

Article

# Synthesis of TiO<sub>2</sub>/WO<sub>3</sub> Composite Nanofibers by a Water-Based Electrospinning Process and Their Application in Photocatalysis

Vincent Otieno Odhiambo<sup>1,\*</sup>, Aizat Ongarbayeva<sup>1</sup>, Orsolya Kéri<sup>1</sup>, László Simon<sup>2</sup> and Imre Miklós Szilágyi<sup>1</sup>

- <sup>1</sup> Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4., H-1111 Budapest, Hungary; ayzatonga@gmail.com (A.O.); orsolyakeri@gmail.com (O.K.); imre.szilagyi@mail.bme.hu (I.M.S.)
- <sup>2</sup> Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary; simon.laszlo92@gmail.com
- \* Correspondence: vincent.odhiambo@mail.bme.hu

Received: 6 April 2020; Accepted: 24 April 2020; Published: 2 May 2020



**Abstract:**  $TiO_2/WO_3$  nanofibers were prepared in a one-step process by electrospinning. Titanium(IV) bis(ammonium lactato)dihydroxide (TiBALDH) and ammonium metatungstate (AMT) were used as water-soluble Ti and W precursors, respectively. Polyvinylpyrrolidone (PVP) and varying ratios of TiBALDH and AMT were dissolved in a mixture of H<sub>2</sub>O, EtOH and CH<sub>3</sub>COOH. The as-spun fibers were then heated in air at 1 °C min<sup>-1</sup> until 600 °C to form TiO<sub>2</sub>/WO<sub>3</sub> composite nanofibers. Fiber characterization was done using TG/DTA, SEM–EDX, FTIR, XRD, and Raman. The annealed composite nanofibers had a diameter range of 130–1940 nm, and the results showed a growth in the fiber diameter with an increasing amount of WO<sub>3</sub>. The photocatalytic property of the fibers was also checked for methyl orange bleaching in visible and UV light. In visible light, the photocatalytic activity increased with an increase in the ratio of AMT, while 50% TiBALDH composite fibers showed the highest activity among the as-prepared fibers in UV light.

**Keywords:** electrospinning; polyvinylpyrrolidone; titanium(IV) bis(ammonium lactato) dihydroxide; ammonium metatungstate; nanofibers; photocatalysis

# 1. Introduction

The main challenges in enhancing the efficiency of the photocatalytic activity of  $TiO_2$  are to increase its light-absorbing range to a higher wavelength and to decrease the speed of the charge carriers to recombine [1–5]. Different methods of overcoming these problems have been reported. One such strategy is to prepare composites of  $TiO_2$  with semiconductor metal oxides that have a narrow bandgap. Tungsten oxide has been widely reported to have excellent photochromic and electrochromic properties. WO<sub>3</sub> has a higher discharge capacity, a smaller bandgap, and is, therefore, a suitable compound to combine with  $TiO_2$  [6–8]. Many methods of coupling  $TiO_2$  with WO<sub>3</sub> have been reported. Smith et al. prepared  $TiO_2$ –WO<sub>3</sub> composite nanotubes by anodic oxidation of their precursors [9]. Szilagyi et al. used electrospinning to synthesize WO<sub>3</sub> fibers and coated them with  $TiO_2$  using atomic layer deposition (ALD) [10]. Reyes et al. incorporated WO<sub>3</sub> into  $TiO_2$  nanotubes by electrodeposition [11]. Chakornpradit et al. used sol-gel and electrospinning methods to prepare  $TiO_2/WO_3$  composite micro-nanofibers [12]. Epifani et al. prepared  $TiO_2/WO_3$  nanocomposites by colloidal processing in solvothermal conditions [13]. The challenge of synthesizing composite  $TiO_2/WO_3$  precursors are water-soluble.



In our previous study, we used a water-soluble precursor to prepare  $TiO_2$  nanofibers by electrospinning [14]. The study presents the possibility of fabricating composite nanofibers from  $TiO_2$  and other metal oxides in a one-step synthesis using electrospinning. Electrospinning has been reported extensively as a suitable method for preparing nanofibers that are uniform and have a large surface area [15–19]. This technique uses an electrically charged jet of polymer solution, or melt is used to form nanofibers that are collected on a grounded target [20–24].

In this study, an aqueous solution of polyvinylpyrrolidone (PVP), titanium(IV) bis(ammonium lactate)dihydroxide (TiBALDH), and ammonium metatangstate (AMT) was electrospun, and the as-synthesized fibers annealed to form TiO<sub>2</sub>/WO<sub>3</sub> composite nanofibers. We investigated how the properties of the electrospun fibers changed when different volume ratios of precursor solutions were used. A simultaneous thermogravimetry/differential thermal analysis (TG/DTA) of the electrospun fibers was done in air and nitrogen to determine the annealing temperatures. By annealing the electrospun fibers at 600 °C in air, the polymer was removed, and the precursors decomposed to form TiO<sub>2</sub>/WO<sub>3</sub> nanofibers. The fibers were studied using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). The specific surface area of the annealed fibers was studied by the Bruneauer–Emmett–Teller (BET) method. The annealed nanofibers were investigated by X-ray diffraction (XRD), Raman spectroscopy and UV-Vis diffuse reflectance spectroscopy as well. The bandgap of the annealed fibers was also determined. The photocatalytic activity of the fibers in UV and visible light was investigated using methyl orange.

#### 2. Materials and Methods

#### 2.1. Materials

All the chemicals were of analytical grade and used as received. Polyvinylpyrrolidone (PVP,  $(C_6H_9NO)_n$ , × K-90), ethyl alcohol, acetic acid, titanium(IV) bis(ammonium lactato)dihydroxide solution (50 wt % in water), and Ammonium metatungstate were obtained from Sigma Aldrich, (Budapest, Hungary).

### 2.2. Preparation and Characterization of TiO<sub>2</sub>/WO<sub>3</sub> Fibers

The polymer solution had 20 wt % PVP dissolved in a 1:1 mixture of acetic acid and ethyl alcohol. An aqueous solution of AMT contained 1 g of AMT in 1 mL of distilled water. The solution for electrospinning was prepared by adding 2 mL of the polymer solution to 2 mL of an aqueous solution containing different TiBALDH: AMT volume ratios 100:0, 90:10, 50:50, 10:90 and 0:100. The solution was magnetically stirred at 25 °C for 6 h. For the electrospinning procedure, the solution was transferred into a 10 mL plastic syringe fitted with a needle. The voltage used was 20 kV, the flow rate was 1 mLh<sup>-1</sup>, and the distance between the needle and the collecting plate was 15 cm.

The thermal properties of the as-spun fibers were studied in air and nitrogen using an A STD 2960 Simultaneous DTA/TGA (TA Instruments Inc., New Castle, DE, USA) thermal analyzer. A heating rate of 10 °C min<sup>-1</sup> was used, and the fibers were heated to 600 °C. The as-spun fibers were calcined in air at 600 °C for 6 h to form nanofibers. The heating rate used was 1 °C min<sup>-1</sup> up to 600 °C.

The morphology of the as-spun and annealed fibers was characterized by SEM using a JEOL JSM-5500LV (Tokyo, Japan) scanning electron microscope coupled with energy dispersive X-ray (EDX). All the fibers were covered with a thin Au/Pd layer, using a sputter coater.

The surface area analysis of the annealed fibers was done by a multipoint Brunauer–Emmett–Teller (BET) method, using nitrogen adsorption/desorption isotherm measurements at 25 °C.

A Nicolet 6700 (Thermo fisher scientific USA) Fourier transform infrared spectrophotometer was used to obtain the FTIR spectra of the fibers in the range of  $400-4000 \text{ cm}^{-1}$  in transmittance mode.

The XRD patterns of the annealed fibers were obtained with a X'pert Pro MPD X-ray diffractometer (PANalytical, Almelo, Netherlands), using Cu K<sub> $\alpha$ </sub> irradiation. Raman spectroscopy was done using

a Jobin Yvon Labram Raman instrument (Horiba, Kyoto, Japan) with an Olympus BX41 microscope (Olympus, Tokyo, Japan) fitted with a green Nd-YAG laser. The measuring range was 72–1560 cm<sup>-1</sup>.

The diffuse reflectance UV-Vis absorption spectra of the annealed fibers were measured by (Avantes BV, Apeldoorn, Netherlands) with fiber optic spectrophotometer between 250 and 800 nm. The bandgap was calculated using the Kubelka–Munk theory from the Tauc plots [25].

# 2.3. Photocatalysis

The photocatalytic activity of the fibers was investigated in both UV and visible light. In a quartz cuvette, 1.0 mg of the annealed fibers mixed with 3 mL of  $4 \times 10^{-5}$  M aqueous methyl orange solution. The samples were left in the dark for 24 h and then exposed to UV and visible light lamps. The decomposition of the methyl orange was checked by measuring the absorbance of its most intense peak (464 nm) every half-hour using a Jasco V-550 UV-VIS spectrometer (Jasco, Tokyo, Japan) for 240 minutes.

# 3. Results and Discussion

Figure 1 shows the TG/DTA curves for the thermal decomposition of the as-spun fibers in air and nitrogen. The decomposition process was continuous in both conditions. The DTA curves for the decomposition process in air showed exothermic peaks because of the decomposition reactions that occurred. In nitrogen, the fiber components decomposed without combustion, and the DTA curves showed endothermic peaks. The residual mass was higher when the fibers were decomposed in nitrogen due to the presence of unburnt carbon [15].

When the fibers were decomposed in air, there was a loss of mass of about 6% at around 100 °C due to the loss of water. The exothermic peaks between 300 and 350 °C (Figure 1a–e) are due to the decomposition and combustion of PVP, and AMT also begins to decompose at this stage. In Figure 1b–e, the exothermic peaks at around 400–480 °C are due to the degradation and decomposition of TiBALDH. In Figure 1a–d, the exothermic peak between 510 and 560 °C can be attributed to the burning of the carbon residue of PVP. The as-formed h-WO<sub>3</sub> also transformed into m-MO<sub>3</sub> in this stage [26]. The decomposition of the polymer and the degradation of the precursors finished at around 560 °C. The resulting fibers showed a significant increase in mass with an increase in the concentration of AMT. This is consistent with the theoretical knowledge, since AMT is about 94.1% WO<sub>3</sub> by mass, while TiBALDH is 27.2% TiO<sub>2</sub> by mass.

The SEM images of the as-spun fibers are shown in Figure 2. The diameter of the fibers increased with an increase in the AMT ratio. The diameter was 630–800 nm for 100% TiBALDH, 720–1050 nm for 90% TiBALDH, 920–1170 nm for 50% TiBALDH, 980–1200 nm for 10% TiBALDH and 1930–2950 nm for 0% TiBALDH.

As shown in Figure 3, the diameter of the fibers reduced after annealing. This can be attributed to the decomposition and degradation of PVP, TiBALDH, and AMT. The fibers had a diameter between 130 and 170 nm for 100% TiBALDH, 420 and 480 nm for 90% TiBALDH, 700 and 740 nm for 50% TiBALDH, 780 and 1020 nm for 10% TiBALDH, and 1610 and 1940 nm for 0% TiBALDH. The elemental composition and the specific surface area of the annealed fibers are shown in Table 1.



**Figure 1.** Thermogravimetry/differential thermal analysis (TG/DTA) curves of as-spun fibers annealed in air and nitrogen: (**a**) 0% titanium(IV) bis(ammonium lactate)dihydroxide (TiBALDH, (**b**) 10% TiBALDH, (**c**) 50% TiBALDH, (**d**) 90% TiBALDH and (**e**) 100% TiBALDH.



**Figure 2.** SEM images of as-spun fibers: (**a**) 0% TiBALDH, (**b**) 10% TiBALDH (**c**) 50% TiBALDH, (**d**) 90% TiBALDH, and (**e**) 100% TiBALDH.



**Figure 3.** SEM images of annealed fibers (**a**) 0% TiBALDH, (**b**) 10% TiBALDH (**c**) 50% TiBALDH, (**d**) 90% TiBALDH, and (**e**) 100% TiBALDH.

**Table 1.** The diameter of as-spun and annealed fibers, elemental composition and specific surface area of annealed fibers.

Fibers	Diameter (d/nm)		Elemental Composition (wt %)			Surface Area (m²/g)
	as-Spun Fibers	Annealed Fibers	Ti	W	0	
100% TiBALDH	630-800	130-170	35.8		64.2	1.5
90% TiBALDH	720-1050	420-480	32.2	6.0	61.8	49.4
50% TiBALDH	920-1170	700-740	12.1	23.1	64.7	25.8
10% TiBALDH	980-1200	780-1020	7.3	28.8	63.9	11.3
0% TiBALDH	1930–2950	1610–1940		36.8	63.2	9.3

The FTIR spectra of the fibers are shown in Figure 4. For the as-spun nanofibers, the vibration peaks at around 3200 cm<sup>-1</sup> are due to the stretching vibrations of –OH from water and –NH functional groups from AMT [27]. Peaks between 2980 and 2870 cm<sup>-1</sup> are associated with the C–H stretching vibrations from the lactato ligands of TiBALDH. The peak at around 1700 cm<sup>-1</sup> corresponds to the C=O stretching and the –NH bending vibrations in TiBALDH, while around 1430 cm<sup>-1</sup> and 1470 cm<sup>-1</sup> bands bending –CH bonds of CH<sub>2</sub> in PVP and deformation mode of the NH<sub>4</sub><sup>+</sup> ion in AMT can be observed. C–O and C–N stretching bands of PVP can be seen in the range 1250–1220 cm<sup>-1</sup>. Stretching and bending vibrations of C=C can be seen at 1550 cm<sup>-1</sup> and 980 cm<sup>-1</sup>, respectively [28]. Peaks at around 700–900 cm<sup>-1</sup> can be attributed to W–O vibrations. The peak at around 550 cm<sup>-1</sup> is assigned to Ti–O stretching motions [29]. After annealing C–H, C=O, C–N, and C=C, vibration peaks disappeared, demonstrating that the annealing process was successful.



**Figure 4.** FTIR spectra of as-spun and annealed fibers: (**a**) 0% TiBALDH, (**b**) 10% TiBALDH, (**c**) 50% TiBALDH, (**d**) 90% TiBALDH and (**e**) 100% TiBALDH.

Figure 5 shows the XRD patterns of the as-spun and annealed fibers. The XRD pattern of the as-spun fibers did not show distinct diffraction peaks due to the amorphous nature of the as-spun fibers. The XRD pattern of 100% TiBALDH fibers was indexed to ICDD 04-022-6651. The pattern had peaks corresponding to the anatase form of TiO<sub>2</sub>. The diffraction peaks at  $2\theta = 25.3$ , 28.6, 48.1, 55.1 and 62.7 corresponded to (101), (112), (200), (105) and (204), respectively [30,31]. The XRD pattern of 0% TiBALDH fibers was indexed to ICDD 04-021-7427 and corresponded to the monoclinic form of WO<sub>3</sub>. The pattern showed the main characteristic peaks corresponding to (002), (020), (200) and (202) planes at  $2\theta = 23.1$ , 23.6, 24.4, and 34.2, respectively [32]. The XRD patterns for 90%, 50%, and 10% TiBALDH showed peaks corresponding to the anatase form of TiO<sub>2</sub> and monoclinic forms of WO<sub>3</sub>.



Figure 5. XRD patterns: (a) as spun fibers, and (b) as annealed fibers.

Figure 6 shows the Raman spectra of the annealed fibers; 100% TiBALDH showed Raman active modes for anatase TiO<sub>2</sub>; 144 cm<sup>-1</sup> (E<sub>g</sub>), 197 cm<sup>-1</sup> (E<sub>g</sub>), 399 cm<sup>-1</sup> (B<sub>1g</sub>), 515 cm<sup>-1</sup> (A<sub>1g</sub>) and 630 cm<sup>-1</sup> (E<sub>g</sub>) [19]. The peaks at 720 cm<sup>-1</sup> and 805 cm<sup>-1</sup> for 0% TiBALDH can be assigned to the O=W=O stretching vibrations characteristic of monoclinic WO<sub>3</sub> [33]. The Raman spectra for annealed 10%, 50%, and 90% TiBALDH showed Raman peaks for both anatase TiO<sub>2</sub> and monoclinic WO<sub>3</sub>.



Figure 6. Raman spectra of annealed fibers.

The diffuse reflectance spectra in Figure 7 showed that the absorption edge of the fibers increased with an increase in the concentration of AMT. The increase in the absorption edge implies that the composite nanofibers can absorb light at a higher wavelength. Therefore, they can utilize light more efficiently during the process of photocatalysis [22]. The bandgap was calculated from the Tauc plots (Figure S1) using Kubelka-Munk theory. The bandgap decreased as the ratio of AMT increased, as shown in Table 2. This confirmed that the electrospinning process resulted in the coupling of  $TiO_2$  with WO<sub>3</sub>, hence a decrease in the bandgap. This is significant, as the decrease in the bandgap can enable the composite fibers to absorb light in the visible region of the electromagnetic spectrum.



**Figure 7.** Diffuse reflectance UV-Vis spectra: (**a**) 100% TiBALDH, (**b**) 90% TiBALDH (**c**) 50% TiBALDH, (**d**) 10% TiBALDH, and (**e**) 0% TiBALDH.

Table 2. Danugap values for the annealed libers.	

Fibers	100% TiBALDH	90% TiBALDH	50% TiBALDH	10% TiBALDH	0% TiBALDH
Bandgap [eV]	3.06	2.96	2.73	2.62	2.58

Figure 8 illustrates the rate of photocatalytic degradation of methyl orange in the presence of annealed fibers in UV and visible light. In UV light, P25 showed higher photocatalytic activity than the annealed fibers. For the as-prepared fibers, 50% TiBALDH fibers showed the highest photocatalytic activity after 240 min, and its activity was very close to that of P25. This can result from the combination of TiO<sub>2</sub> and WO<sub>3</sub>, which decreased the rate of recombination of photogenerated electrons and holes during the photocatalytic process. In visible light, 0% TiBALDH fibers had the greatest photocatalytic activity. For the composite fibers, the photocatalytic activity increased with the increase in the ratio of AMT. The fibers had increased absorption edges and could absorb light at a higher wavelength.

The reaction constants for the degradation of methyl orange was calculated using a pseudo first-order kinetics model. A plot of  $-\ln(A/A^{\circ})$  against time gave a straight line (Figures S2 and S3), and the slope represented the apparent rate constant ( $k_{app}$ ) for the degradation reactions, as shown in Tables 3 and 4. The  $k_{app}$  was consistent with the photocatalytic activity of the as-spun fibers. The fibers that showed better photocatalytic activity had higher  $K_{app}$  values.

The photocatalytic efficiency of the 50% TiBALDH fibers compared favorably with other composite TiO2/WO3 fibers reported by other authors, as shown in Table 5.



**Figure 8.** The degradation rate of methyl orange by annealed fibers in (**a**) UV light, and (**b**) visible light.

**Table 3.** Reaction rate constant and  $r^2$  values for the photocatalytic degradation of methyl orange in UV light.

Sample	k <sub>app</sub> (min <sup>-1</sup> )	r <sup>2</sup>
100% TiBALDH	0.0009	99.6
90% TiBALDH	0.0007	99.8
50% TiBALDH	0.0009	98.9
10% TiBALDH	0.0003	82.7
0% TiBALDH	0.0002	98.4
Bare Methyl Orange	0.00006	86.6
P25	0.001	99.8

**Table 4.** Reaction rate constant and  $r^2$  values for the photocatalytic degradation of methyl orange in visible light.

Sample	k (min <sup>-1</sup> )	r <sup>2</sup>
100% TiBALDH	0.0001	86.1
90% TiBALDH	0.0002	91.4
50% TiBALDH	0.0001	87.2
10% TiBALDH	0.0002	78.1
0% TiBALDH	0.0002	92.0
Bare Methyl Orange	0.0006	86.0

Table 5. Comparison of photocatalytic efficiency of various WO<sub>3</sub>/TiO<sub>2</sub> nanofibers.

Photocatalyst	Method of Preparation	A/A°	Authors
WO <sub>3</sub> /TiO <sub>2</sub> films	Electrospinning and deposition	0.85	Soares et al. [34]
$WO_3/TiO_2$ core shell nanofibers	Electrospinning and ALD	0.65	Szilagyi et al. [10]
WO <sub>3</sub> /TiO <sub>2</sub> -wood fibers	Hydrothermal synthesis	0.2	Gao et al. [35]
WO <sub>3</sub> /TiO <sub>2</sub> nanoparticles	Hydrothermal sol-gel synthesis	0.2	Paula et al. [36]

# 4. Conclusions

 $TiO_2/WO_3$  composite fibers were successfully synthesized by electrospinning, using water-soluble precursors and annealing. The fibers were characterized by TG/DTA, SEM-EDX, FTIR, XRD, and Raman. Annealed fibers had the anatase form of  $TiO_2$  and the monoclinic form of  $WO_3$ . Different precursor ratios were used to investigate how the concentration of the precursors affected different properties of the fibers. The diameter of the fibers depended on the precursor ratio and increased with the increasing

concentration of AMT. Composite fibers with 50% TiBALDH had higher photocatalytic activity in UV light than pure fibers. This can be as a result of the reduction in the rate of recombination of the charge carriers. The photocatalytic activity of the fibers in visible light increased with an increasing ratio of AMT. Coupling TiO<sub>2</sub> with WO<sub>3</sub> can increase the absorption edge of the fibers, hence making the fibers absorb light at a higher wavelength of the spectrum, thereby improving the photocatalytic property of TiO<sub>2</sub>.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2079-4991/10/5/882/s1, Figure S1: Tauc plots for annealed fibers (a) 100% TiBALDH (b) 90% TiBALDH (c) 50% TiBALDH (d) 10% TiBALDH (e) 0% TiBALDH, Figure S2: Graph for apparent rate constant and r<sup>2</sup> values for the photocatalytic degradation of methyl orange in UV light, Figure S3: Graph for apparent rate constant and r<sup>2</sup> values for the photocatalytic degradation of methyl orange in Visible light.

Author Contributions: Conceptualization, I.M.S., V.O.O. and O.K.; methodology, L.S., V.O.O. and O.K.; investigation, A.O. and V.O.O.; funding acquisition, I.M.S.; resources, I.M.S.; supervision, I.M.S.; writing—original draft preparation, V.O.O.; writing—review and editing, A.O., O.K., L.S. and I.M.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** An NRDI K 124212 and an NRDI TNN\_16 123631 grants are acknowledged. The research within project No. VEKOP-2.3.2-16-2017-00013 was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund. The research reported in this paper was supported by the Higher Education Excellence Program of the Ministry of Human Capacities in the frame of Nanotechnology and Materials Science research area of Budapest University of Technology (BME FIKP-NAT) and Stipendium Hungaricum scholarship grant.

**Acknowledgments:** The authors thank Tamas Igricz (Budapest University of Technology and Economics, Department of Organic Chemistry and Technology) for help in the Raman measurements and Krisztina László (Budapest University of Technology and Economics, Department of Physical Chemistry and Materials Science) for help in specific surface area measurements.

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

### References

- Etacheri, V.; Di Valentin, C.; Schneider, J.; Bahnemann, D.; Pillai, S.C. Visible-light activation of TiO2 photocatalysts: Advances in theory and experiments. *J. Photochem. Photobiol. C Photochem. Rev.* 2015, 25, 1–29. [CrossRef]
- Chen, Z.; Zhao, J.; Yang, X.; Ye, Q.; Huang, K.; Hou, C.; Zhao, Z.; You, J.; Li, Y. Fabrication of TiO<sub>2</sub>/WO<sub>3</sub> Composite Nanofibers by Electrospinning and Photocatalystic Performance of the Resultant Fabrics. *Ind. Eng. Chem. Res.* 2016, 55, 80–85. [CrossRef]
- 3. Nagy, D.; Firkala, T.; Drotár, E.; Szegedi, Á.; László, K.; Szilágyi, I.M. Photocatalytic WO3/TiO2 nanowires: WO3 polymorphs influencing the atomic layer deposition of TiO2. *RSC Adv.* **2016**, *6*, 95369–95377. [CrossRef]
- 4. Justh, N.; Mikula, G.J.; Bakos, L.P.; Nagy, B.; László, K.; Parditka, B.; Erdélyi, Z.; Takáts, V.; Mizsei, J.; Szilágyi, I.M. Photocatalytic properties of TiO2@polymer and TiO2@carbon aerogel composites prepared by atomic layer deposition. *Carbon N. Y.* **2019**, *147*, 476–482. [CrossRef]
- Liu, H.; Zhang, Z.-G.; He, H.-W.; Wang, X.-X.; Zhang, J.; Zhang, Q.-Q.; Tong, Y.-F.; Liu, H.-L.; Ramakrishna, S.; Yan, S.-Y.; et al. One-Step Synthesis Heterostructured g-C3N4/TiO2 Composite for Rapid Degradation of Pollutants in Utilizing Visible Light. *Nanomaterials* 2018, *8*, 842. [CrossRef]
- Nakata, K.; Liu, B.; Goto, Y.; Ochiai, T.; Sakai, M.; Sakai, H.; Murakami, T.; Abe, M.; Fujishima, A. Visible Light Responsive Electrospun TiO2 Fibers Embedded with WO3 Nanoparticles. *Chem. Lett.* 2011, 40, 1161–1162. [CrossRef]
- Song, Y.-Y.; Gao, Z.-D.; Wang, J.-H.; Xia, X.-H.; Lynch, R. Multistage Coloring Electrochromic Device Based on TiO2 Nanotube Arrays Modified with WO3 Nanoparticles. *Adv. Funct. Mater.* 2011, 21, 1941–1946. [CrossRef]
- 8. Gao, H.; Zhang, P.; Hu, J.; Pan, J.; Fan, J.; Shao, G. One-dimensional Z-scheme TiO2/WO3/Pt heterostructures for enhanced hydrogen generation. *Appl. Surf. Sci.* **2017**, *391*, 211–217. [CrossRef]
- 9. Smith, Y.R.; Sarma, B.; Mohanty, S.K.; Misra, M. Formation of TiO2–WO3 nanotubular composite via single-step anodization and its application in photoelectrochemical hydrogen generation. *Electrochem. commun.* **2012**, *19*, 131–134. [CrossRef]

- 10. Szilágyi, I.M.; Santala, E.; Heikkilä, M.; Pore, V.; Kemell, M.; Nikitin, T.; Teucher, G.; Firkala, T.; Khriachtchev, L.; Räsänen, M.; et al. Photocatalytic properties of WO3/TiO2 core/shell nanofibers prepared by electrospinning and atomic layer deposition. *Chem. Vap. Depos.* **2013**, *19*, 149–155. [CrossRef]
- 11. Reyes, K.R.; Stephens, Z.D.; Robinson, D.B. Composite WO3/TiO2 nanostructures for high electrochromic activity. *ACS Appl. Mater. Interfaces* 2015, 7, 2202–2213. [CrossRef] [PubMed]
- 12. Chakornpradit, P.; Phiriyawirut, M.; Meeyoo, V. Preparation of TiO<sub>2</sub>/WO<sub>3</sub> Composite Nanofibers by Electrospinning. *Key Eng. Mater.* **2017**, *751*, 296–301. [CrossRef]
- Epifani, M.; Comini, E.; Díaz, R.; Andreu, T.; Genç, A.; Arbiol, J.; Siciliano, P.; Faglia, G.; Morante, J.R. Acetone Sensing with TiO2-WO3 Nanocomposites: An Example of Response Enhancement by Inter-oxide Cooperative Effects. *Procedia Eng.* 2014, *87*, 803–806. [CrossRef]
- Otieno, O.V.; Csáki, E.; Kéri, O.; Simon, L.; Lukács, I.E.; Szécsényi, K.M.; Szilágyi, I.M. Synthesis of TiO2 nanofibers by electrospinning using water-soluble Ti-precursor. *J. Therm. Anal. Calorim.* 2020, 139, 57–66. [CrossRef]
- Kéri, O.; Bárdos, P.; Boyadjiev, S.; Igricz, T.; Nagy, Z.K.; Szilágyi, I.M. Thermal properties of electrospun polyvinylpyrrolidone/titanium tetraisopropoxide composite nanofibers. *J. Therm. Anal. Calorim.* 2019, 137, 1249–1254. [CrossRef]
- Pradeep, D.; Dubey, R.S. Experimental Study of Electrospun TiO2 Nanofibers. Int. Res. J. Eng. Technol. 2017, 4, 1082–1083.
- Nasikhudin Ismaya, E.P.; Diantoro, M.; Kusumaatmaja, A.; Triyana, K. Preparation of PVA/TiO<sub>2</sub> Composites Nanofibers by using Electrospinning Method for Photocatalytic Degradation. *IOP Conf. Ser. Mater. Sci. Eng.* 2017, 202, 012011. [CrossRef]
- 18. Thenmozhi, S.; Dharmaraj, N.; Kadirvelu, K.; Kim, H.Y. Electrospun nanofibers: New generation materials for advanced applications. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2017**, *217*, 36–48. [CrossRef]
- 19. Zhang, H.; Yu, M.; Qin, X. Photocatalytic Activity of TiO2 Nanofibers: The Surface Crystalline Phase Matters. *Nanomaterials* **2019**, *9*, 535. [CrossRef]
- 20. Li, D.; Xia, Y. Fabrication of Titania Nanofibers by Electrospinning. Nano Lett. 2003, 3, 555–560. [CrossRef]
- 21. Im, J.S.; Kim, M.I.; Lee, Y.-S. Preparation of PAN-based electrospun nanofiber webs containing TiO2 for photocatalytic degradation. *Mater. Lett.* **2008**, *62*, 3652–3655. [CrossRef]
- 22. Liu, R.; Ye, H.; Xiong, X.; Liu, H. Fabrication of TiO2/ZnO composite nanofibers by electrospinning and their photocatalytic property. *Mater. Chem. Phys.* **2010**, 121, 432–439. [CrossRef]
- 23. Szilágyi, I.M.; Nagy, D. Review on one-dimensional nanostructures prepared by electrospinning and atomic layer deposition. *J. Phys. Conf. Ser.* **2014**, *559*, 012010. [CrossRef]
- Contreras-Cáceres, R.; Cabeza, L.; Perazzoli, G.; Díaz, A.; López-Romero, J.M.; Melguizo, C.; Prados, J. Electrospun Nanofibers: Recent Applications in Drug Delivery and Cancer Therapy. *Nanomaterials* 2019, *9*, 656. [CrossRef] [PubMed]
- 25. Bakos, L.P.; Karajz, D.; Katona, A.; Hernadi, K.; Parditka, B.; Erdélyi, Z.; Lukács, I.; Hórvölgyi, Z.; Szitási, G.; Szilágyi, I.M. Carbon nanosphere templates for the preparation of inverse opal titania photonic crystals by atomic layer deposition. *Appl. Surf. Sci.* **2020**, *504*, 144443. [CrossRef]
- Szilágyi, I.M.; Santala, E.; Heikkilä, M.; Kemell, M.; Nikitin, T.; Khriachtchev, L.; Räsänen, M.; Ritala, M.; Leskelä, M. Thermal study on electrospun polyvinylpyrrolidone/ammonium metatungstate nanofibers: Optimising the annealing conditions for obtaining WO3 nanofibers. *J. Therm. Anal. Calorim.* 2011, 105, 73–81. [CrossRef]
- 27. Zheng, M.; Gu, M.; Jin, Y.; Jin, G. Preparation, structure and properties of TiO2-PVP hybrid films. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2000**, *77*, 55–59. [CrossRef]
- 28. Yang, T.L.; Pan, C.T.; Chen, Y.C.; Lin, L.W.; Wu, I.C.; Hung, K.H.; Lin, Y.R.; Huang, H.L.; Liu, C.F.; Mao, S.W.; et al. Synthesis and fabrication of silver nanowires embedded in PVP fibers by near-field electrospinning process. *Opt. Mater.* **2015**, *39*, 118–124. [CrossRef]
- 29. Boga, B.; Székely, I.; Pap, Z.; Baia, L.; Baia, M. Detailed Spectroscopic and Structural Analysis of TiO2/WO3 Composite Semiconductors. *J. Spectrosc.* **2018**, *2018*, 6260458. [CrossRef]
- Lee, J.-S.; Lee, Y.-I.; Song, H.; Jang, D.-H.; Choa, Y.-H. Synthesis and characterization of TiO2 nanowires with controlled porosity and microstructure using electrospinning method. *Curr. Appl. Phys.* 2011, *11*, S210–S214. [CrossRef]

- Jo, M.; Cho, J.; Wang, X.; Jin, E.; Jeong, S.; Kang, D.-W. Improving of the Photovoltaic Characteristics of Dye-Sensitized Solar Cells Using a Photoelectrode with Electrospun Porous TiO2 Nanofibers. *Nanomaterials* 2019, 9, 95. [CrossRef] [PubMed]
- 32. Lu, R.; Zhong, X.; Shang, S.; Wang, S.; Tang, M. Effects of sintering temperature on sensing properties of WO 3 and Ag-WO 3 electrode for NO 2 sensor. *R. Soc. Open Sci.* **2018**, *5*, 171691. [CrossRef] [PubMed]
- Ernawati, L.; Wahyuono, R.A.; Muhammad, A.A.; Nurislam Sutanto, A.R.; Maharsih, I.K.; Widiastuti, N.; Widiyandari, H. Mesoporous WO3/TiO2 Nanocomposites Photocatalyst for Rapid Degradation of Methylene Blue in Aqueous Medium. *Int. J. Eng.* 2019, *32*, 1345–1352.
- 34. Soares, L.; Alves, A. Photocatalytic properties of TiO<sub>2</sub> and TiO<sub>2</sub>/WO<sub>3</sub> films applied as semiconductors in heterogeneous photocatalysis. *Mater. Lett.* **2018**, *211*, 339–342. [CrossRef]
- 35. Gao, L.; Gan, W.; Qiu, Z.; Zhan, X.; Qiang, T.; Li, J. Preparation of heterostructured WO3/TiO2 catalysts from wood fibers and its versatile photodegradation abilities. *Sci. Rep.* **2017**, *7*, 1102. [CrossRef]
- 36. Paula, L.F.; Hofer, M.; Lacerda, V.P.B.; Bahnemann, D.W.; Patrocinio, A.O.T. Unraveling the photocatalytic properties of TiO2/WO3 mixed oxides. *Photochem. Photobiol. Sci.* **2019**, *18*, 2469–2483. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).