

1 Article

# 2 Enhanced visible-light active WO<sub>3</sub> thin films towards 3 air purification: effect of the synthesis conditions

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12 **Abstract:** Taking into consideration, our current environmental situation in the world people should face with  
13 growing problem of air and water pollution. Heterogeneous photocatalysis is highly promising tool to  
14 improve both, air and water quality through decomposition/mineralization of contaminations directly into  
15 harmless CO<sub>2</sub> and H<sub>2</sub>O under ambient conditions. In this contribution we focused on the synthesis of self-  
16 assembly WO<sub>3</sub> thin films *via* an electrochemical approach in the aqueous electrolyte containing fluoride ions  
17 towards air purifications. The effect of preparation conditions such as applied potential (10 – 50 V),  
18 anodization time (15 – 120 minutes), concentration of H<sub>2</sub>SO<sub>4</sub> (0.5 – 1.5 M) and NaF (0.1 – 1.0 wt.%) on the  
19 morphology, photocurrent response and photocatalytic activity addressed to removal of air pollutant in the  
20 presence of as-prepared WO<sub>3</sub> samples were thoroughly examined and presented. The results revealed the  
21 growth of nanoplatelets and their gradual transformation into flower-like structure. The oxide layers and  
22 platelets thickness of the WO<sub>3</sub> samples were found to be proportionally related with the synthesis conditions.  
23 The photocatalytic ability towards air purification was evaluated by degradation of toluene from air mixture  
24 using low-powered LEDs as an irradiation source ( $\lambda_{\max} = 415 \text{ nm}$ ). The highest photoactivity was achieved  
25 in presence of the sample which possessed well-ordered, regular shape and repeatable distribution of flower  
26 buds (100% of degradation). The results have confirmed that the oxide layer thickness of the anodic WO<sub>3</sub>  
27 significantly affected the photocatalytic activity, which increased with the increasing thickness of WO<sub>3</sub> (to  
28 1.05  $\mu\text{m}$ ) and then had a down trend. The photocurrent response evidenced that well-organized sample had  
29 the highest ability in photocurrent generation under UV-Vis and Vis irradiation. Finally, a possible growth  
30 mechanism of WO<sub>3</sub> NFs was also discussed.

31 **Keywords:** WO<sub>3</sub> nanoflowers; electrochemical anodization; toluene degradation; visible light  
32 induced photocatalysis;  
33

## 34 1. Introduction

35 Air pollutions are the major cause of global environmental threats. They contribute to the  
36 formation of respiratory diseases, infectious diseases, acute toxic effects, cancers as well as  
37 reproductive disorders and allergies. The World Health Organization reports that every year over 4.2  
38 million deaths is a result of exposure to ambient air pollutant[1]. Moreover, air pollutants adversely  
39 affect the world, disrupting photosynthesis, transpiration and respiration. Secondly, they  
40 contaminate water and soil. They increase the acidity of drinking water as well as content of heavy  
41 metals such as lead, copper, zinc or cadmium in the water. Acidified water destroys plumbing  
42 installations, washing away various toxic substances from it. They cause corrosion of metals and  
43 building materials. Air pollutants have also negative impact on climate change. The main problem  
44 which needs to be solved today it is a successful decomposition/mineralization of air contamination.  
45 Therefore, an innovative and effective method of removing harmful substances from environmental  
46 are sought.

47 Advanced oxidation processes (AOPs) have been extensively studied to reduce a great variety  
48 of pollutants present in various environmental media[2–4]. Among them, special attention has been  
49 paid for the application of heterogeneous photocatalysis in environmental applications for the  
50 remediation of polluted air and water. The photocatalytic effects exerted by redox reaction are caused  
51 by photoinduced of electrons ( $e^-$ ) from the valence band to the conduction band leaving positive holes  
52 ( $h^+$ ) behind in very short time (femtoseconds) under the influence of UV-Vis irradiation. Several  
53 reactive species, including formation of the high reactive hydroxyl radicals ( $\bullet OH$ ) and superoxide  
54 radicals ( $O_2^{\bullet -}$ ), are generated through reaction of  $e^-$  and  $h^+$  which are considered to be involved in the  
55 oxidative and reductive reactions in photocatalysis. The generated reactive oxygen species react with  
56 adsorbed gas and/or water pollutants leading to the degradation/mineralization them into  $CO_2$  and  
57  $H_2O$ [5,6]. Successful photocatalytic air purification relies on the following parameters: (i) photon  
58 absorption of semiconductor photocatalysts and (ii) surface properties of photocatalysts, in  
59 particular, keeping clean photocatalyst surface free from the accumulation of recalcitrant  
60 intermediates and products during the processes[7,8].

61 Currently, the most studied photocatalyst which holds a great potential as very effective  
62 photoinduced photocatalyst is frequently used to decompose organic and inorganic contaminations  
63 from water and air due to its good chemical stability, high oxidizability, non-toxicity and low-cost  
64 preparation of nano- and microparticles is titanium dioxide ( $TiO_2$ ). However, the main drawback of  
65 it is wide band gap (3.2 eV for anatase) and consequently only small fraction of the solar irradiation  
66 can be absorbed by this material ( $\sim 4\%$ )[9,10]. Many studies reported that sufficient doping of cations  
67 or anions into  $TiO_2$  layers to create certain states within the band gap energy may led to achieved  
68 visible light driven  $TiO_2$  photocatalysts[11]. However, those modification have a number of fails, such  
69 as its thermal instability and formation of recombination centres for photoinduced charge carriers,  
70 which significantly decrease its photocatalytic ability[12]. Therefore, designing and/or further  
71 development of an efficient visible light active photocatalyst is particularly critical need for air  
72 purification.

73 From a practical point of view, tungsten trioxide ( $WO_3$ ) became an alternative photocatalytic  
74 material with interesting optical, electrical and structural properties [13]. In terms of chemical  
75 stability and inertness,  $WO_3$  exhibits the same attributes as  $TiO_2$ . In addition, it possess a lower band  
76 gap energy level (between 2.4 and 2.8 eV), stable physicochemical properties and strong resilience to  
77 photocorrosion effects[10,14]. Furthermore, it has been considered a great interest due to ability to (i)  
78 decontaminate polluted water[15,16], (ii) detect hazardous gases[17–19] and (iii) solar energy  
79 conversion[20,21].

80 Numerous studies reported different synthesis approach of  $WO_3$  nanostructures including sol-  
81 gel technique[22–24] electrochemical deposition[25], chemical vapour deposition[26,27],  
82 electrochemical oxidation[28,29], magnetron sputtering[30–32], ion-beam evaporation[33,34] and  
83 atomic layer deposition[35] have been described. Among them, an anodization technique attracts  
84 considerable attention due to low cost and simplicity of a synthesis route. Furthermore, the possibility  
85 of controlling and adjusting a growth process by tuning anodization parameters (such as applied  
86 potential, synthesis time and temperature) as well as electrolyte composition makes this technique  
87 more interesting for fabricating metal oxide nanostructures with controllable pore size, good  
88 uniformity, and conformability over large areas[36–38]. However, several studies have reported that  
89 it is still a challenge to obtain well-aligned and uniformity of anodic  $WO_3$  nanostructures instead of  
90 nanoporous[13,39–41]. First mention about preparation of porous  $WO_3$  using galvanostatic  
91 anodization of W foil in oxalic acid electrolyte, was described by Grimes *et al.*[42]. It was found that  
92 the obtained nanoporous tungsten oxide exhibited more regular surface with smaller pore size in  
93 compare with results described previously for other methods. Self-organized nanoporous structure  
94 by anodizing W foil in electrolyte composed of 1 M sulphate acid and 0.5 wt.% sodium fluoride was  
95 reported by Schmuki *et al.*[37]. The ability to control the synthesis conditions allowed them to obtain  
96 desired self-ordered oxide structure exhibiting higher photocurrent efficiency than a compact oxide  
97 layer. Sadek *et al.* described the growth process of  $WO_3$  nanoplatelets during the anodization of  
98 tungsten foil in a nitric acid environment at higher temperatures[43]. The combination of the

99 synthesis parameters with high temperature led the authors to obtained relatively thick films of  
100 nanoplatelets with potential application in photosensitive devices. Flower-shaped tungsten oxide  
101 nanostructure prepared in an acidified electrolyte solution containing fluoride ions was reported by  
102 Amal *et al.*[29,44]. The resultant thin oxide film, with enhanced surface area and thickness, exhibited  
103 a higher photocurrent density. What is more, the annealing temperature and crystallite of the as-  
104 anodized WO<sub>3</sub> nanostructures was found as a critical factor e. g. in water splitting reaction[44].  
105 Despite many reports describing synthesis approach of WO<sub>3</sub> nanostructures with electrochemical  
106 method, there is still lack of knowledge about the effect of synthesis parameters (such as electrolyte  
107 composition, applied potential and time period duration) on the geometrical parameters, optical and  
108 photocatalytic properties with photoactivity of the WO<sub>3</sub> nanoflowers.

109 Motivated by this, we propose, for the first time, a novel synthesis method of the self-assembly  
110 three-dimensional tungsten oxide nanoflowers (3D WO<sub>3</sub> NFs) thin film with improved optical and  
111 photoelectrochemical properties and exhibited enhanced photocatalytic activity in the reaction of  
112 toluene degradation under visible irradiation. The objectives of the present study are, therefore: (i) to  
113 optimize synthesis conditions of the WO<sub>3</sub> NFs, (ii) to correlate morphological dimensions and  
114 photoactivity and (iii) to find optimal synthesis conditions to assure that the nanostructures do not  
115 decompose under illumination and its remains stable in time.

## 116 2. Materials and Methods

### 117 2.1 Materials

118 Isopropanol (p.a., POCh. S.A., Gliwice, Poland), acetone, methanol (p.a., P.P.H. STANLAB,  
119 Lublin, Poland) and deionized water (DI, with conductivity of 0.05 μS) were used during sonication  
120 process. WO<sub>3</sub> NFs were synthesis with using anodic oxidation of tungsten foil (0.127 mm, 99.9%  
121 purity, Sigma Aldrich, Sigma Aldrich) in the aqueous electrolyte composed of sulphuric acid solution  
122 (96%, p. a., P.P.H. STANLAB, Lublin, Poland) and sodium fluoride (p. a., P.P.H. STANLAB, Lublin,  
123 Poland).

### 124 2.2 Synthesis of WO<sub>3</sub> nanoflowers

125 W foils were cut into 2 × 2 cm samples and ultrasonically cleaned in acetone, isopropanol,  
126 methanol and deionised water for 10 minutes in each solvent and then dried in an air stream[45,46].  
127 The as-cleaned samples were contacted with a Cu spring and pressed against an O-ring in an  
128 anodization cell, which consists of a two-electrode configuration with W foil as the working electrode  
129 (anode) and the platinum foil as the counter electrode (cathode). All the experiments were performed  
130 at room temperature. The electrolytes containing various concentration of sodium fluoride (0.1, 0.2,  
131 0.5, 0.7 and 1.0 wt.%) and sulphuric acid (0.5, 1 and 1.5 M) were used. A sets of analysis were  
132 conducted for 15, 30, 45, 60, 90 and 120 minutes during anodization at the voltage range of 10 – 50 V  
133 using programmable power supply (MCP M10-QS1005). The as-anodized samples were raised with  
134 deionized water, dried overnight at 60°C and then annealed at 400°C for 4 h with a ramping rate of  
135 4°C/min in the air environment.

### 136 2.3 Material characterization

137 A high resolution scanning electron microscopy (HRSEM, JEOL, JSM – 7610F) was used to  
138 analysed the morphology parameters of WO<sub>3</sub> NFs. Cross-sectional images were obtained in which  
139 the samples were scrunched and measured at the angle of 30° tilted view to determine the thickness  
140 of the films. The crystal structure of the samples was determined from X-Ray diffraction patterns  
141 recorded in the range of 2θ = 20 – 80°, using an X-Ray diffractometer (XRD, Rigaku MiniFlex 600)  
142 with Cu Kα radiation. UV-Visible absorption spectra of the samples in the wavelength of 200 - 800 nm  
143 were collected by using diffuse reflectance UV–Vis spectroscopy (Thermo Scientific) equipped with  
144 an integrating sphere with baseline determined with barium sulphate as reference. The  
145 photoluminescence (PL) measurements were carried out at room temperature using a  
146 photoluminescence spectrometer LS-50B (PerkinElmer) equipped with Xenon discharge lamp as an

147 excitation source and a R928 photomultiplier as detector. The excitation radiation (300 nm) was  
148 directed on the surface of the samples at an angle of 90°. The Raman spectra were collected with a  
149 Thermo Scientific DXR Smart Raman spectrometer with a 532 nm laser as the excitation source under  
150 ambient conditions.

#### 151 2.4 Photocatalytic performance

152 The photocatalytic activity of the as-prepared WO<sub>3</sub> thin films was tested by the visible-light-  
153 driven degradation of toluene (200 ppm) from an air mixture, used as a model contaminant. The  
154 measurements were carried out in a flat stainless steel reactor of a volume of ca. 35 cm<sup>3</sup> equipped  
155 with a quartz window, two valves and a septum. The irradiation source consisted of a LED array  
156 with  $\lambda_{\max} = 415$  nm was located above the sample. The as-anodized foil was placed at the bottom side  
157 and the reactor was closed with a quartz window. Subsequently, the gaseous mixture was passed  
158 through the reactor for 1 min. Then, the valves were closed and the reactor was kept in dark for  
159 30 min in order to achieve equilibrium. Before starting the irradiation, a reference toluene sample was  
160 taken. The concentration was determined by using a gas chromatograph (TRACE 1300, Thermo  
161 Scientific), equipped with an ionization flame detector (FID) and a Phenomenex capillary column  
162 (30 mm x 25 mm, 0.5  $\mu$ m). The samples (200  $\mu$ L) were dosed with a gastight syringe each 10 min.  
163 Intensity of irradiation was measured by an optical power meter and reached 15 mW/cm<sup>2</sup>.

#### 164 2.5 Photoelectrochemical activity

165 Photocurrent measurements were performed using an AutoLab PGSTAT 204 potentiationstat-  
166 galvanostat (Metrohm) with the three-electrode system. Prepared samples were used as working  
167 electrodes with Ag/AgCl/0.1 M KCl and Pt mesh as the reference and counter electrodes, respectively.  
168 The active surface area of the electrode was 0.25 cm<sup>2</sup>. Prior to the measurement, the electrolyte 0.1 M  
169 Na<sub>2</sub>SO<sub>4</sub> water solution, was purged with argon for 1 h. Similarly, the space above the electrolyte  
170 during the measurements was purged with argon. Photocurrent measurements under UV-Vis and  
171 visible irradiation were analyzed using a 250 W Xe light source with a 420 nm cut-off filter (for visible  
172 light irradiation).

### 173 3. Results

174 To investigate the effect of the synthesis conditions and electrolyte composition, (anodization  
175 potential, reaction time, concentration of H<sub>2</sub>SO<sub>4</sub> and NaF) on the morphological, photoactivity and  
176 photoelectrochemical properties of the anodic oxide WO<sub>3</sub>, a series of the samples were prepared. The  
177 labels of the as-prepared samples together with the synthesis conditions, morphological parameters,  
178 optical band gap and efficiency of toluene degradation are presented in Table 1.

**Table 1.** Sample label, morphology parameters, optical band gap and efficiency of toluene degradation of the obtained samples.

Sample label	Preparation conditions (electrolyte composition and anodization parameters)		Flower diameter (nm)	Oxide layer thickness ( $\mu\text{m}$ )	Platelets thickness (nm)	Optical band gap (eV)	Efficiency of toluene degradation after 60 minutes of irradiation (%)
	Constant parameters	Variable parameters					
WO_10 V	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 90 min	10V	-**	0.1±0.1	11.8±0.1	2.75	36
WO_20 V	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 90 min	20V	-**	0.3±0.1	12.8±0.2	2.61	67
WO_30 V	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 90 min	30V	0.72±0.1	0.8±0.1	13.6±0.2	2.65	90
WO_40 V*	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 90 min	40V	1.21±0.1	1.05±0.1	14.9±0.3	2.52	100
WO_50 V	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 90 min	50V	0.81±0.2	1.2±0.1	16.9±0.3	2.65	73
WO_15 min	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 40V	15 min	-**	0.1±0.02	11.2±0.1	2.66	15
WO_30 min	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 40V	30 min	0.91±0.1	0.3±0.05	12.3±0.1	2.64	25
WO_45 min	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 40V	45 min	1.04±0.2	0.5±0.1	13.1±0.2	2.56	55
WO_40 V*	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 40V,	90 min	1.21±0.1	1.05±0.2	14.9±0.2	2.52	100
WO_120 min	1.0 M H <sub>2</sub> SO <sub>4</sub> , 0.5 wt.% NaF, 40V	120 min	1.52±0.2	1.35±0.1	15.6±0.2	2.40	78
WO_0.5 M H <sub>2</sub> SO <sub>4</sub>	0.5 wt.% NaF, 40V, 90 mi	0.5 M H <sub>2</sub> SO <sub>4</sub>	1.15±0.1	1.17±0.1	13.4±0.2	2.63	86
WO_40 V*	0.5 wt.% NaF, 40V, 90 min	1.0 M H <sub>2</sub> SO <sub>4</sub>	1.21±0.1	1.05±0.1	14.9±0.2	2.52	100
WO_1.5 M H <sub>2</sub> SO <sub>4</sub>	0.5 wt.% NaF, 40V, 90 min	1.5 M H <sub>2</sub> SO <sub>4</sub>	1.10±0.1	1.0±0.1	15.3±0.3	2.55	90
WO_0.1 wt.% NaF	1.0 M H <sub>2</sub> SO <sub>4</sub> , 40V, 90 min	0.1 wt.% NaF	-**	1.0±0.01	11.3±0.1	2.79	26
WO_0.2 wt.% NaF	1.0 M H <sub>2</sub> SO <sub>4</sub> , 40V, 90 min	0.2 wt.% NaF	-**	1.02±0.1	12.1±0.2	2.62	61
WO_40 V*	1.0 M H <sub>2</sub> SO <sub>4</sub> , 40V, 90 min	0.5 wt.% NaF	1.21±0.1	1.05±0.01	14.9±0.3	2.52	100
WO_0.7 wt.% NaF	1.0 M H <sub>2</sub> SO <sub>4</sub> , 40V, 90 min	0.7 wt.% NaF	-**	1.1±0.01	15.9±0.3	2.55	86
WO_1.0 wt.% NaF	1.0 M H <sub>2</sub> SO <sub>4</sub> , 40V, 90 min	1.0 wt.% NaF	-**	1.15±0.01	17.8±0.3	2.66	74

\*The WO\_40 V sample was synthesised in the following conditions: 90 min, 40 V, 0.5 wt.% NaF and 1.0 M H<sub>2</sub>SO<sub>4</sub> in each series to compare the influence of preparation conditions.

\*\*The formation of the flower buds was not observed.

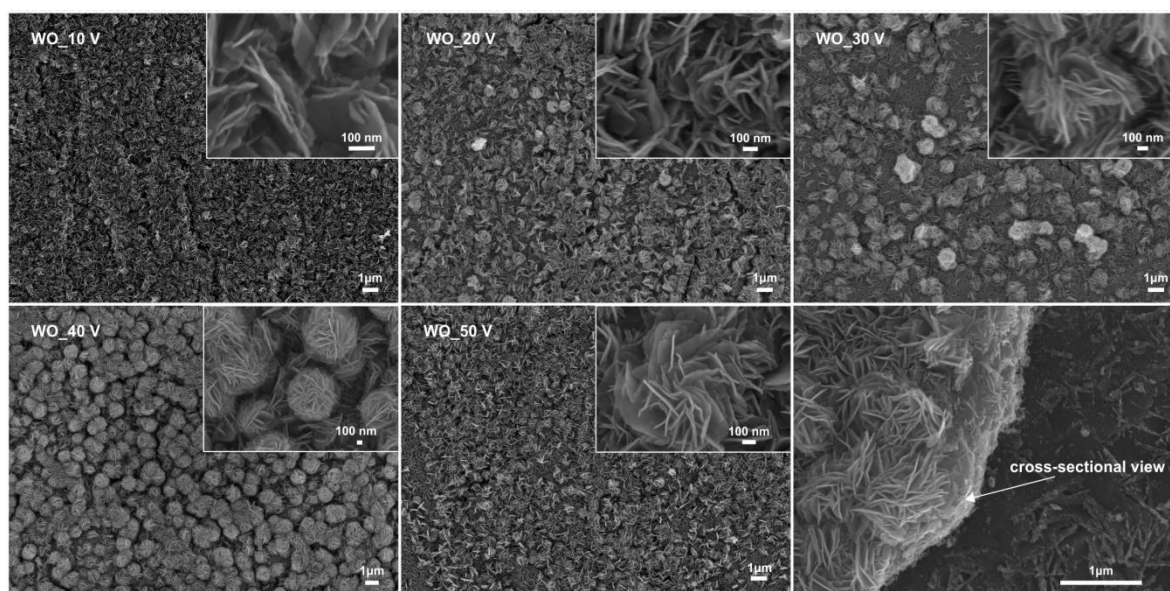




183 3.1. Morphology

184 3.1.1 Effect of the anodization potential

185 Series of samples in the range of 10 to 50 V were synthesized to determine the effect of the  
 186 anodization potential on the growth of the WO<sub>3</sub> nanostructure. The results are displayed in Figure 1.  
 187 Too low anodization potential (below 20 V) resulted in the formation of the anodic oxide layer  
 188 possessing platelets nanostructure. Its irregular shape has been gradually transformed into flower-  
 189 like structure when the anodization potential increased to 30 V and revealed growth of the irregular,  
 190 sparsely spread flower buds with the diameter of  $0.72 \pm 0.1 \text{ nm}$ . Regular shape and repeatable  
 191 distribution were observed for the sample anodized at 40 V with the diameter of the flowers buds  
 192 equaled  $1.21 \pm 0.1 \text{ }\mu\text{m}$ . However, further increase to 50 V caused decrease of the flowers buds  
 193 abundance (see Figure 1). Decrease in the diameter of WO<sub>50</sub> V to  $0.81 \pm 0.2 \text{ nm}$  was also observed.  
 194 Moreover, it was found that the nanoplatelets started to deform – were rounded and looked like  
 195 developed buds. On the other hand, increasing the anodization potential resulted in an increase in  
 196 the oxide layer thickness and platelets thickness from  $0.1 \pm 0.1 \text{ }\mu\text{m}$  and  $11.8 \pm 0.1 \text{ nm}$  for the WO<sub>10</sub> V  
 197 sample to  $1.2 \pm 0.1 \text{ nm}$  and  $16.9 \pm 0.3 \text{ nm}$  for WO<sub>50</sub> V, respectively. Additionally, higher applied  
 198 voltage resulted in sharpening the edges of the nanoplatelets.

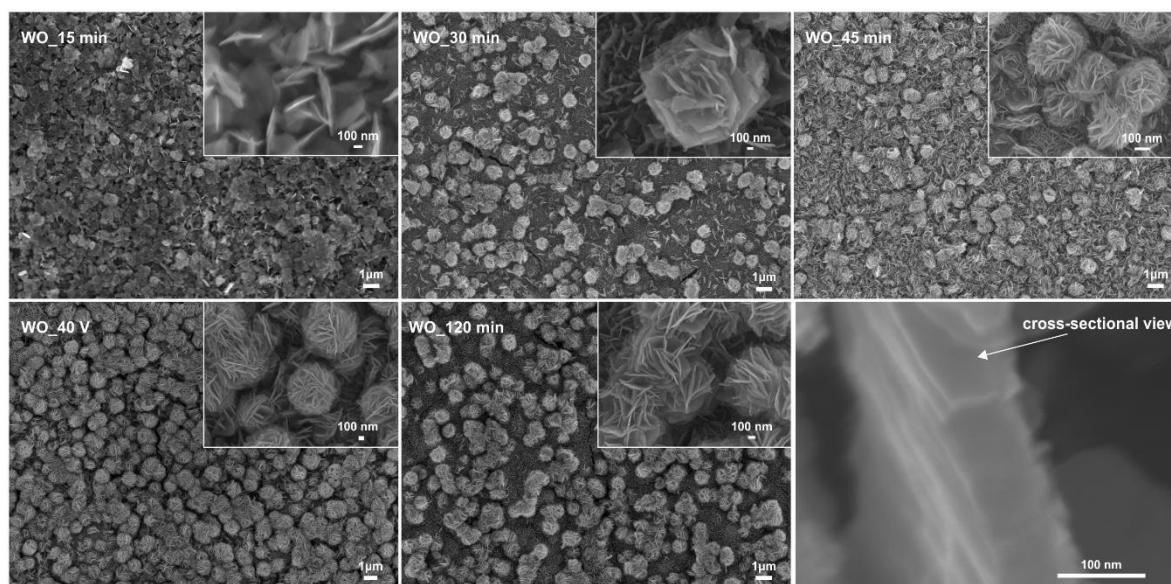


199  
 200 **Figure 1.** Effect of the anodization potential on the morphology of WO<sub>3</sub> NFs. Fluoride content  
 201 0.5 wt.%, H<sub>2</sub>SO<sub>4</sub> concentration 1.0 M, anodization time 90 min.

202 3.1.2 Effect of the anodization time

203 To investigate the effect of the anodization time on the growth of the nanoflowers, a series of  
 204 experiments were conducted for different durations and the results are presented in Figure 2. The  
 205 sample anodized at 40 V has been chosen to explore further its anodization time because it exhibited  
 206 the most ordered, regular shape of flower-like structure. It established that the obtained layers  
 207 consisted of irregular buds when the anodization time decreased below 90 minutes. Moreover, in  
 208 shorter time fewer pores were formed and an increase in heterogeneity of the layers was observed. It  
 209 could be assume that the growth of well-ordered flowers buds require soluble species which are  
 210 formed by the initial anodic growth of the oxide layer, which will be further discussed in this paper.  
 211 We suggest that the continuously increase in the anodization time allows to achieve steady state while  
 212 the diameter of the flower buds, the thickness of the oxide layer and the platelets thickness were still  
 213 improved. Diameter increased to 1150 nm, oxide layer thickness from  $0.1 \pm 0.02$  to  $1.35 \pm 0.1 \text{ }\mu\text{m}$ , and

214 platelets thickness from  $11.2 \pm 0.1$  to  $15.6 \pm 0.2$  nm, respectively for WO\_15 min and WO\_120 min (see  
 215 Table 1). It was found the flowers buds were evenly distributed on the layer for the anodizing time  
 216 of 90 min (Figure 2). However, further extension of the anodization time had a negative effect on  
 217 the WO<sub>3</sub> nanostructures, whereby the regular flower-like nanostructure of WO<sub>3</sub> was destroyed and  
 218 the anodic oxide was composed of irregular, poorly distributed flower buds. Moreover, slow  
 219 transformation of the flower buds again into nanoplatelets was observed. The reason might be  
 220 attributed to the higher etching rate on the WO<sub>3</sub> surface layer with extension of the anodization time  
 221 up to 120 minutes (see Fig. 2). Similar observation of the flower-like structure growth with an  
 222 extension of the anodization time was also studied and published by Amal group[29].



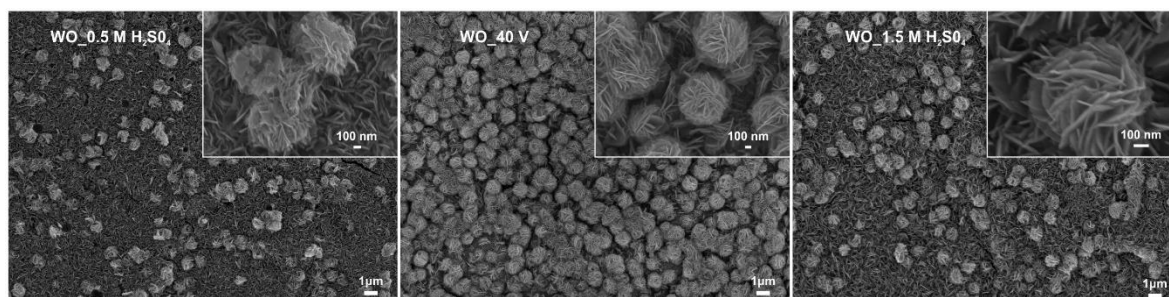
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224 **Figure 2.** Effect of the anodization time on the morphology of the WO<sub>3</sub> NFs. Fluoride content 0.5 wt.%,  
 225 H<sub>2</sub>SO<sub>4</sub> concentration 1.0 M, anodization potential 40 V.

### 226 3.1.3 Effect of the sulphuric acid concentration

227 A significant impact of the sulphuric acid concentration on the homogeneity of the samples was  
 228 noticed. Too low (0.5 M) or too high (1.5 M) concentration caused disorganization of the nanoplatelets  
 229 forming the oxide layer. Moreover, for the both mentioned concentrations, the layers consisted of  
 230 evenly distributed nanoplatelets with poorly formed irregular buds. According to the literature, for  
 231 the initial oxidation step occurs, the W foil needs to be in contact with the oxidizing acid which  
 232 initially oxidize into WO<sub>2</sub><sup>2+</sup> and results in the formation of the continues oxide film[29,43]. However,  
 233 we assume that too low acid concentration resulted too slow nucleation rate (WO\_0.5 M H<sub>2</sub>SO<sub>4</sub>).  
 234 Furthermore, it was found that the increase in the acidity of the environment resulted in etching of  
 235 the ions WO<sub>2</sub><sup>2+</sup> ions as it was confirmed from the Pourbaix diagram [47] and thus less distributed  
 236 flower-buds were observed (see Figure 3). El-Basiouney *et al.* also concluded that the dissolution of  
 237 WO<sub>3</sub> oxide layer in acidic medium takes place, which is consistent with the below proposed  
 238 mechanism. The optimal concentration for forming regular flower buds was 1.0 M reaching the  
 239 highest diameter of  $1.21 \pm 0.1$  nm. The increase of the acid concentration had a slight influence on the  
 240 oxide layer and platelets thickness, the changes from  $1.17 \pm 0.1$  to  $1.0 \pm 0.1$  μm and from  $13.4 \pm 0.2$  to  
 241  $15.3 \pm 0.3$  nm, respectively for WO\_0.5 M H<sub>2</sub>SO<sub>4</sub> and WO\_1.5 M H<sub>2</sub>SO<sub>4</sub>, were observed.





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243

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**Figure 3.** Effect of the sulphuric acid concentration on the morphology of  $\text{WO}_3$  NFs. Fluoride content 0.5 wt.%, anodization potential 40 V, anodization time 90 min.

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### 3.1.4 Effect of the sodium fluoride concentration

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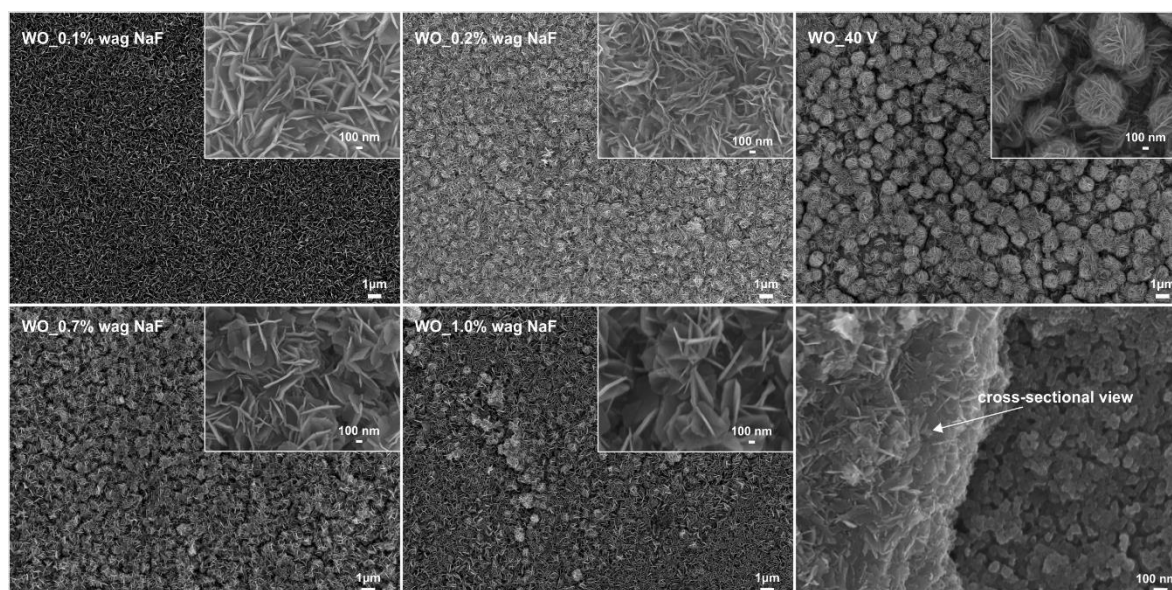
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The effect of fluoride content concentration was investigated by the anodization of the samples at 40 V for 90 minutes in the electrolyte containing 0.5 M  $\text{H}_2\text{SO}_4$  in the range of 0.1 to 1.0 wt.% NaF. The small content of  $\text{F}^-$  ions resulted in a growth of the layers consisted of the regular nanoplakelets (0.1 wt.%). The self-assembly flower buds have already occurred at 0.2 wt.% NaF. Regularly formed buds were found for the WO\_0.5 wt.% NaF sample with the diameter equalled  $1.21 \pm 0.1$  nm. Further increased of the NaF concentration led to deformations of the flowers buds morphology to single, packed nanoplakelets. Moreover, the results revealed that with the increasing amount of NaF concentration, increase of sharpened edges of the nanoplakelets was observed. The oxide layer and platelets thickness increased slightly from  $1.0 \pm 0.01$  to  $1.15 \pm 0.01$   $\mu\text{m}$  and from  $11.3 \pm 0.1$  to  $17.8 \pm 0.3$  nm, respectively for WO\_0.1 wt.% NaF and WO\_1.0 wt.% NaF, implying that the NaF concentration was mainly responsible for the flower buds formation.



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**Figure 4.** Effect of the sodium fluoride concentration on the morphology of the  $\text{WO}_3$  NFs.  $\text{H}_2\text{SO}_4$  concentration 1.0 M, anodization potential 40 V, anodization time 90 min.

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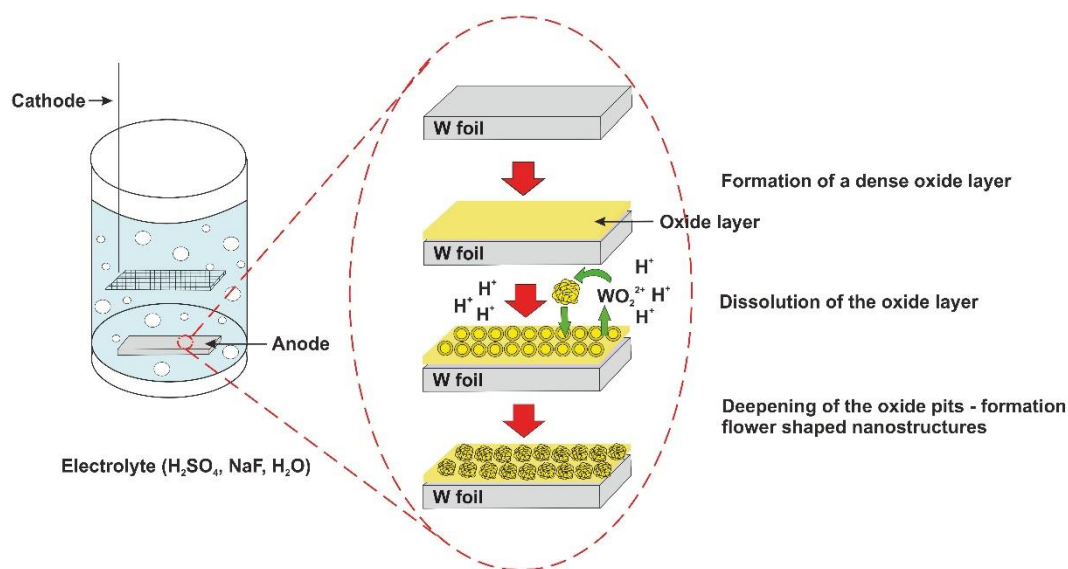
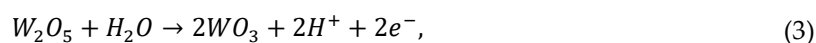
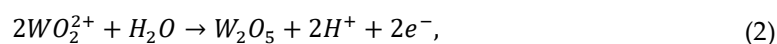
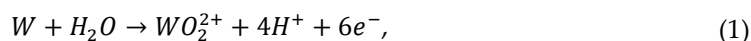
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Similarly to the formation of the anodized titanium dioxide nanotubes films ( $\text{TiO}_2$  NTs) in the electrolyte containing fluorine ions [48,49], the  $\text{WO}_3$  NFs films were formed as a result of field-assisted oxide growth and localized chemical dissolution. Based on the above results and literature reports [28,29,50], we propose the following mechanism of the  $\text{WO}_3$  NFs thin film growth process: (i) formation of a dense oxide layer on W foil, (ii) activation of the barrier oxide layer by fluoride ions resulting in chemical dissolution of the oxide layer and (iii) deepening of the oxide pits that in time branch out formation flower shaped nanostructures (Scheme 1). The proposed schematic illustration of the anodic growth of oxide layer is presented on Scheme 1 according to the following equations:





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**Scheme 1** Schematic illustration of the WO<sub>3</sub> NFs thin film growth process.

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Reaction 1 describes the electrochemical dissolution of tungsten foil and formation of an oxide layer of WO<sub>2</sub><sup>2+</sup> on the surface. Subsequently, the WO<sub>2</sub><sup>2+</sup> ions are attracted by water molecules and form an intermediate W<sub>2</sub>O<sub>5</sub> oxide. Since the WO<sub>2</sub><sup>2+</sup> and intermediate W<sub>2</sub>O<sub>5</sub> are decomposed in an aqueous environment, the oxide layer growth. Further oxide growth is controlled by the field enhanced ion transport through the growing oxide. This process is self-limiting under a constant applied voltage, as the field within the oxide layer is progressively reduced by the increasing oxide thickness, thus resulting in the growth of a compact WO<sub>3</sub> film with finite thickness. During the initial step, disordered pits are formed and a nanoporous structure is subsequently developed by the chemical dissolution of the oxide layer or the direct complexation of WO<sub>2</sub><sup>2+</sup> at the oxide electrolyte interface and form soluble fluoride complexes[49]. The anodic growth of the WO<sub>3</sub> oxide layer became a competition between its and the chemical dissolution of the tungsten oxide layer in a fluoride containing electrolyte solution[51,52]. During the anodization process, the constant growth and chemical dissolution of the tungsten oxide layer occurs simultaneously and a steady state is established when the growth rate at the metal oxide interface occurs at the same as the dissolution rate of oxide film at the outer interface[13,28].

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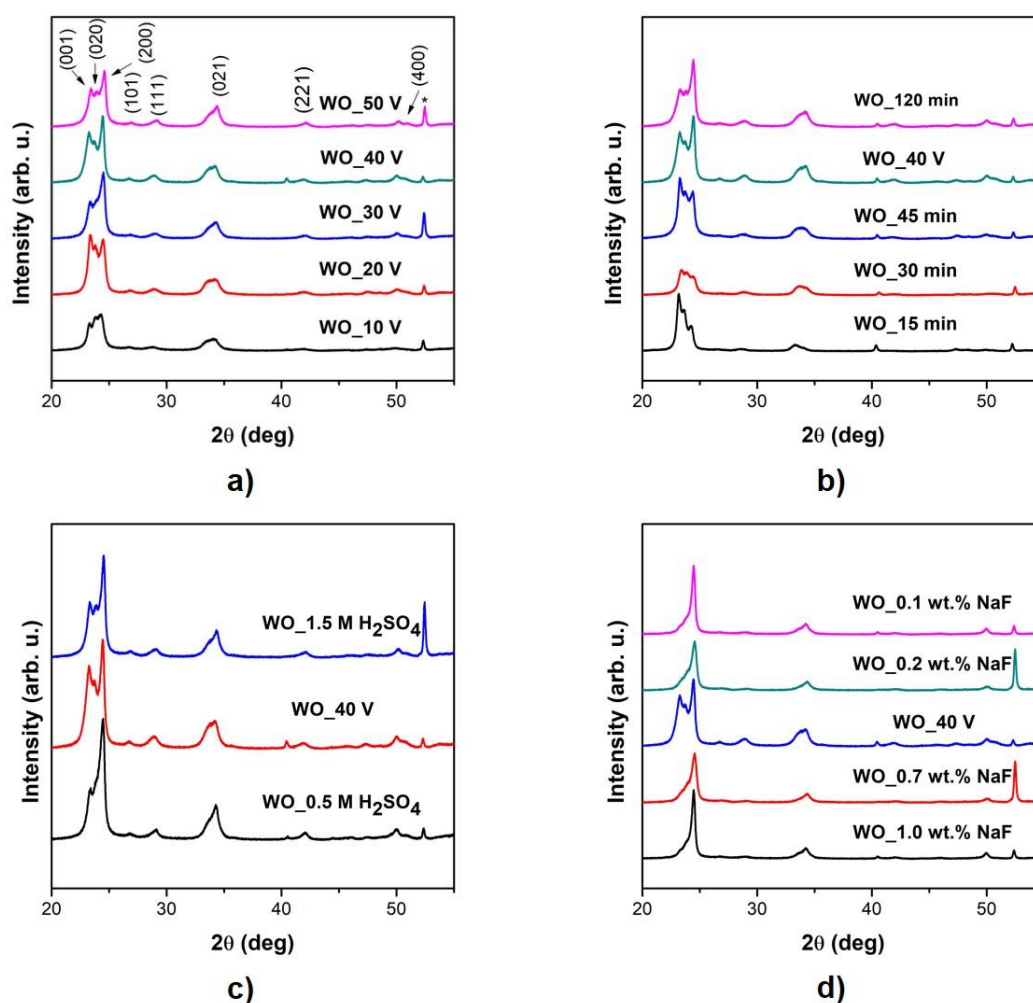
As mentioned above, the anodic growth of the compact oxide on the metal surface and the formation of pores is governed by chemical dissolution of the formed oxide layers induced by fluoride ions from the electrolyte solution and formation of a soluble fluoride complex. The key point is to find an optimize amount of the fluoride content, needed to form a porous structure, allows for the successful formation of the flower-like structure. Too low or too high concentration revealed presence of the nanoplatelets instead of nanoflowers (see Figure 4) indicating that the presence of fluoride ions is essential to generate soluble ions (WO<sub>2</sub><sup>2+</sup>) and form the flower-like structure. Moreover, an increase in the NaF concentration (to 1.0 wt.%) resulted in slowly etching of the oxide

293 layer and exhibited poorly organized flowers buds co-existence together with nanoplatelets (see  
294 Figure 2). Lai [53] also investigated the influence of the fluoride content on the growth of anodic  $\text{WO}_3$   
295 nanotubular structure and realised that optimization of fluoride ions played crucial role in controlling  
296 formation the chemical dissolution reaction on the interface of  $\text{W}/\text{WO}_3$  and thus growth of the  
297 nanotubes. It should be remarked that dissolution of  $\text{WO}_3$  occurs over the entire  $\text{W}$  foil, thus with  
298 extending oxidation time we observed gradual transformation of the nanoplatelets into flower-like  
299 structure after 90 minutes of the anodization process. Further time extension resulted in an opposite  
300 effects (Figure 2). Moreover, literature survey reports that the dissolution of  $\text{WO}_3$  in acid medium  
301 takes place *via* the formation of  $\text{WO}_2^{2+}$  species[54]. Therefore, it might lead to the precipitation of  
302 primary formed  $\text{WO}_2^{2+}$  and allows for thickening of the  $\text{WO}_3$  nanostructured film. However, we  
303 observed that the increase of the acid concentration resulted in the formation of slightly thinner oxide  
304 layer (see Table 1). Therefore, we assume that the dissolution of the oxide layer could be driven by  
305 the instability of  $\text{WO}_2^{2+}$  in the presence of aqueous electrolyte solution at room temperature and  
306 presence of high anodization potential.

### 307 3.2 Crystallographic structure

308 Figure 5 displays the X-ray patterns of the self-assembled  $\text{WO}_3$  NFs film. The reflection patterns  
309 of the  $\text{WO}_3$  could be indexed to a triclinic phase. The  $\text{WO}_3$  phase was represented by the peaks (001),  
310 (020), (200), (101), (111), (021), (221) and (400) crystal planes at  $2\theta$  located around  $23.3^\circ$ ,  $23.8^\circ$ ,  $24.4^\circ$ ,  
311  $26.8^\circ$ ,  $28.9^\circ$ ,  $33.8^\circ$ ,  $41.4^\circ$  and  $50.5^\circ$ . The peaks indexed to  $\text{W}$  foils were found at  $2\theta$  of approximately  
312  $52.5^\circ$  (denoted in Figure 5 “\*”),  $58.5^\circ$  and  $73.4^\circ$ . The XRD patterns of the samples anodized for 90  
313 minutes in the potential range of 10 – 50 V are given in Figure 5a. As noted, the potential of 10 V was  
314 too low for successful formation of the oxide layers thus it was hard to establish any of the peaks in  
315 range of  $23^\circ$ – $25^\circ$ . It was found that with increasing anodization potential the intensity of the peak  
316 (200), characteristic for triclinic phase of  $\text{WO}_3$ , increased. However, further rise to 50 V resulted in the  
317 intensity decrease. As the anodization time increased we observed that the intensity of the (001) peak  
318 decrease whereas the (200) one started to intensively arise and reached its highest intensity with an  
319 oxidation time of 120 minutes (see Figure 5b). As the sulphuric acid concentration increased, the  
320 intensity of the (200) peak started to decrease whereas the intensity of peaks indexed to (001) and  
321 (020) became higher (Figure 5c). An optimum concentration which allowed for the growth of the  
322 oxide layer was 1.0 M. Interestingly, concentration of fluoride content strongly affected on the peaks  
323 height indexed to  $\text{WO}_3$  (Figure 5d). Only the  $\text{WO}_{0.5}$  wt.% NaF sample revealed the presence of the  
324 peaks (001), (020), (200), (101) and (111), whereas the rest of the samples in this series possessed the  
325 intensive peak indexed to (200). Reduction of the (001) peak and thus enhancement of the (200) peak  
326 intensity in all the samples could be ascribed to the improvement of the nanostructured layer and  
327 compact oxide layers obtained at different conditions. The  $\text{WO}_3$  NFs samples possessed analogous  
328 crystallinity, while different synthesis conditions resulted in changes of the refined lattice parameters  
329  $a$ ,  $b$ , and  $c$  as well as unit cell volume, which are gathered in Table S1.





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**Figure 5.** XRD patterns of the  $\text{WO}_3$  NFs samples differing in (a) applied potential, (b) anodization time, (c)  $\text{H}_2\text{SO}_4$  and (d) NaF concentration.

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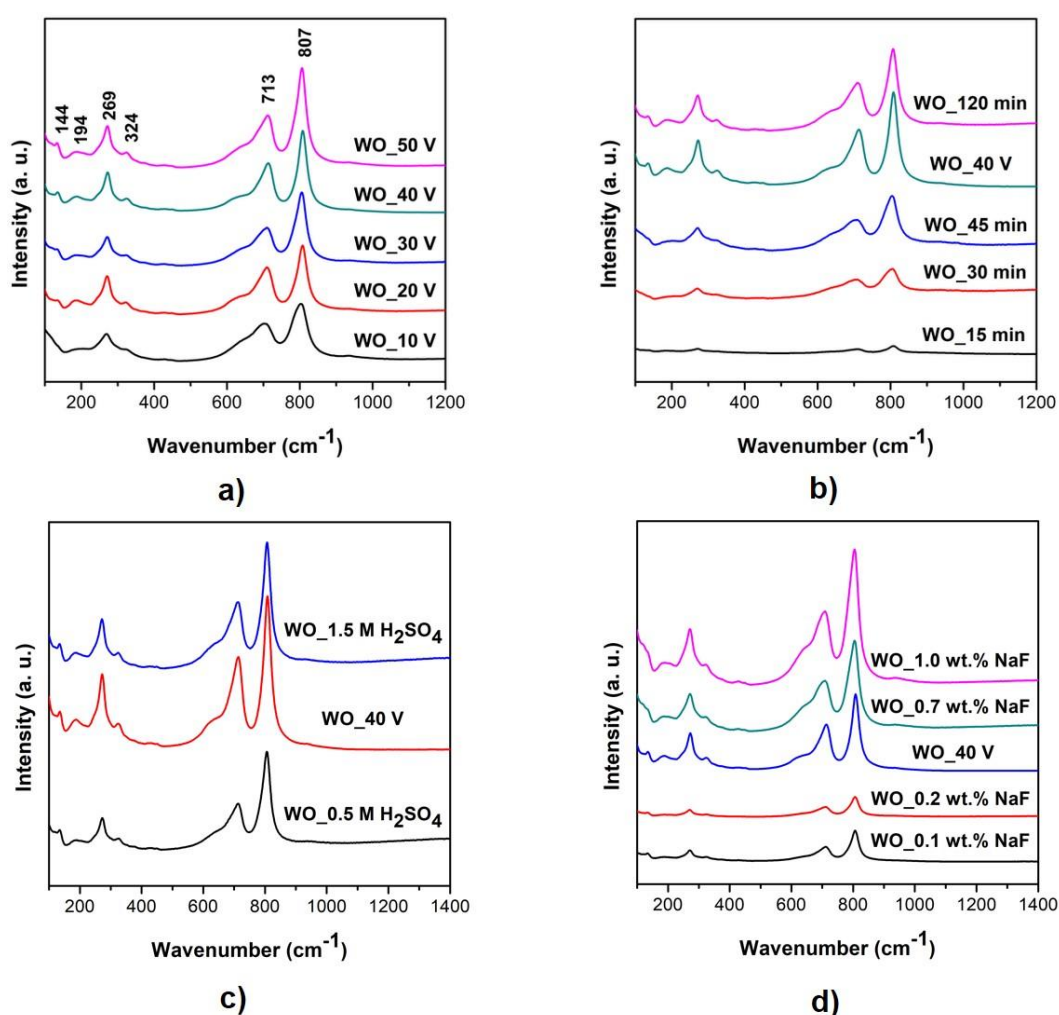
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The Raman spectra of the samples are displayed in Figure 6. As it can be seen, we can determine three frequency regions. The first one appeared at lower frequencies (below  $200\text{ cm}^{-1}$ ) in regards to the relative translational or rotational motions of the  $\text{WO}_6$  octahedral. The second region occurs between wave\_numbers of  $200 - 400\text{ cm}^{-1}$  indicating the O-W-O bending mode. The last region with peaks located at around  $600 - 900\text{ cm}^{-1}$  is indexed to the O-W-O stretching modes[55]. The Raman spectra confirmed the  $\text{WO}_3$  triclinic phase due to the presence of the characteristic peaks at around  $144, 194, 269, 324, 713$  and  $807\text{ cm}^{-1}$ . No Raman signal corresponding to the tungsten was observed. The bands of  $269$  and  $324\text{ cm}^{-1}$  can be attributed to the  $\delta$  bending (O-W-O) and  $\nu$  (W-O-W) vibrations modes of the bridging oxygen[56]. The strongest peaks observed at  $713$  and  $807\text{ cm}^{-1}$  can be assigned to the stretching modes arising from O-W-O[23,56]. All the samples exhibited the same features but as the preparation conditions changed, an intensity of the peaks starts to arising (especially at around  $269$  and  $807\text{ cm}^{-1}$ ) indicated the formation of the oxide layer (see Figure 6 a-d).





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**Figure 6.** Raman spectra of the  $\text{WO}_3$  NFs samples differing in (a) anodization potential, (b) anodization time (c)  $\text{H}_2\text{SO}_4$  and (d) NaF concentration.

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### 3.3. Optical and photoluminescence properties

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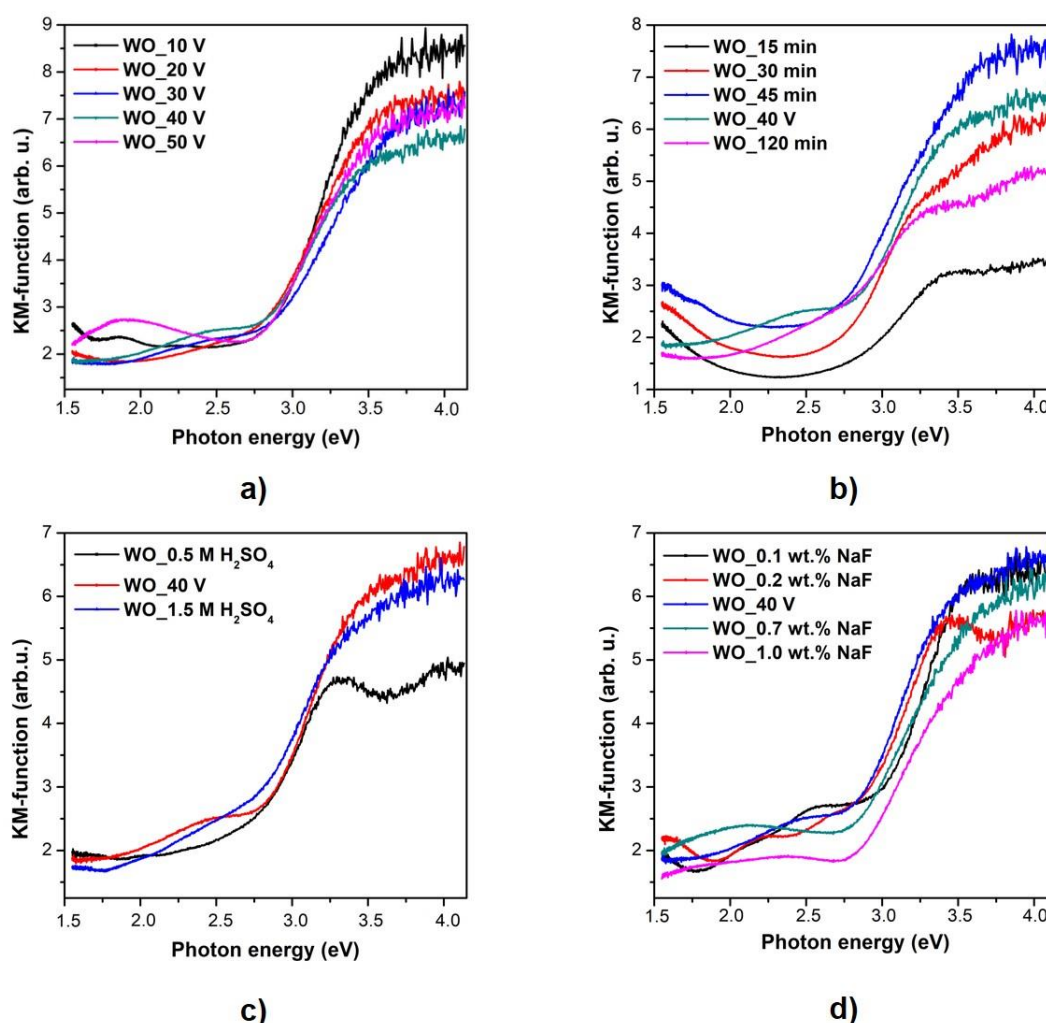
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The change in the optical properties of the as-prepared  $\text{WO}_3$  films by the photoabsorption studies (Figure S1) and corresponding optical band gap energy as presented in Figure 7 were investigated. The absorption edge of the series differing in the applied potential was located approximately of 470 nm for all samples (Figure S1a). As the anodization time increase from 15 to 120 minutes the absorption edge shifted from 460 to 540 nm (see Figure S1b), respectively. Higher acid concentration practically did not influence on the absorption edge which was around 475 nm (Figure S1c). For the series differing in fluoride ions concentration, the absorption edge was around 450 nm for all sample except the one obtained with the lowest amount of NaF (0.1 wt.%) – approximately 430 nm (Figure S1d). An absorption shift in the 450 – 800 nm range was observed for all samples, confirming changes in the structure of the obtaining samples. Raised absorbance values at higher wavelengths could be attributed to the presence of oxygen vacancies on the surface film. Furthermore, it was found that as the anodization time increased the photoabsorbance values decreased due to decrease in amount of suboxides and oxygen vacancies. A similar observation was described by Amal et al. who analysed the influence of duration time period on the flower-shaped  $\text{WO}_3$  growth[29].

364 The band gap of WO<sub>3</sub> NFs films can be determined by considering the indirect transition  
 365 between 2p electrons from the valence band (VB) of oxygen and the 5d the conduction band (CB) of  
 366 tungsten based on the Tauc's plot according to the following equation[57,58]:

$$\alpha h\nu = A(h\nu - E_g)^n, \quad (4)$$

367 where  $\alpha$ ,  $\nu$ , A and  $E_g$  are absorption coefficient, light frequency, proportionality constant, and  
 368 band gap, respectively. The band gap energies of the WO<sub>3</sub> NFs samples were calculated with equation  
 369 4 and the data were collected in Table 1 and displayed on Figure 7. The values were in accordance  
 370 with the literature, where the band gap values for the flower-shaped WO<sub>3</sub> film was around 2.5 -  
 371 2.75 eV[37,40].

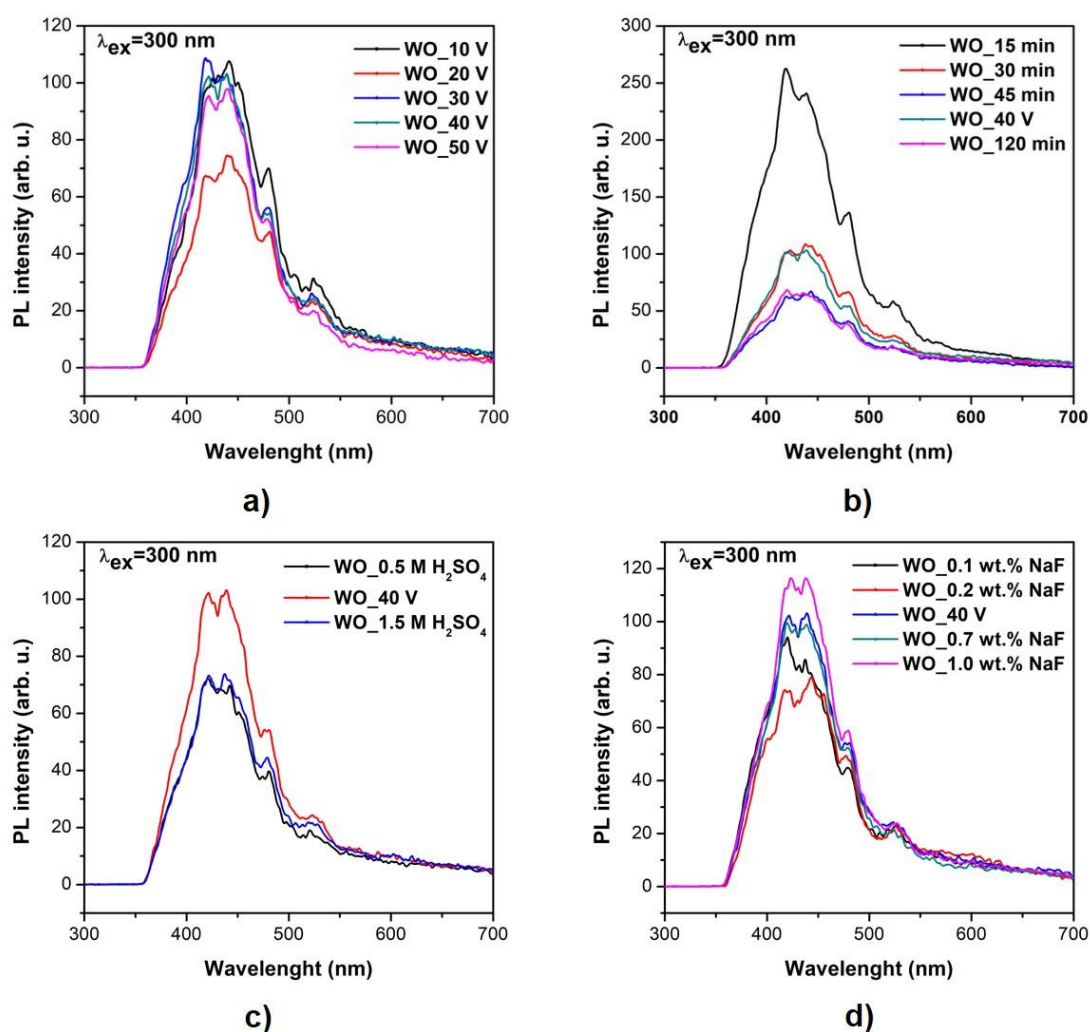


372  
 373 **Figure 7.** Optical band gap spectra of the WO<sub>3</sub> NFs samples differing in (a) anodization potential,  
 374 (b) anodization time (c) H<sub>2</sub>SO<sub>4</sub> and (d) NaF concentration.

375 Photoluminescence spectra for the as-obtained WO<sub>3</sub> NFs samples in four different series are  
 376 shown in Figure 8 a-d. Typically for the oxygen metal based semiconductors, the PL spectra are  
 377 composed of UV emission and a visible emission band attributed to the surface defects. All the  
 378 samples exhibited the same PL features with different intensity depending on the preparation  
 379 conditions. The emission was positioned at around 420, 438, 481 and 527 nm. The values at around  
 380 420, 438 and 481 nm might be attributed to the presence of intrinsic defects such as oxygen vacancies  
 381 giving rise to donor states located below the CB. The emission located at wavelength of 527 nm



382 indicated the possibility of band recombination (intrinsic states rather than surface states). The values  
 383 are consistent with those reported for the others semiconductors, such as TiO<sub>2</sub> and ZnO[59,60].



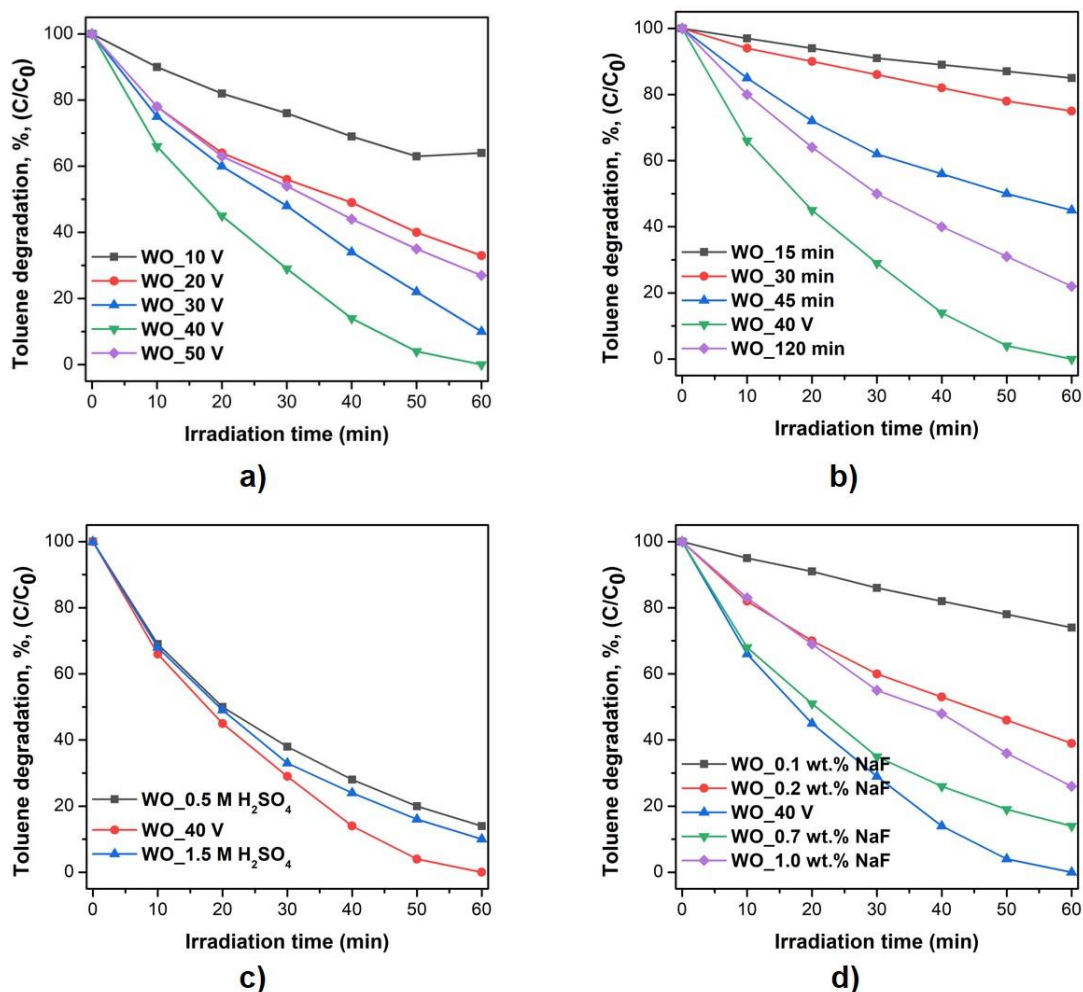
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385 **Figure 8** Photoluminescence spectra of the WO<sub>3</sub> NFs samples differing in (a) anodization potential,  
 386 (b) anodization time (c) H<sub>2</sub>SO<sub>4</sub> and (d) NaF concentration.

### 387 3.4 Photocatalytic activity

388 The potential environmental applications of the as-prepared WO<sub>3</sub> samples were investigated in  
 389 a model reaction of toluene degradation from the air mixture to simple degradation products like  
 390 CO<sub>2</sub> and H<sub>2</sub>O. This approach was employed to analyse the effect of the preparation conditions,  
 391 anodization potential and time, as well as electrolyte composition, concentration of sulphuric acid  
 392 and sodium fluoride, on the WO<sub>3</sub> NFs photoactivity. The obtained results are displayed in Figure 9  
 393 and Table 1. It was found that samples preparation route by changing applied potential, anodization  
 394 time and fluoride content significantly influenced the photocatalytic activity. In the case of different  
 395 H<sub>2</sub>SO<sub>4</sub> concentration, the samples WO<sub>0.5</sub> M H<sub>2</sub>SO<sub>4</sub>, WO<sub>1.0</sub> M H<sub>2</sub>SO<sub>4</sub> and WO<sub>1.5</sub> M H<sub>2</sub>SO<sub>4</sub> had  
 396 comparable efficiency, 86%, 100% and 90%, respectively. As shown in Figure 9 a-d the highest  
 397 photocatalytic activity, reaching 100% of toluene removal after 60 minutes of irradiation, achieved  
 398 the sample prepared in the following conditions: anodization potential 40 V, anodization time  
 399 90 min, fluoride content 0.5 wt.% and H<sub>2</sub>SO<sub>4</sub> concentration 0.5 M. Besides, further increase of the each  
 400 parameter resulted in an opposite effect, decrease of photoactivity was observed for WO<sub>50</sub> V,  
 401 WO<sub>120</sub> min, WO<sub>1.5</sub> M H<sub>2</sub>SO<sub>4</sub> and WO<sub>0.1</sub> wt.% NaF, 73%, 78%, 90% and 74%, respectively.





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**Figure 9** Photoactivity of the WO<sub>3</sub> NFs samples in gas phase degradation of toluene under Vis light irradiation ( $\lambda_{\max} = 415$  nm) differing in (a) anodization potential, (b) anodization time (c) H<sub>2</sub>SO<sub>4</sub> and (d) NaF concentration.

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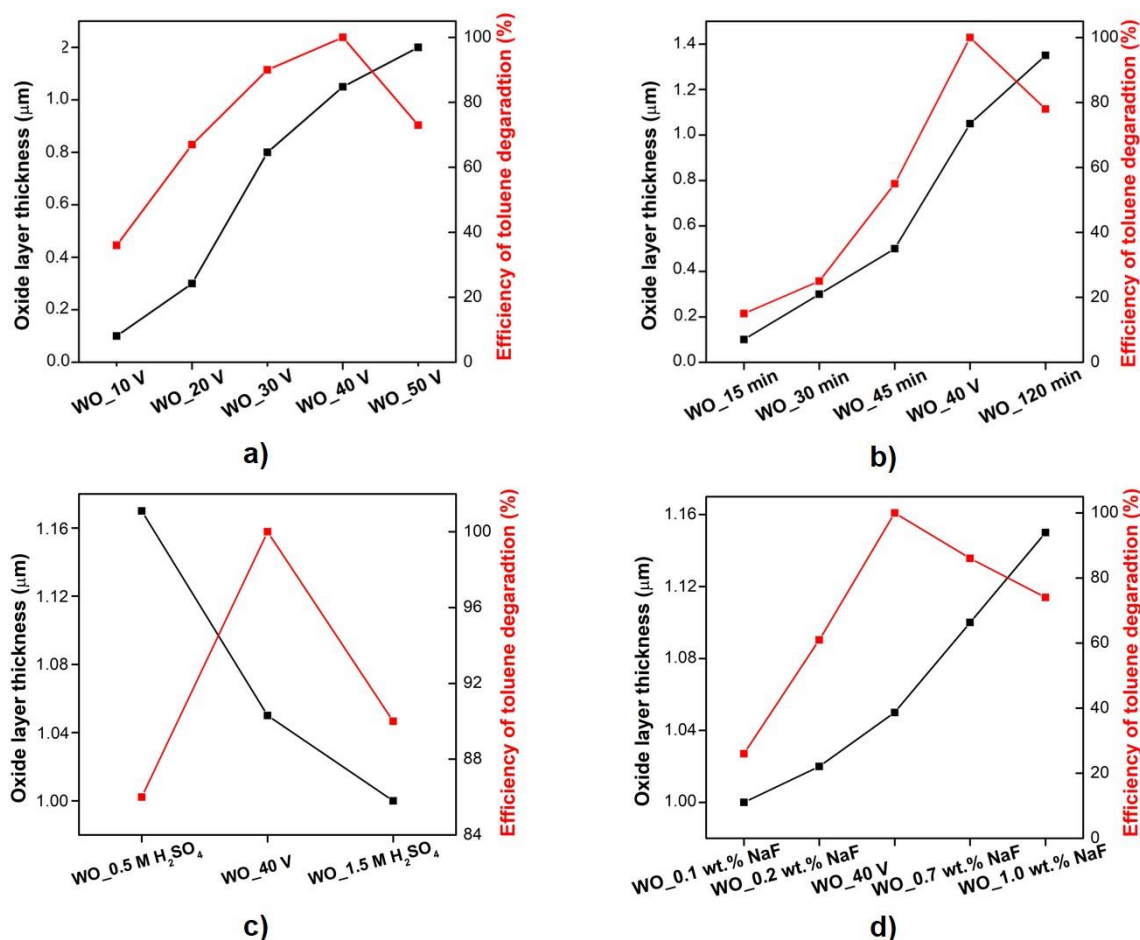
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In line with the other photocatalysts, the photoactivity of WO<sub>3</sub> depends on the lifetime of photogenerated charge carriers. Surface electron-hole recombination is extremely high with most of charge carriers recombining on the photocatalyst surface before the redox reactions and this recombination rate must be reduced in order to improve the photocatalytic activity. It seems that a simple toluene degradation route in presence of the WO<sub>3</sub> samples relies on the attack of the OH• radical to the methyl group of toluene. The key parameter that influence the improvement of the photocatalytic activity towards air pollutants degradation is morphology control. According to the literature, it was found that the flower-like three-dimensional (3D) structure photocatalysts possesses (i) larger surface area and (ii) plenty of mesopores with ordered open pore frameworks, into which photocatalyst may effectively harvest visible light due to multiple scattering[61,62]. Moreover, the large surface of flower-like structure could decrease the recombination efficiency of the photoexcited carries and favours their transfer to the surface to react with organic pollutants. When comparing the photoactivity of the as-prepared WO<sub>3</sub> samples with their morphological parameters, it was obvious that well-ordered, regular shape of nanoflowers array films were more efficient than the random occurred flowers buds or nanoplatelets (Table 1, Figure. 10). It could be ascribed to the more effective separation for the photogenerated electron-hole pairs and the larger surface area of the nanoflowers structure[63]. As apparent from the above discussed experimental data, the highest photocatalytic activity in the reaction of toluene decomposition (100%) after 60 min of LED irradiation ( $\lambda_{\max} =$

424 415 nm) was reached for the WO<sub>40</sub> V sample prepared in the following conditions: 40 V, 90 min,  
 425 1.0 M H<sub>2</sub>SO<sub>4</sub> and 0.5 wt.% NaF. This sample also possessed the most uniform distribution and regular  
 426 shape of the flowers buds with the diameter equalled to  $1.21 \pm 0.1 \mu\text{m}$ . We noticed that the efficiency  
 427 of toluene degradation increased with increasing thickness of WO<sub>3</sub> array film, and then had a down  
 428 trend (Fig. 10 a-d). The experimental results indicated that the 1.05  $\mu\text{m}$  thick WO<sub>3</sub> film appeared with  
 429 a maximum photodegradation efficiency of the toluene removal. Previous literature suggests that if  
 430 the metal oxide thin film is thicker than the depth of light penetration, the bottom film absorbs only  
 431 few incident photons and serves as an inter support and resulted in the decrease of the photocatalytic  
 432 activity for a thick film[64].



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**Figure 10.** Influence of the oxide layer thickness on the efficiency of toluene degradation in the series differing in (a) applied potential, (b) anodization time, (c) H<sub>2</sub>SO<sub>4</sub> and (d) NaF concentration.

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### 3.5 Photoelectrochemical activity

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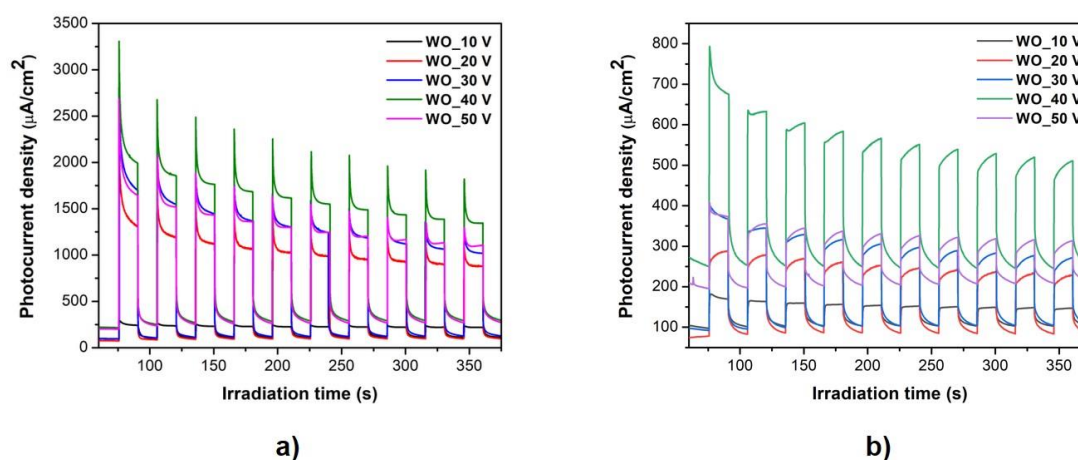
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Photoelectrochemical response of the samples prepared at different applied potential was evaluated as photocurrent measurements in light off/on cycles with 1.5 V applied voltage. Photocurrent was registered under both UV-Vis (Figure 11a) and Vis irradiation (Figure 11b). No significant decay of the photocurrent was observed during the photoelectrochemical measurements under both sources of irradiation indicating good stability of obtained photoelectrodes. The photocurrent under UV-Vis light was approximately 5 times higher in comparison with visible light irradiation. In addition, the same tendency in sample photoelectroactivity was observed for both types of light sources, namely as the anodizing voltage increased to 40 V, the measured photocurrent increased and then decreased (for a sample obtained at 50 V). This could be related to the high ordering of the platelet structure and the improvement of the nanostructured layer thickness with larger surface area which was achieving with increasing anodization voltage (up to 40 V). Prepared

448 samples, especially the most photoactive sample (WO\_40 V), exhibited the large surface of flower-  
 449 like structure which increased the interface between oxide layer and electrolyte, facilitating incident  
 450 photons absorbance and the charge transfer for the separation of photoexcited hole – electrons pairs.



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452 **Figure 11.** Photocurrent response of selected WO<sub>3</sub> samples under a) UV-Vis and (b) Vis irradiation  
 453 ( $\lambda > 420$  nm) at 1.5 V in 0.1 M Na<sub>2</sub>SO<sub>4</sub>. The switch on/off period is 30 s.

## 454 5. Conclusions

455 In summary, we have described a simple and environmental friendly one-step anodization  
 456 synthesis method of the WO<sub>3</sub> NFs thin films in the aqueous solution containing fluoride ions. The  
 457 effect of synthesis conditions, applied potential and anodization time, as well as electrolyte  
 458 composition, concentration of H<sub>2</sub>SO<sub>4</sub> and NaF contents, on the morphology, photocatalytic activity  
 459 and photoelectrochemistry properties of the WO<sub>3</sub> photocatalysts was presented. The results revealed  
 460 the growth of the nanoplatelets which were slowly transformed into the nanoflowers structure  
 461 depending on the synthesis parameters. The optimal conditions allowing the synthesis of the well-  
 462 organize, regular shaped flower buds with the diameter of 1.21  $\mu$ m were: anodization potential of  
 463 40 V, anodization time 90 minutes, the electrolyte containing 1.0 M H<sub>2</sub>SO<sub>4</sub> and 0.5 wt.% NaF. The  
 464 photocatalytic activity of the as-prepared WO<sub>3</sub> samples towards decomposition of air contaminants  
 465 was investigated in the model reaction of toluene degradation. Moreover, we found that the  
 466 morphology control was the key avenue to improve the photocatalytic activity. Hence, the samples  
 467 which consisted of the irregular shaped nanoplatelets exhibited lower photocatalytic activity than  
 468 those with the flower-like structure. The highest photoactivity in toluene degradation and in  
 469 photocurrent generation under UV-Vis and Vis irradiation achieved the sample with the most  
 470 ordered and regular flower buds, WO<sub>40</sub> V. Moreover, we noticed that the thickness of the oxide  
 471 layer was directly related with the photocatalytic efficiency. The thicker WO<sub>3</sub> layer was, the higher  
 472 decline in the photoactivity was observed because of difficulties of light penetration into deeper  
 473 layers. Although, the highest photoactivity exhibited the sample with thick of 1.05  $\mu$ m (100%,  
 474 WO<sub>40</sub> V) and further increase of the oxide layer thickness resulted in an opposite effect. These  
 475 finding suggest that self-assembly, regular shape flower-like WO<sub>3</sub> thin film activated with low-  
 476 powered LEDs as an irradiation source ( $\lambda_{\text{max}} = 415$  nm) could be a promising material for air  
 477 purification. The synthesis of visible light active and stable photocatalyst can boost the technology of  
 478 air purification since they exploit a renewable energy source and allow to avoid an extra operational  
 479 costs and other limitations associated with artificial illumination.

480 **Supplementary Materials:** Figure S1: Photoabsorption spectra of the WO<sub>3</sub> NFs samples from four series each  
 481 with a different (a) applied potential, (b) anodization time, (c) H<sub>2</sub>SO<sub>4</sub> and (d) NaF concentration., Table S1: Lattice  
 482 parameters of the WO<sub>3</sub> NFs samples.



483 **Author Contributions:** Conceptualization, P.M.; investigation, A.P., M.R., A.Z.-M., J.L., P.M.; supervision, J.L.,  
484 A.Z.-M. and P.M.; writing (review and editing) A.P., A.Z.-M., J.L., P.M.

485 **Conflicts of Interest:** The authors declare no conflict of interest.

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