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Property Analysis of β -Tetragonal Bismite Thin Films: Varied Concentrations and Enhanced Photocatalytic Efficiency

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Abstract

In this study, we thoroughly examine β -Bi₂O₃ 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 β -Bi₂O₃ 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, MoS₂, ZrO₂ [11], and TiO₂, were used for photocatalysis [12]. Among them, Bi₂O₃ 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]. Bi₂O₃ generally exhibits six crystallographic phases viz α -Bi₂O₃ (monoclinic), β - Bi₂O₃ (tetragonal), γ -Bi₂O₃ (body-centered cubic), δ -Bi₂O₃ (face-centered cubic), ϵ -Bi₂O₃ (orthorhombic), and ω -Bi₂O₃ (triclinic) [16].

Moreover, heat of the stable low-temperature polymorph α -Bi₂O₃ results in the formation of the δ -Bi₂O₃ phase at about 730 °C, which, melts at roughly 825 °C. However, two transitions can occur during cooling: δ -Bi₂O₃ to β -Bi₂O₃ at 650 °C or δ -

۲۵ Bi₂O₃ to γ - Bi₂O₃ at 640 °C [17]. A variety of deposition methods are used to produce
۲۶ Bi₂O₃ 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 Bi₂O₃, Wu Xiaohong et al. demonstrated
۴۰ that Bi₂O₃ 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 Bi₂O₃ films synthesized by sol-gel method [27]. These studies have not
۴۶ investigated the influence of the precursor concentration of Bi₂O₃ 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 Bi₂O₃ 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 Bi₂O₃ Thin Films*

62 The following technique was used to elaborate nanostructured Bi₂O₃ films: Bi-
63 (NO₃)₃.5H₂O was dissolved in a 48.4 mL nitric acid solution (67.5% purity) with
64 volume ratio [1:8 HNO₃: H₂O]. Then, 4 mL of polyethylene glycol
65 (HO(CH₂CH₂O)₂₀₀H) 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-C₆H₄-(OCH₂CH₂)_x. 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**.

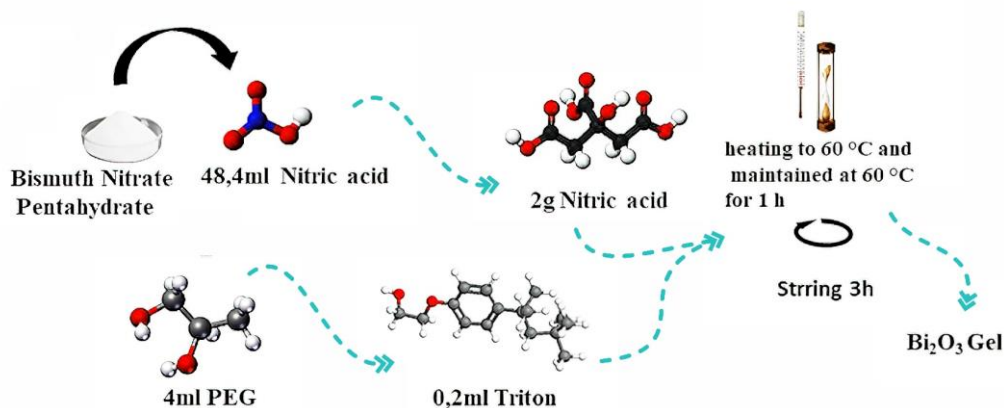


Fig .1. Schematic diagram of Bi_2O_3 preparation by sol-gel synthesis.

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:

Bi_2O_3 thin films were characterized by using different physical techniques. Bi_2O_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

89 2θ range of 20–80°. The crystallite size micro strain and dislocation density of the
90 samples determined XRD from spectrum peak broadening.

91 The 3D surface topography and surface roughness were assessed using a Tencor P-
92 7 mechanical profilometer, which was operated under standard environmental
93 conditions at room temperature. This evaluation utilized the 2-bar method with a
94 customized filter adjustment, specifically employing a Gaussian filter with a cut-off
95 value of 0.800 μm , while addressing edge effects as well.

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

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

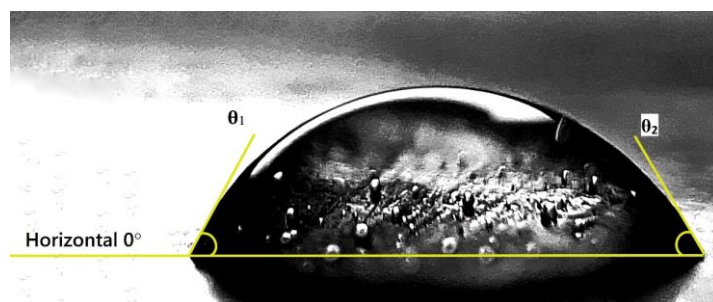
104 2.3. Contact angle measurement

105 The contact angle measurement reflects the ability of a liquid to spread over a surface
106 by wettability. The contact angles of water drop for various bismuth thin films were
107 measured at room temperature in ambient atmosphere by homemade method.
108 Micropipette (*SCIOLOGEX-iso 9001/13485*) was used to meticulously measure the
109 volume of each drop (10 μl), and the distance between micropipette needle and the
110 sample was fixed at 7 mm. All contact angles were averaged from five measurements
111 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 θ_1 and θ_2 ($^\circ$), θ_1 is the angle on the left of a
116 water drop ($^\circ$), θ_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 Bi_2O_3 photocatalysts were evaluated by the
121 photodegradation of MB dye under sunlight irradiation at ~ 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 Bi_2O_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>		β -Bi ₂ O ₃	β -Bi ₂ O ₃	β -Bi ₂ O ₃	β -Bi ₂ O ₃
<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 Bi₂O₃ 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, λ is
 ۱۴۳ the wavelength of the X-rays, and β is the full width at half maximum (FWHM) of X-
 ۱۴۴ ray diffraction peaks in radians [32]. The average crystallite size of the Bi₂O₃ films

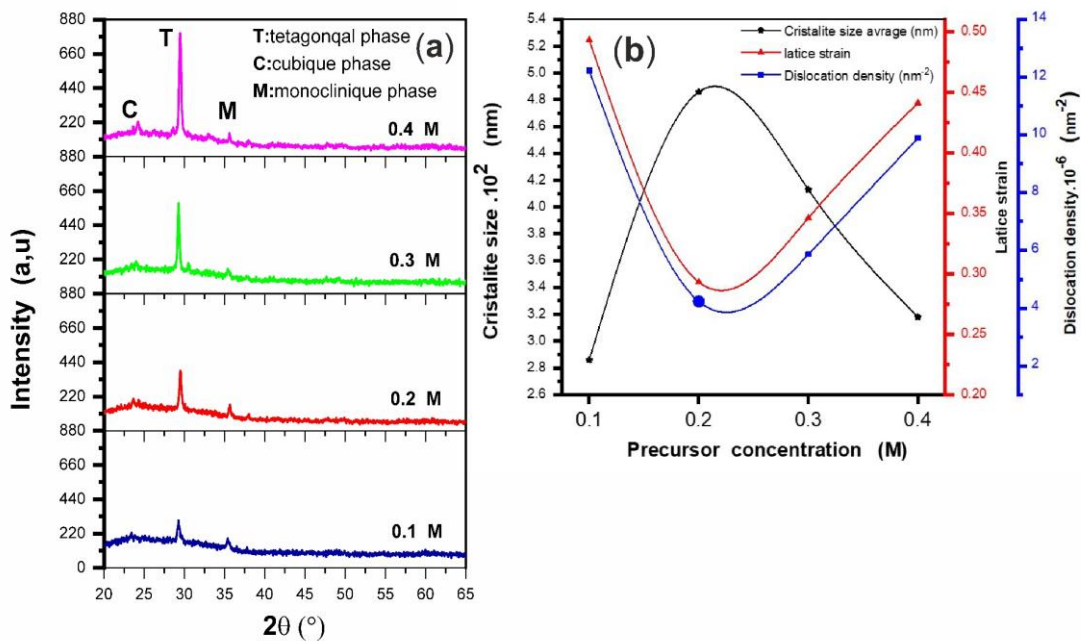
140 prepared by molar precursors of 0.1, 0.2, 0.3, and 0.4 M was found to be 506, 480, 407,
 146 and 360 nm, respectively.

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

148 The dislocation density (δ), 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]:

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

152 The structural parameters such as crystallite size, strain ($\epsilon_{\text{average}}$), and dislocation
 153 density (δ_{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.

109 It was noticed that the crystallite size varies (from 286 to 486 nm) has inverse relation
 160 with the full width at half maximum FWHM. The small value of (δ) obtained in the
 161 present study confirmed the good crystallinity of the Bi_2O_3 thin films [35]. There is a
 162 direct correlation between dislocation density (from $9.88 \cdot 10^{-6}$ to $1.22 \cdot 10^{-5}$) FWHM as
 163 well as strain, since the more strain creates more dislocations in the structure of the
 164 crystal. This result is in agreement with the previously reported [36].

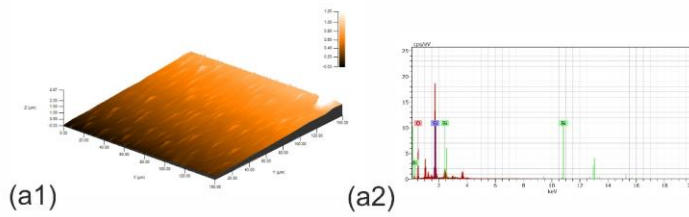
165 **Tables 2.** The structural parameters of various concentration precursor Bi_2O_3 thin films.

<i>Precursor concentration</i>	<i>Position $2\theta(\text{deg})$</i>	<i>d spacing</i>	<i>FWHM $B_T(\text{deg})$</i>	<i>D(nm)</i>	<i>δ dislocation density (nm^{-2})</i>	<i>ε 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

166

167 3.2. Bi_2O_3 thin films morphological and 3D surface topography

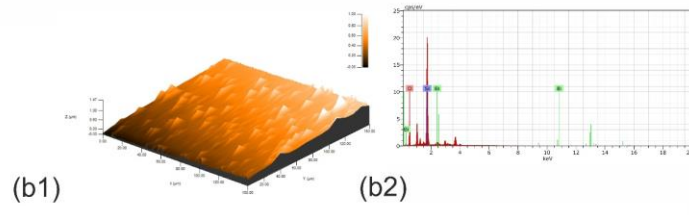
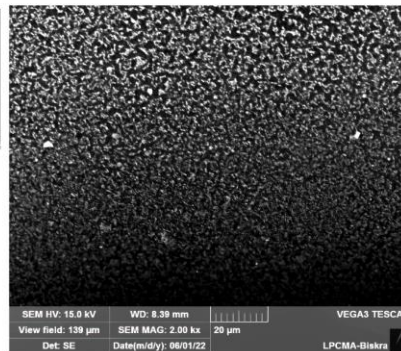
168 The surface morphology of Bi_2O_3 films (from 0.1 to 0.4 M) was carried out using
 169 Scanning Electron Microscope (SEM), as shown in **Fig. 4(a-d)**, respectively. All the
 170 films have irregular island morphology with good overall coverage. **Fig. 4a** shows
 171 isolated islands that are not clustered with each other. When the precursor concentration
 172 is increased, the island grains size increase, this is due to agglomeration in thicker film
 173 resulting grains growth as shown in **Fig. 4(b)** and slightly decreases until the film surface
 174 appears as big grains that are more compact and denser, as shown in **Fig. 4(d)**.



(a1)

(a2)

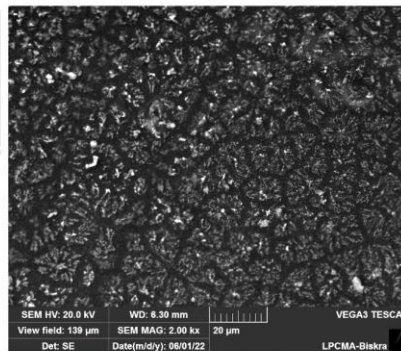
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	20.26	50.14	39.78	0.89
O	8	K-series	17.25	42.69	59.45	2.28
Bi	83	L-series	2.90	7.17	0.76	0.21
Total:			40.41	100.00	100.00	



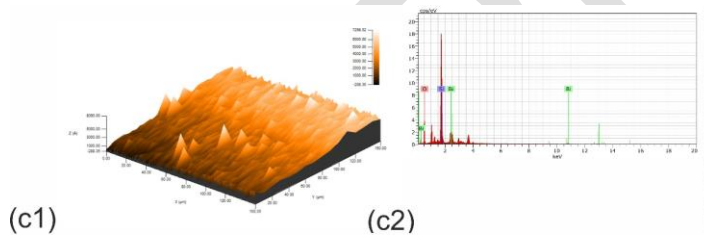
(b1)

(b2)

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	



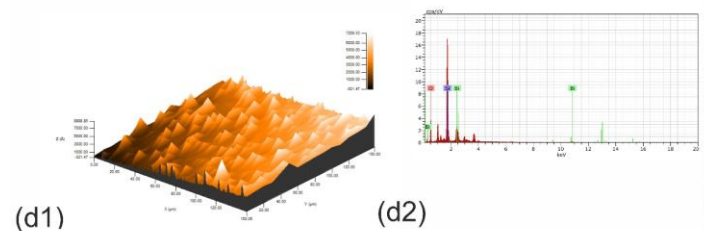
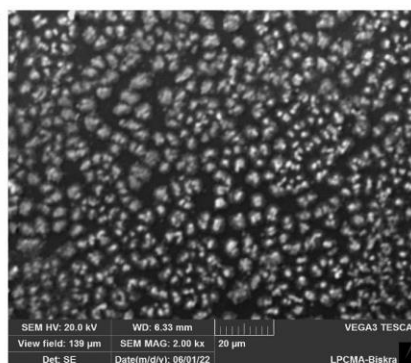
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(c1)

(c2)

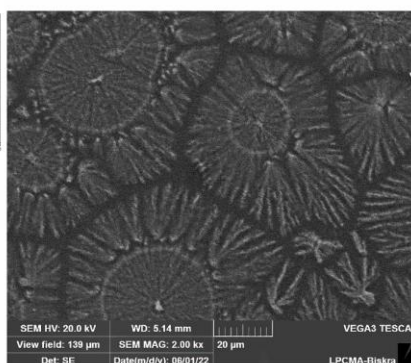
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Si	14	K-series	24.38	42.36	43.49	1.07
O	8	K-series	16.79	29.17	52.58	2.33
Bi	83	L-series	16.39	28.48	3.93	0.69
Total:			57.55	100.00	100.00	



(d1)

(d2)

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 Bi₂O₃ films synthesized by the different
178 precursor concentrations: (a2) 0.1, (b2) 0.2, (c2) 0.3, and (d2) 0.4 M.

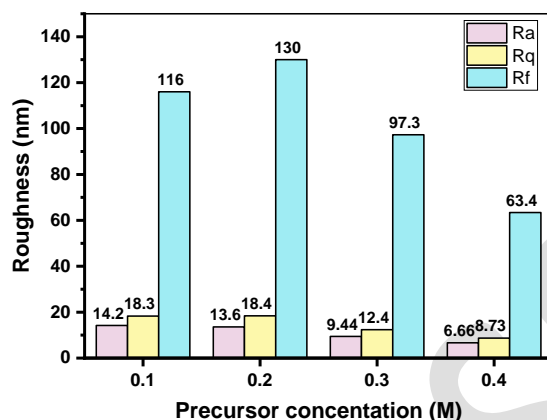
179 The result of cross-sectional SEM images supports the XRD patterns that increasing
180 the intensity of all diffraction peaks are influenced by the thickness of film. Which is
181 good agreement with reported [37]. A quantitative analysis of the surface topography
182 was performed from the data 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 Bi₂O₃
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 Rt of Bi₂O₃ films prepared at various
202 molar concentrations.

203 3.3. Bi₂O₃ 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

213 The optical properties of Bi₂O₃ thin films prepared by using various precursor
214 concentrations were studied by UV–visible spectrophotometer in the range of 300–900
215 nm at room temperature, is depicted in **Fig. 7(a)**. As noticed, the transmittance increases
216 with increasing wavelength, and its average value in the visible region of the spectrum
217 is (78, 67.66%, 67.68%, and 63%); in the ultraviolet region, it is (51, 32, 34%, and
218 18%), with rising precursor concentrations (from 0.1 to 0.4 M), respectively. The
219 transmittance can be associated with the values of grain size, RMS, porosity, and
220 thickness of the films. It is generally expected that increased thickness and surface
221 roughness lead to reduced transmittance, while decreasing porosity and grain size
222 decrease transmittance [42]. The gravimetric weight differential method (weight
223 increase method) was used to determine the thickness of the Bi₂O₃ films.

$$224 \quad D = \Delta m / A \cdot \rho \quad (4)$$

225 Where Δm is the mass difference in grams, A is the area of deposited films in cm², and
226 ρ is the density of the deposited material (Bi₂O₃= 9.17 g/cm³) [43]. **Fig. 7(d)** shows the
227 average thickness variation as a function of concentration precursor values. The film
228 thickness increased (from 40 to 115 nm) as the precursor concentration increased (from
229 0.1 to 0.4 M); this is due to the high viscosity of the solution. The absorption coefficient
230 α of the mentioned films was obtained via the following equation:

$$231 \quad \alpha = \ln I_0/I \cdot 1/d \quad (5)$$

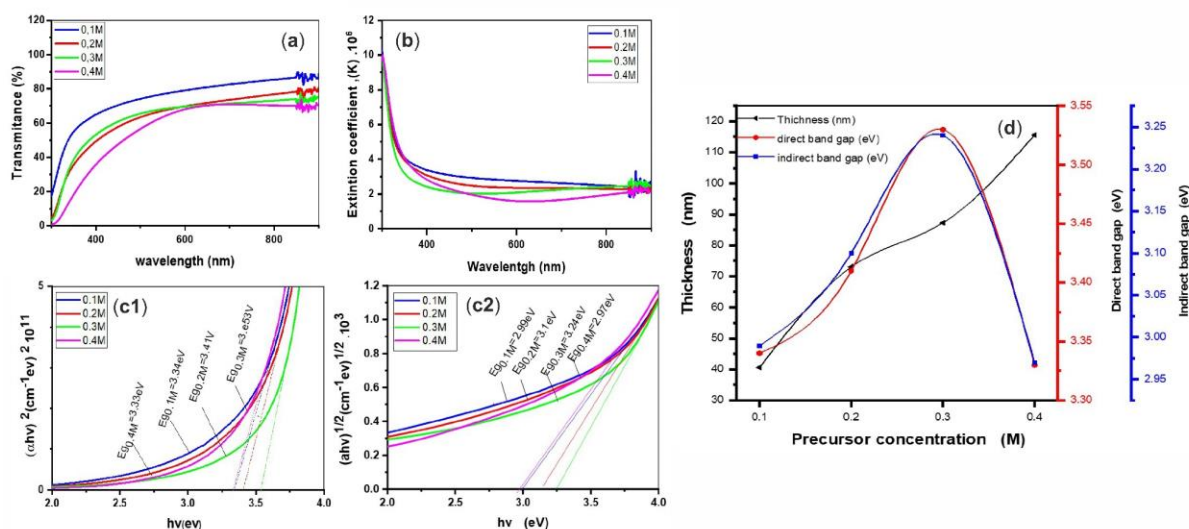
232 Where, d is film thickness, and I_0/I is the ratio of incident beam intensity to emergent
233 beam [17][30]. Band gap values are calculated from absorption spectra, and the method
234 was described in previous literature [45]. The data were analyzed using the following
235 classical relationship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

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

۲۳۷ Where α , h , ν , 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 Bi_2O_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.

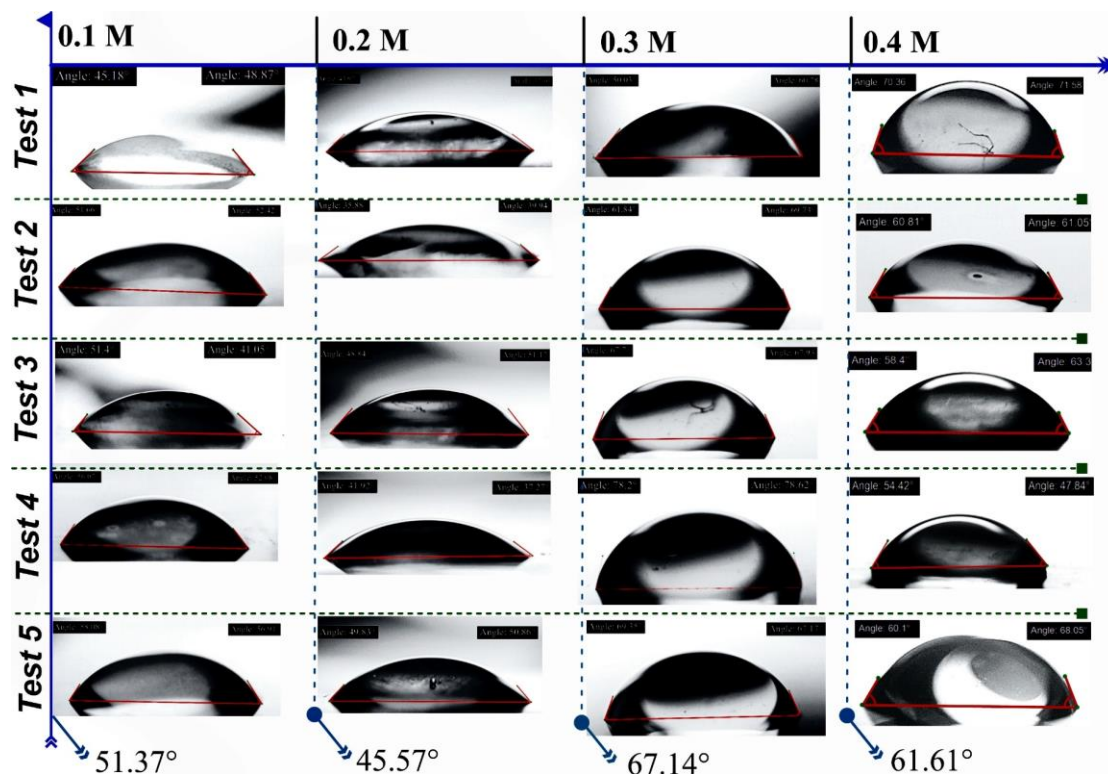


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۲۵۵ **Fig. 7.** (a) Optical transmittance spectrum of Bi_2O_3 synthesized by the different
 ۲۵۶ precursor concentrations. (b) Variation of extinction coefficient (k) versus wavelength
 ۲۵۷ with various molar concentrations. (c1) Direct and (c2) indirect band gap of the Bi_2O_3
 ۲۵۸ films. (d) Variation of thickness and band gap with different precursor concentrations.

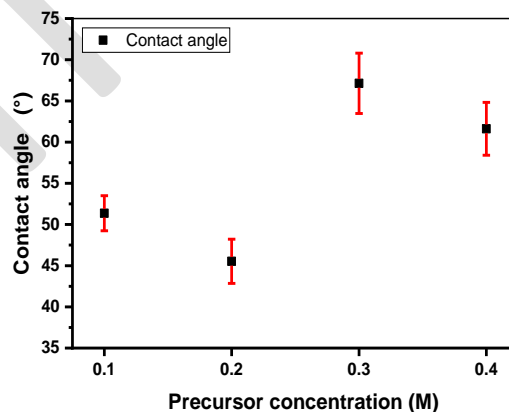
۲۵۹ 3.5. Wettability analysis

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 Bi_2O_3 films, as depicted in **Fig. 8**, water contact
 ۲۶۶ angle measurements were conducted.



۲۷۱ **Fig. 8.** Contact angles measurements images of Bi_2O_3 thin films.

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



۲۷۵ **Fig. 9.** Average contact angles of distilled water (H_2O) on the Bi_2O_3 substrates.

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

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

278 3.6. The photocatalytic efficiency

279 The photocatalytic efficiency of Bi₂O₃ thin films synthesized with variable precursor
280 concentrations was evaluated by MB (2 ppm) photobleaching in an aqueous solution.

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

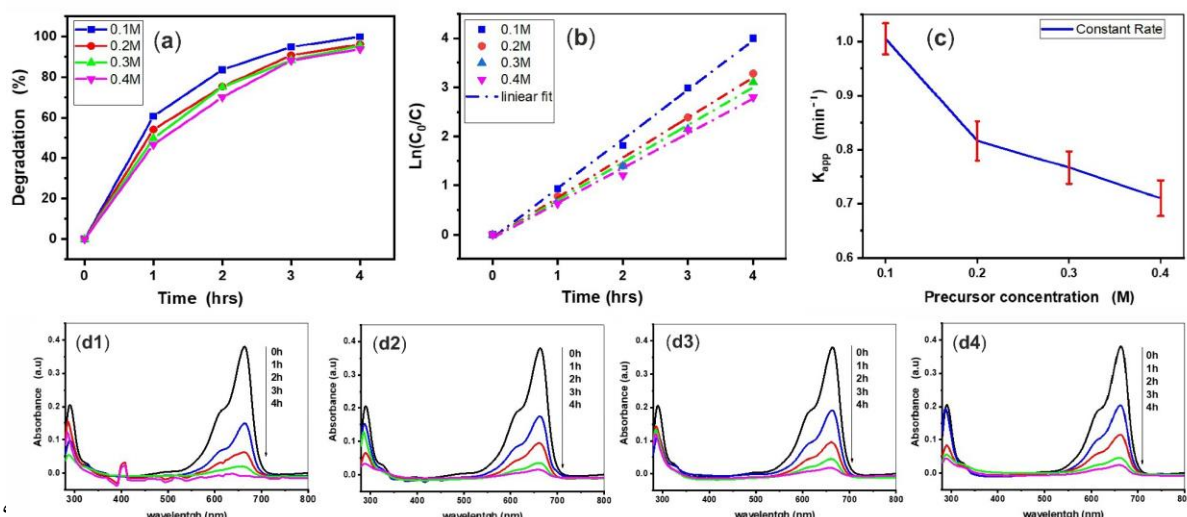
282 **10(a)** shows the time-dependent visible light photocatalysis of thin films (0.1, 0.2, 0.3,
283 0.4 M) which decomposes the MB dye with a total exposure time of 4 h.

284 **Table 4.** Change in temperature, wind, humidity, and the amount of solar radiation
285 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^o)</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				

286

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



۲۸۶

۲۹۰ **Fig. 10.** (a) The degradation rate of MB dye by Bi_2O_3 thin films. (b) Photocatalytic
 ۲۹۱ kinetics for the all Bi_2O_3 thin films. (c) Effects of varying precursor concentrations of
 ۲۹۲ Bi_2O_3 thin films on MB removal under irradiation time. Absorbance spectra of the
 ۲۹۳ MB solutions by Bi_2O_3 thin films prepared with different precursor concentrations:
 ۲۹۴ (d1) 0.1, (d2) 0.2, (d3) 0.3, and (d4) 0.4 M.

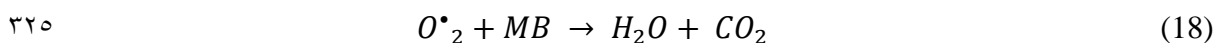
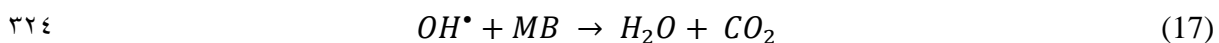
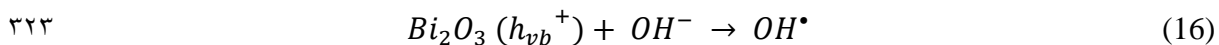
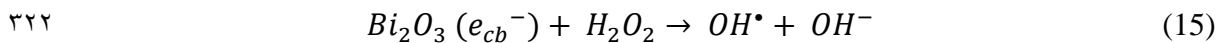
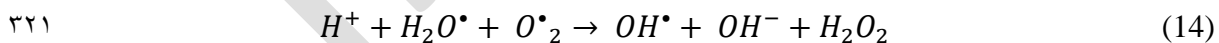
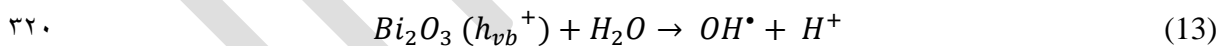
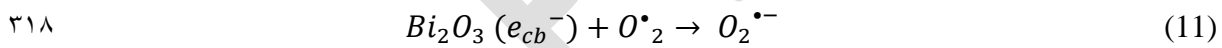
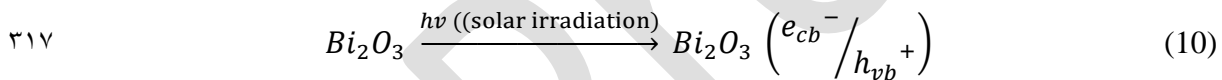
۲۹۵ The degradation rate of MB dye is revealed in the presence of thin films as a catalyst.
 ۲۹۶ The following equation was used to calculate the photo degradation rate: [51]

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

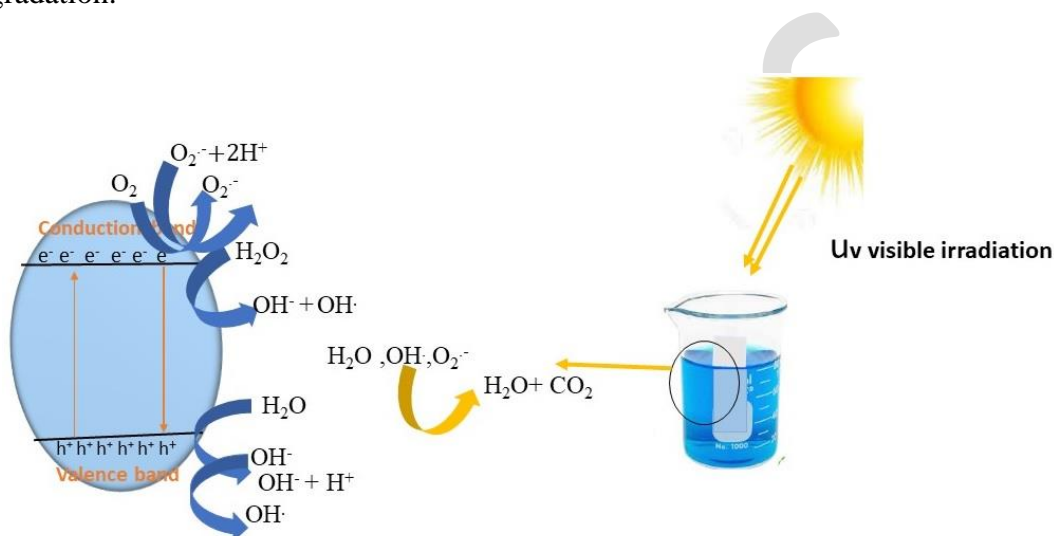
۲۹۸ Where A_0 is the initial absorbance at time $t = 0$ h, A_t is the absorbance after time t . The
 ۲۹۹ absorbance of MB dye over the Bi_2O_3 thin films under sun irradiation for 4 h is shown
 ۳۰۰ in **Fig. 10(d(1, 2, 3, and 4))**. It was observed that after 2h the relative amounts of MB
 ۳۰۱ decomposed by photocatalysis were 47.09, 49.47, 53.97, and 83.60 % when Bi_2O_3
 ۳۰۲ synthesized at 0.1, 0.3, 0.4, and 0.5 M was used as photocatalyst, respectively. Bi_2O_3
 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 (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 Bi_2O_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 Bi_2O_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_2O_3 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 ($-\text{OH}$, $\bullet\text{OH}$, H_2O_2 , etc.) are capable
 ۳۴۱ of oxidizing organic molecules, such as MB into simpler molecules such as CO_2 , H_2O
 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>
β -Bi ₂ O ₃ (0.1M), Thin film	Methylene blue, 0.002 g/l	Dip-coating (glass Substrate)	~99	240	Visible light	Current study
β -Bi ₂ O ₃ , Thin film	Methylene blue, 10 ⁻⁶ mol/l	Spin-coating Deposition (Pt-coated silicon substrates)	~100	1440	Solar lamp (Ultra-Vitalux 300 W, Osram)	[59]
β -Bi ₂ O ₃ , 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 ₃ O ₄ (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 ₃ O ₄ (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 ₃ /Co ₃ O ₄ , 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, Bi₂O₃ films are deposited by sol-gel technique. The structural,
۳۴۸ morphological, optical, and photocatalytic properties of Bi₂O₃ 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 Bi₂O₃
۳۵۱ films was not gradually affected by the change in precursor concentration or film
۳۵۲ thickness. The morphology of the Bi₂O₃ 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 Bi₂O₃
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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