



Article

Wide Response Range Photoelectrochemical UV Detector Based on Anodized TiO₂-Nanotubes@Ti@quartz Structure

Youqing Wang ^{1,*} , Miaomiao Zhang ¹, Wenxuan Wu ¹, Ze Wang ¹, Minghui Liu ^{1,2}, Tiantian Yang ¹ and Renqianzhuoma ¹

¹ Research Center for Semiconductor Materials and Devices, Shaanxi University of Science and Technology, Xi'an 710021, China

² School of Mechatronic Engineering, Xi'an Technological University, Xi'an 710021, China

* Correspondence: wangyouqing@sust.edu.cn

Abstract: Conventional sandwich structure photoelectrochemical UV detectors cannot detect UV light below 300 nm due to UV filtering problems. In this work, we propose to place the electron collector inside the active material, thus avoiding the effect of electrodes on light absorption. We obtained a TiO₂-nanotubes@Ti@quartz photoanode structure by precise treatment of a commercial Ti mesh by anodic oxidation. The structure can absorb any light in the near-UV band and has superior stability to other metal electrodes. The final encapsulated photoelectrochemical UV detectors exhibit good switching characteristics with a response time below 100 ms. The mechanism of the oxidation conditions on the photovoltaic performance of the device was investigated by the electrochemical impedance method, and we obtained the optimal synthesis conditions. Response tests under continuous spectroscopy confirm that the response range of the device is extended from 300–400 nm to 240–400 nm. This idea of a built-in collector is an effective way to extend the response range of a photoelectrochemical detector.

Keywords: UV detectors; photoelectrochemical; TiO₂ nanotubes; anodization; response range



Citation: Wang, Y.; Zhang, M.; Wu, W.; Wang, Z.; Liu, M.; Yang, T.; Renqianzhuoma. Wide Response Range Photoelectrochemical UV Detector Based on Anodized TiO₂-Nanotubes@Ti@quartz Structure. *Nanomaterials* **2024**, *14*, 439. <https://doi.org/10.3390/nano14050439>

Academic Editors: Andrea Orsini and Stefano Salvatori

Received: 26 January 2024

Revised: 21 February 2024

Accepted: 24 February 2024

Published: 28 February 2024



Copyright: © 2024 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

UV light refers to light with wavelengths ranging from 10 nm to 400 nm, which has numerous beneficial uses and unfavorable effects [1,2]. Therefore, it is important to quantitatively detect UV light. The UV detector is a device that converts light signals into electrical signals and is designed to detect UV light [3]. In recent years, UV detectors have been widely used in fields such as light curing, environmental monitoring, biomedicine, military, fire fighting, cultural relics protection, etc. [4–9]. Compared with traditional photoconductive UV detectors, a new type of photoelectrochemical (PEC) UV detector that has recently emerged has attracted much attention due to its advantages such as a simple preparation process, easy availability of raw materials, and no need for additional external voltage [10].

The traditional PEC UV detector consists of three parts: photoanode, electrolyte and counter electrode [11]. The photoanode is mainly composed of a transparent conductive substrate (such as FTO/ITO) and a semiconductor nanostructured thin film [12]. As the core part of the entire device, the role of the photoanode is to absorb UV light, generate electron–hole pairs, and conduct photogenerated electrons [10]. Ni et al. prepared a core–shell-structured self-powered UV photodetector with MgO-modified TiO₂ nanowires (NWs) using FTO glass as a conductive electrode, which has high responsiveness and high switching ratio [13]. However, due to the filtering effect of FTO/ITO thin films on UV light, traditional PEC UV detectors cannot detect UV light below 300 nm. To address the above issues and broaden the response range, Wei et al. reported a newly designed PEC UV detector that used a special stainless-steel-mesh-based electrode through which UV light

can directly reach the active material. The detector showed good photoelectric conversion ability and considerable switching performance, even under very weak irradiation [14]. Furthermore, Wang et al. prepared a novel PEC device with Ag NWs as conductive electrodes, quartz glass as the substrate, and TiO_2 nanoparticles as photoactive layers, and the response range of the UV detector was extended [15]. However, all of the above devices are complex to fabricate and have unstable performance. Both stainless steel and Ag metal are unstable under I^-/I_3^- electrolyte systems, which seriously affects the service life of the devices [16]. In addition, the active material attached to the electrode surface also falls off very easily during long-term operation.

As a wide band gap semiconductor, TiO_2 has received widespread attention due to its good photochemical properties, stability, easy availability of raw materials, and nontoxicity. Various methods for preparing nanostructured TiO_2 active layers have been reported. Compared with simple TiO_2 nanoparticles, TiO_2 nanotubes (NTs) have a larger specific surface area, faster electron transmission speed and lower electron recombination efficiency [17–19]. The electrochemical anodizing method as a common method for preparing TiO_2 -NTs generally uses pure Ti materials as the anode, and graphite or Pt sheets as the cathode [20]. Electrochemical oxidation can prepare TiO_2 -NTs with three-dimensional (3D) structures on different Ti substrates. Due to the ability of TiO_2 -NTs to absorb reflected and refracted light, the photon loss caused by scattering effects in the electrolyte can be minimized [21–24]. Currently, the TiO_2 -NTs/(FTO/ITO) structures have been applied in dye-sensitized solar cells (DSSC) and photocatalysis [25–27]. As far as we know, there are no reports of applying anodizing TiO_2 -NTs to the PEC UV detector.

In this work, we used the anodization method to generate the TiO_2 -NTs network structure on the Ti mesh in situ. Under precise control, the unoxidized Ti wire inside can serve as a conductive electrode to conduct photogenerated electrons to the external circuit. Finally, quartz glass with high transmittance throughout the entire UV region was used as the substrate to form a TiO_2 -NTs@Ti@quartz (abbreviated as TOTQ) type PEC-UV detector. This particular collector-built PEC UV detector successfully solves the problem of UV utilization of conventional structures and broadens the response range of the device from 300–400 nm to 240–400 nm. The in situ one-step preparation process improves the stability of the photoanode, while the all-Ti material system can be adapted to various electrolytes.

2. Materials and Methods

All the chemicals used in the experiment were analytical grade without further purification. The preparation process of the PEC-UV detector based on TOTQ is shown in Figure 1.

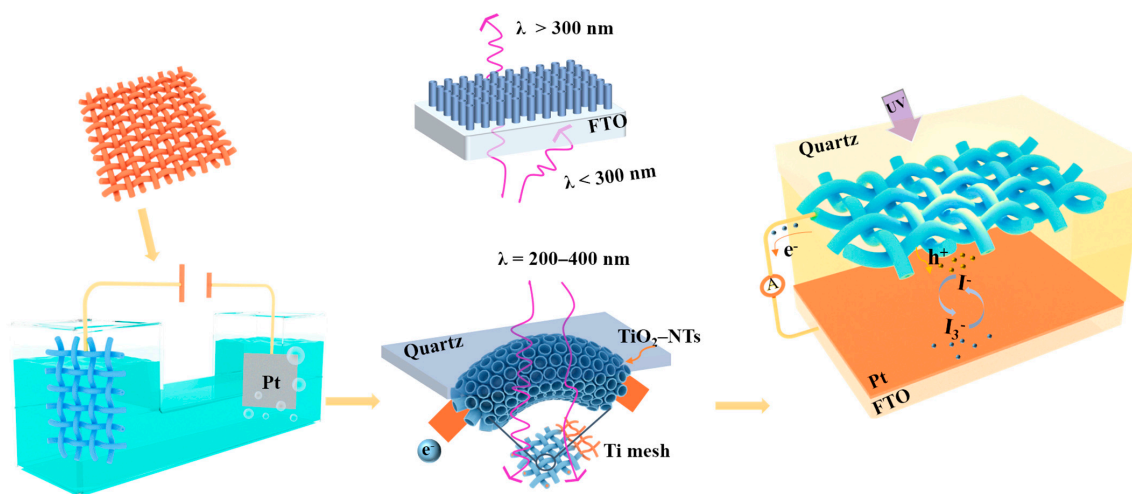


Figure 1. The preparation process and working principle of TOTQ PEC UV detector. The cleaned Ti mesh is anodized to form NTs, which are then attached to quartz glass to form a photoanode. PEC UV detector can be formed by packing the photoanode with the counter electrode and injecting electrolyte in the middle.

2.1. Preparation of Photoanodes

The raw material of Ti mesh used was sponge Ti with a purity of 99.5%. Firstly, the Ti mesh was cut into small square pieces of $8 \times 14 \text{ mm}^2$, which were then cleaned with acetone, absolute ethanol, and deionized water for 5 min, respectively. The traditional two-electrode system was used for anodic oxidation with Ti mesh as the working electrode and a Pt sheet with purity above 99.99% as the counter electrode. The distance between the two electrodes was about 2.5 cm. Anodization was carried out under the drive of a direct-current (DC) power supply (120 V, 3 A). The electrolyte consisted of 0.25 wt% NH_4F + 0.75 vol% H_2O glycol solution [28]. The oxidation was divided into two groups: control the oxidation voltage and oxidation time, respectively. The first group was oxidized at 15, 30, 45, 60, 75 and 90 V for 60 min, and the second group was oxidized for 30, 60, 90, 120, 150 and 180 min at 60 V. After anodization, the samples were rinsed with deionized water and then ultrasonically cleaned for 30 s. The purpose of ultrasonic cleaning was to remove the organic impurities on the oxide surface. After treatment, the samples were annealed in a muffle furnace at 550°C for 3 h [29].

2.2. Encapsulation of PEC UV Detectors

The prepared TiO_2 -NTs/Ti mesh was pasted on the quartz glass; then, the counter electrode was packaged and the distance between the photoanode and the counter electrode was controlled to be about $100 \mu\text{m}$. Finally, a drop of electrolyte was injected into the gap. The counter electrode was prepared by dropping the H_2PtCl_6 solution onto the FTO glass and annealing at 400°C for 30 min. The iodine-based electrolyte contained 1.12 g of 1,3-dimethylimidazole iodide, 0.038 g of iodine, 0.06 g of guanidine thiocyanate, 0.34 g of tert-butyl pyridine, 0.0335 g of lithium iodide, 4.25 mL of acetonitrile, and 0.75 mL of butyl cyanide. See previous works for more details [30,31].

2.3. Characterization

TiO_2 -NTs were prepared with a DC power supply. The microstructure of TiO_2 -NTs/Ti mesh was observed with a field emission scanning electron microscope (FESEM, Hitachi S-4800). UV transmission performance was tested with a UV-vis photometer. The crystal structure was tested with an X-ray diffractometer (XRD). The detection performance of PEC UV detectors was tested with the electrochemistry workstation.

3. Results and Discussion

3.1. Characteristics of TiO_2 -NTs@Ti Mesh Photoanode

The morphology and XRD patterns of the Ti mesh before and after anodization are shown in Figure 2. The surface of the Ti mesh is smooth with no cracking before anodization (Figure 2a). As shown in Figure 2b, the TiO_2 -NTs prepared by anodic oxidation on Ti mesh finally show cracks, which are mainly based on the difference perimeter between the bottom and the top of the connection point, as well as the van der Waals force and capillary force during the drying process [26]. The cracks between NTs are conducive to the diffusion of the electrolyte, but if the cracks are too deep, they will lead to a recombination reaction between the Ti core in the middle and the electrolyte directly. Figure 2c shows the digital images of the Ti mesh before (i) and after (ii) anodization. The color of the Ti mesh changes from silver gray to dark gray, and the reaction is intensified due to the rapid transfer of electrons at the electrolyte interface, leading to faster formation of NTs and higher transmittance of the Ti mesh. We peeled the TiO_2 -NTs formed by anodizing at 60 V for 60 min from the Ti substrate; as shown in Figure 2d,e, the average length of the TiO_2 -NTs is $2.8 \mu\text{m}$, the inner diameter is 46.82 nm, and the wall thickness is 18.11 nm. High-temperature annealing is an important means to transform TiO_2 from the amorphous phase to the anatase and rutile phases, and a high content of the anatase phase of TiO_2 is conducive to electronic transmission. The XRD pattern after annealing at 550°C is shown in Figure 2f. After high-temperature treatment for 3 h, the TiO_2 -NTs are transformed into the anatase phase.

Since the anatase phase of TiO_2 starts to transform into the rutile phase at around 450°C , the diffraction peaks of the rutile phase can also be seen in the plots.

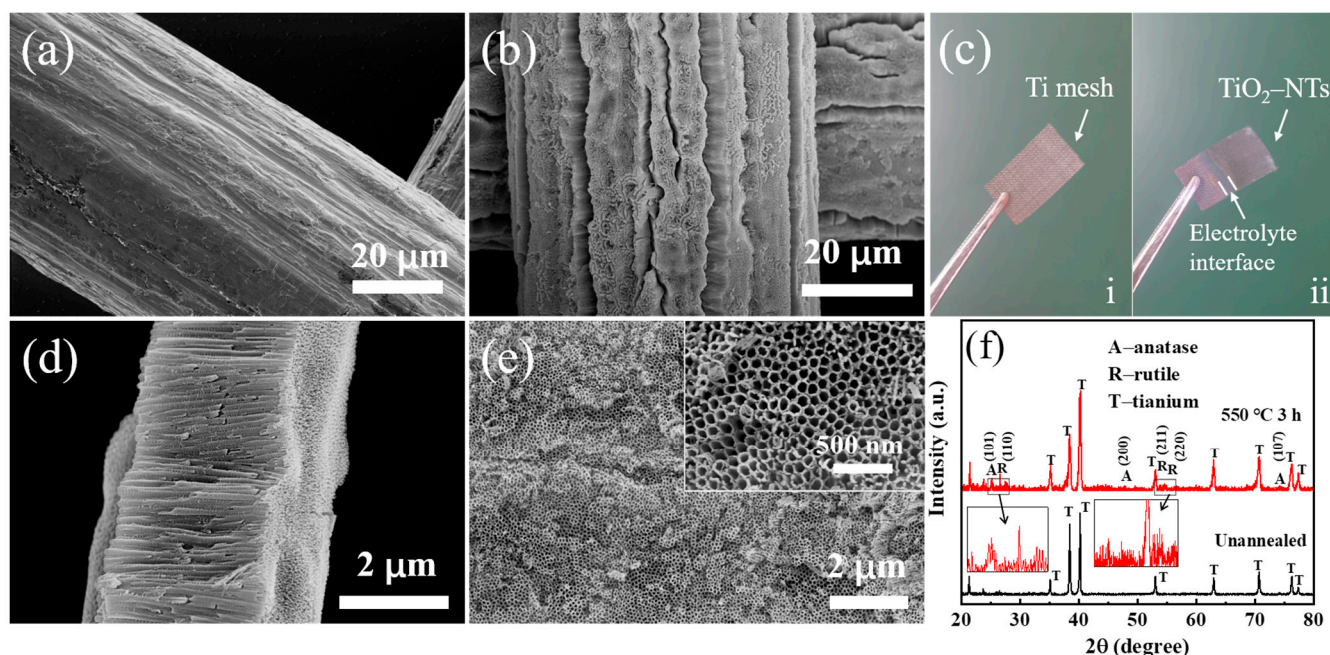


Figure 2. SEM morphology of (a) Ti mesh and (b) anodized Ti mesh. (c) Physical image of Ti mesh before and after anodizing, i (before oxidation), ii (after oxidation). (d) Characterization of the length of TiO_2 -NTs. (e) Morphological characterization of TiO_2 -NTs. (f) XRD spectrum of TiO_2 -NTs@Ti mesh.

It is important to ensure that the Ti core in the center has good electrical conductivity after oxidation. As illustrated in Figure 3a, the resistance of the Ti mesh before anodization is $0.6\ \Omega$, and the conductivity remains stable after 90 min of anodization at 90 V, with a resistance of $0.9\ \Omega$. The resistance between the Ti-conducting channels at both ends and the NT surface is also low at $1.7\ \Omega$. This provides a strong guarantee for the transport of photogenerated carriers. The TiO_2 -NTs@Ti structure obtained by anodizing on the surface of the Ti mesh naturally has the function of a photoanode for the PEC UV detector. Therefore, when the packaging devices, only a high transmittance substrate needs to be added. The curves in Figure 3b show the transmittance of five different substrates. Due to the filtering problem of FTO/ITO to UV light, traditional devices cannot respond below 300 nm. In contrast, quartz glass has a high transmittance of 90% in the entire near-UV and visible regions, which can be used as an ideal substrate material for PEC UV devices. Therefore, in the subsequent study, we chose quartz glass as the substrate to form the TOTQ-structured PEC UV detector. On the other hand, the Ti mesh has a low transmittance of about 30%, indicating that most of the light sources can be effectively utilized, and there is no significant difference in transmittance between the UV and visible regions. The slight decrease in the transmittance of TiO_2 -NTs@Ti after anodizing indicates that more light is being utilized, which is due to the light scattering induced by the NT structure that enhances the light absorption.

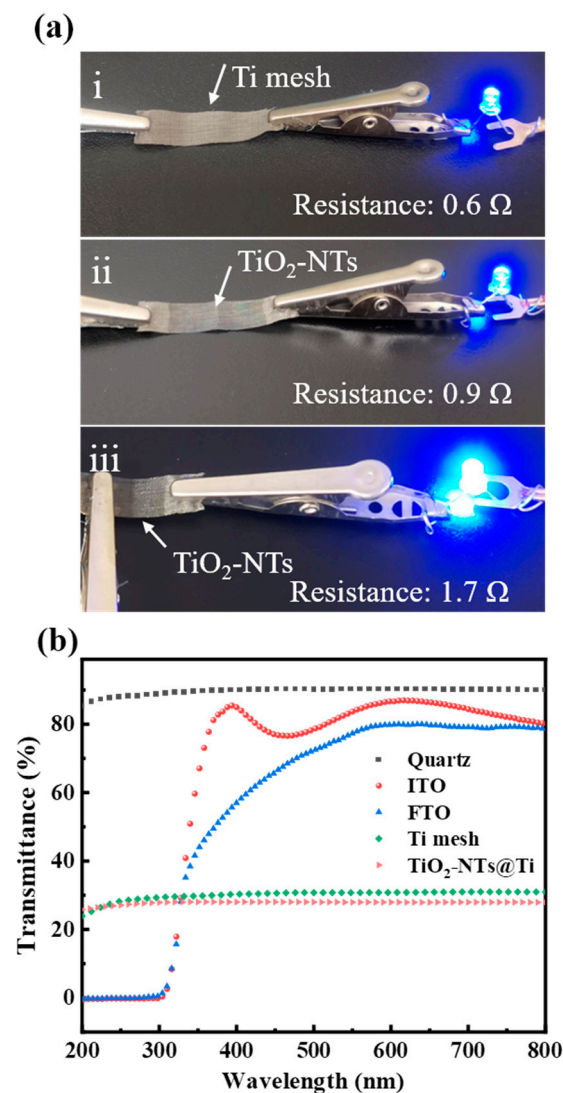


Figure 3. (a) Changes in resistance of Ti mesh at both ends before and after anodizing (90 V, 90 min), before anodizing (i), after anodizing (ii), between TiO₂-NTs and Ti mesh (iii). (b) Transmission spectrum of FTO, ITO, quartz, Ti mesh, and TiO₂-NTs@Ti mesh.

3.2. Performance of PEC UV Detectors

The volt ampere characteristic test is an important characterization to reflect the photovoltaic conversion capability of PEC UV detectors [32]. Figure 4a,b show the J–V curves of devices prepared under different oxidation voltage conditions, where Figure 4a refers to the tests at 254 nm (300 $\mu\text{W}/\text{cm}^2$), and Figure 4b refers to the tests at 365 nm (180 $\mu\text{W}/\text{cm}^2$).

As the oxidation voltage increases, the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) of the device show a trend of first increasing and then decreasing, and the best performance comes from the device prepared at 60 V. The V_{oc} and J_{sc} of the device reach 0.45 V and 4.53 $\mu\text{A}/\text{cm}^2$ at 365 nm, respectively. When the voltage is too low, it is difficult to produce an effective anodic oxidation reaction, and very little TiO₂-NT is formed, which subsequently affects light absorption and charge exchange at the interface. When the voltage is too high, the rapid response causes the destruction of the nanostructure, while the internal Ti core is overconsumed, introducing a large charge transfer impedance. SEM images of samples obtained at different voltages are shown in Figure S1. It can be seen that when the voltage is low, it is difficult to form a tubular structure, and only a TiO₂ nanofilm is formed instead.

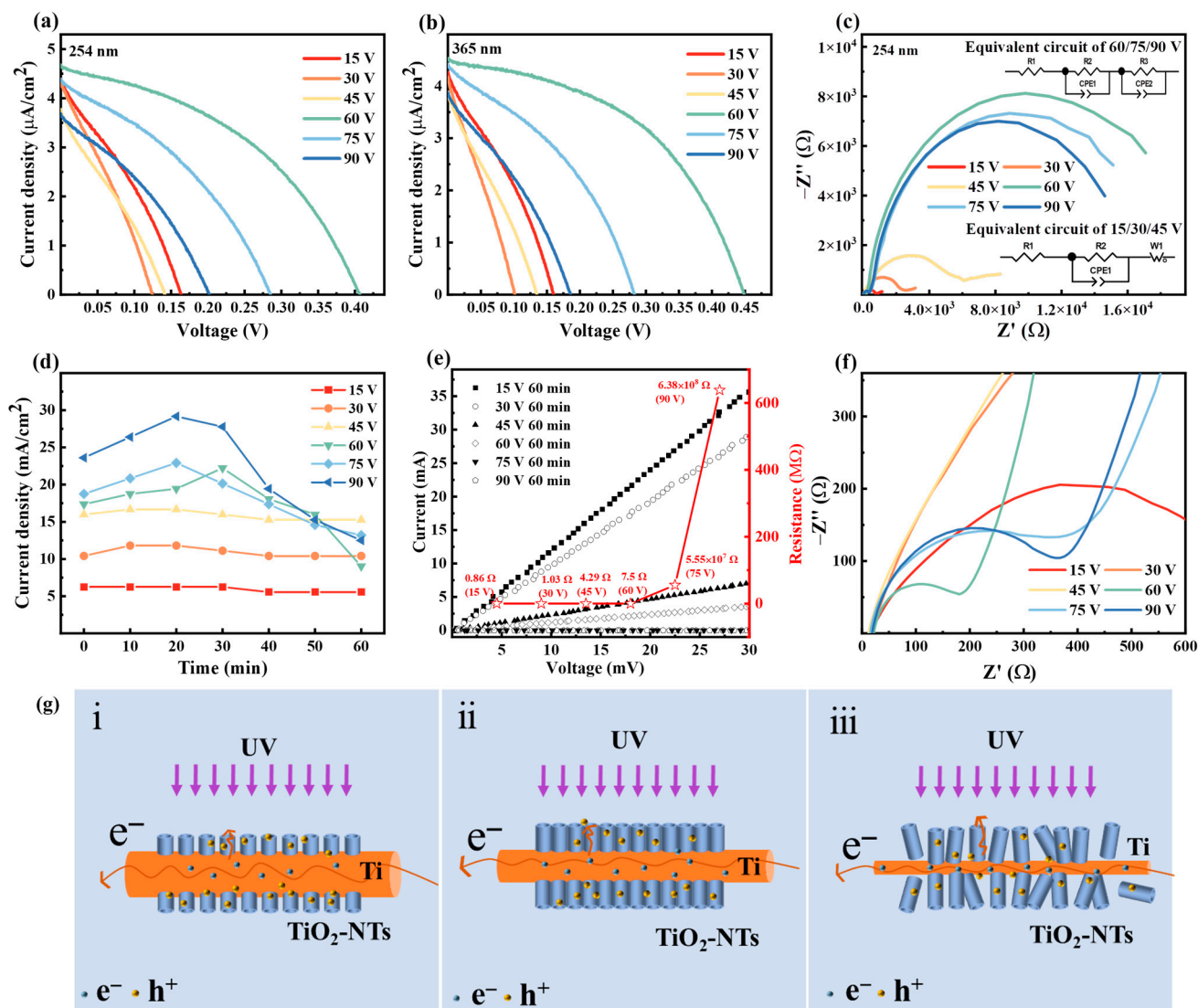


Figure 4. (a,b) J–V curves of the PEC UV detector based on different oxidation voltages for 60 min at 254 nm and 365 nm, respectively. (c) Electrochemical impedance spectroscopy (tested at 254 nm), the illustration shows the equivalent circuit diagram. (d) Time-dependent curve of anodic oxidation current density. (e) Changes in resistance of Ti mesh under different oxidation voltages. (f) Partial enlarged view of Figure 4c. (g) Schematic diagram of Ti mesh oxidation, low voltage (i), optimum voltage (ii), high voltage (iii).

We further investigated the mechanism of the reaction voltage on the performance by impedance spectroscopy. The Nyquist map is used to characterize electron transfer between interfaces [33]. Usually, the electrochemical impedance spectrum consists of high-frequency semicircles and low-frequency oblique straight lines or semicircles. The spectrum composed of high-frequency semicircles and low-frequency oblique lines represents the charge transfer and diffusion processes. When the spectrum is composed of high-frequency small semicircles and low-frequency large semicircles, the small semicircle represents the impedance (R_{ce}) of the interface between the counter electrode and electrolyte, and the large semicircle represents the impedance (R_{ct}) of the electron recombination process at the interface between the photoanode and electrolyte [34,35]. By fitting the Nyquist diagram with an equivalent circuit (illustrated in Figure 4c), the series resistance (R_s) and charge transfer resistance (R_{ce}/R_{ct}) can be estimated.

The intersection of the Nyquist curve and the real part represents the series impedance (R_s), which is mainly derived from the resistance of the electrolyte [34]. Due to the use

of iodine-based electrolytes in the same amount, the solution resistance of each device is maintained at around $15\ \Omega$. The curves in Figure 4c show that the Nyquist spectrum consists of high-frequency semicircles and low-frequency oblique lines when the voltage is 15 V, 30 V, and 45 V. As the voltage increases, the radius of the semicircle increases. This may be due to the increase in voltage leading to an increase in the roughness of the generated TiO_2 film, and the charge transfer resistance increases. The consistent slopes of the low-frequency oblique line indicate that the diffusion rate of electrons in the electrolyte is the same. When the voltage is 60 V, 75 V, and 90 V, the Nyquist curve consists of two semicircles, where the diameter of the low-frequency small semicircle increases as the voltage increases, while the diameter of the high-frequency large semicircle decreases as the voltage increases. The difference in morphology and structure between the NTs and the nanofilms leads to a change in the electronic conduction of the devices during operation, which changes the Nyquist pattern.

The relationship between the current density and the time of oxidation reaction is shown in Figure 4d. As the voltage increases, the current density of the oxidation reaction increases and the oxidation reaction becomes more intense until 20 min of oxidation, when the current density reaches its maximum value. At the beginning of the anodic oxidation reaction, the Ti mesh loses electrons and reacts with water in the electrolyte to form a TiO_2 oxide layer, resulting in an increase in current density. When the reaction lasts for about half an hour, the TiO_2 oxide layer is gradually corroded by F^- in the electrolyte to form a porous structure, and the current density decreases with time. When the electrochemical oxidation rate and chemical dissolution rate tend to be equal, the current density no longer changes, and the prepared TiO_2 -NTs tend to stabilize and no longer change. In this work, when the oxidation potential was set to 60 V, it was found through monitoring that the current density did not change after 90 min of oxidation (Figure S2). The I–V curves and resistance of TiO_2 -NTs@Ti photoanode structures prepared under different oxidation voltages are shown in Figure 4e. The linear test results indicate that no Schottky barriers are present in the structure. The resistance of Ti mesh increases with the increase in oxidation voltage. When the voltage is greater than 60 V, the generated TiO_2 -NTs have very poor contact with the Ti substrate due to the intense reaction. After high-temperature calcination, TiO_2 -NTs will separate from the substrate, resulting in poor conductivity. This result further confirms that 60 V is the optimal preparation voltage.

Figure 5a,b display the photovoltaic characteristic of the device measured by controlling the oxidation time under the oxidation voltage of 60 V. As the oxidation time changes, the V_{oc} and J_{sc} of the device both show a trend of increasing first and then decreasing later, reaching the optimal value at an oxidation time of 90 min. Figure 5c,d show the Nyquist spectra of devices corresponding to different oxidation times. The results indicate that the sample has the lowest electron transfer impedance and the highest electron recombination impedance under the optimum synthesis parameter.

As the device is illuminated, TiO_2 absorbs UV photons to produce photogenerated electrons, which diffuse along the TiO_2 -NTs to the Ti core for transport. When the oxidation time is short or the oxidation voltage is low, the NTs are not formed or are relatively short and sparse, which does not ensure that most of the UV light is absorbed (as shown in Figure 4g(i)). When the oxidation time is longer or the oxidation voltage is higher, the NTs are prone to fracture and peeling, resulting in the electrolyte directly contacting the Ti core, which in turn leads to a severe recombination reaction between the electrons in Ti and the ions in the oxidation state (as shown in Figure 4g(iii)). In addition, besides the depth of the NT array, the oxidation voltage has an important effect on the morphology and structure of the NTs. Therefore, it is important to optimally control the oxidation time and oxidation voltage considering the light absorption, carrier transport and recombination.

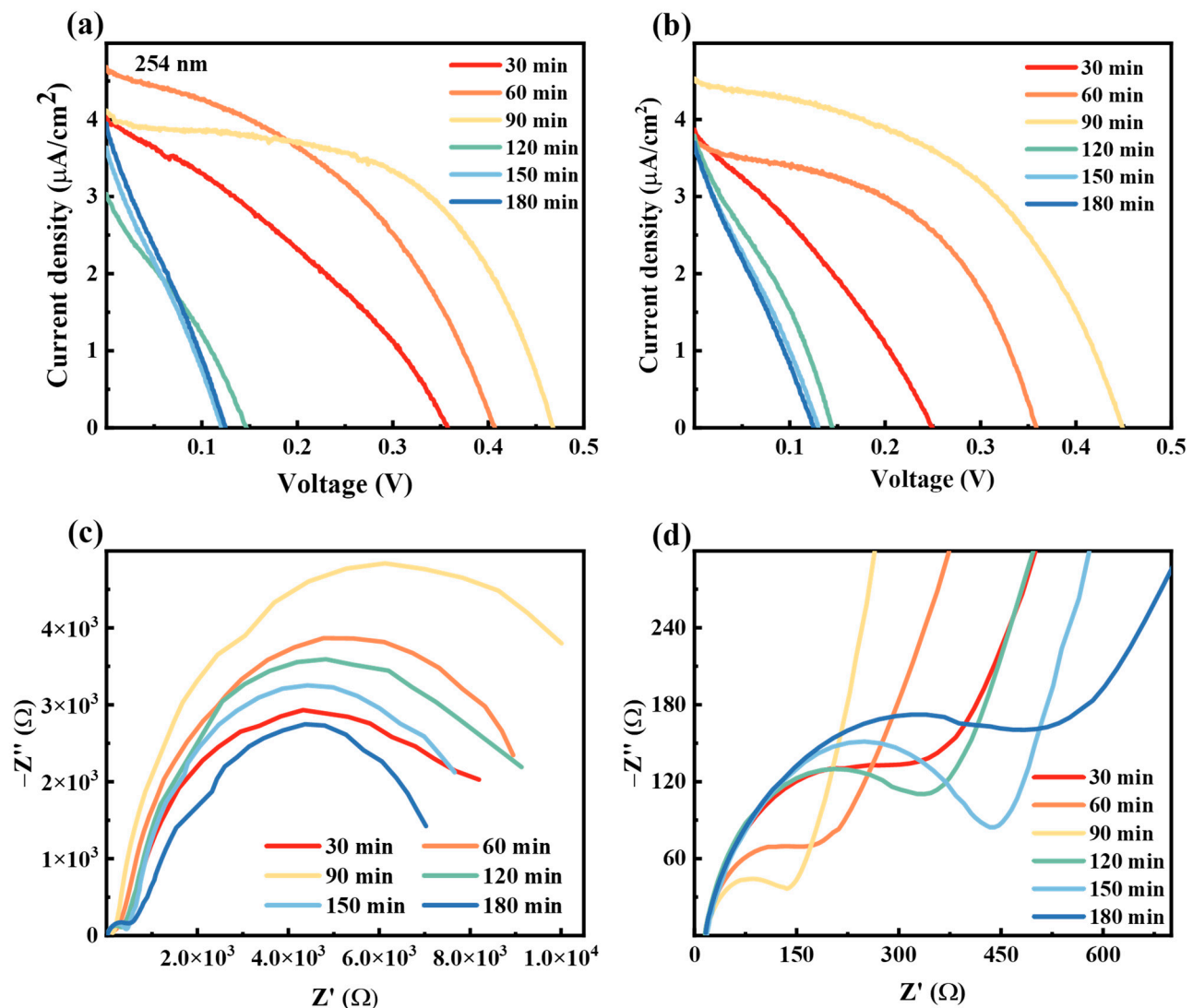


Figure 5. (a,b) J–V performance test of samples obtained at different preparation times (preparation voltage control to 60 V). (c,d) Electrochemical impedance spectroscopy (tested at 254 nm).

In order to study the sensitivity of TOTQ PEC UV detectors, we irradiated the devices with UV light in the form of rectangular pulses, with a switching time interval of 15 s. The response speed of the device is mainly affected by carrier diffusion and interface reaction rate [32]. The results show that the detector can operate normally at 0 V bias. As shown in Figure 6a,c, the devices exhibit good switching response at both 365 nm (UVA band) and 254 nm (UVC band). The relative response current under different conditions is consistent with the volt-ampere characteristic test results, and the optimal synthesis conditions are 60 V and 90 min. Under the best conditions, the switching response curve is nearly rectangular, and the current responds very quickly with the light source, and the response current is close to 1 $\mu\text{A}/\text{cm}^2$. The time sensitivity of the device can be obtained by enlarging the response side and recovery side of the switching curve; as shown in Figure 6f, the typical response time and recovery time are both about 1 s, which is much faster than the photoconductive device.

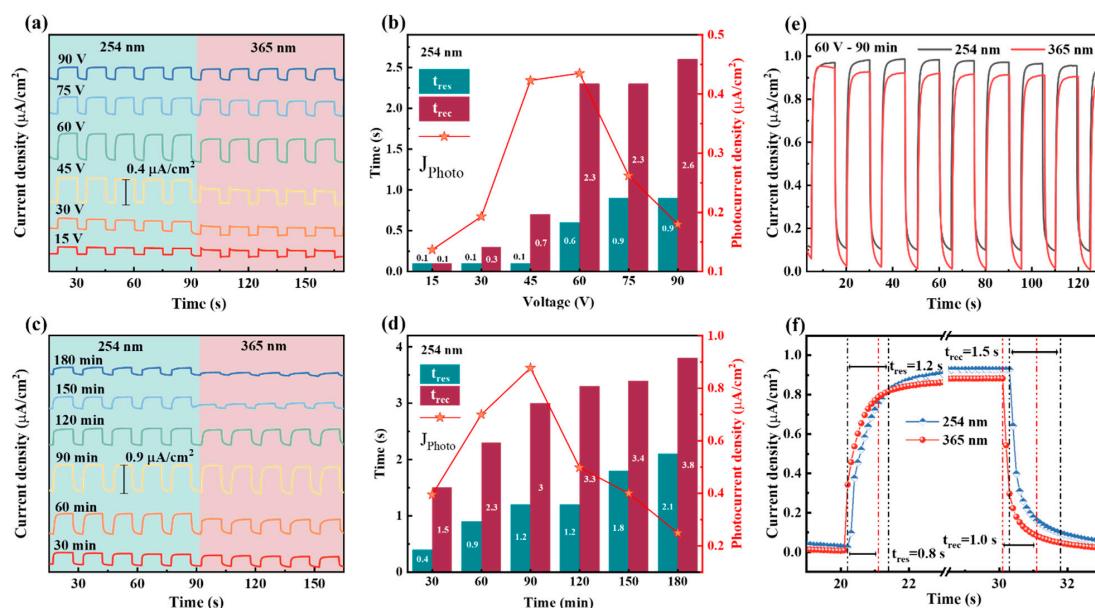


Figure 6. (a,c) Photocurrent response corresponding to different oxidation voltages and oxidation times. (b,d) Measurement of response speed under different preparation conditions (t_{res} indicates the response time and t_{rec} indicates the recovery time). (e) The switching performance of the UV detectors. The switching period is 15 s. (f) Enlarged time response curves.

The time response curve of the device consists of a rising edge of the photo-current response and a falling edge of the dark reaction, and the rising curve is mainly affected by the rapid excitation and transmission of electrons under UV light, while the falling curve is mainly affected by the charge diffusion after stopping illumination. Figure 6b,d show the statistical data of response time (t_{res}) and recovery time (t_{rec}) of devices under different conditions. As the oxidation voltage increases, both the t_{res} and t_{rec} of the device increase, and the t_{rec} of the same device is longer than the t_{res} . This may be due to the fact that with the increase in oxidation voltage, the TiO_2 active layer becomes thicker, increasing the diffusion distance of photogenerated carriers, and thus extending the response time and recovery time. It should be noticed that the t_{res} and t_{rec} of the device remain between 0.1 s and 0.2 s when the voltage is less than 60 V. This is because the TiO_2 nanofilm generated at a lower voltage has better contact with the Ti substrate, resulting in faster electron transfer. However, when the voltage is 60 V or above, more TiO_2 -NT structures are generated, and after high-temperature treatment, the separation of the NT from the Ti substrate hinders electron conduction. The length of preparation time also has a similar effect on the response speed.

3.3. Extension of the Detection Range

Conventional PEC UV detectors use transparent conductive oxide (TCO) as electrodes to form a sandwich-like structure. During operation, the UV light needs to penetrate the TCO substrate (FTO or ITO) to reach the active layer; however, the TCO substrate has a severe filtering effect on the UV light, which affects the responsiveness of the device and leads to a narrow response range (300–400 nm). Most of the current research work focuses on the synthesis and modulation of the photoanode active material, neglecting the important parameter of response range. The TiO_2 -NTs@Ti core-shell structure obtained by in situ anodic oxidation in this work successfully solved the above problem. (1) The electron collector of the TOTQ structure is located inside the active material, and the UV light of any wavelength can reach the TiO_2 through the encapsulated quartz without obstacles, which greatly improves the utilization of the light source of the device and thus broadens the response range. (2) The structure with the built-in collector can shorten the diffusion distance of photogenerated electrons, which is conducive to the enhancement of the photo

response. (3) The mechanical and chemical stability of the one-step synthesized all-Ti-based structure is superior to the work reported in the literature, for example, the use of stainless steel mesh loaded with the active substance as the electrode, and the use of Ag NWs as the UV-transparent electrode [14]. In addition, TiO_2 -NTs have a large specific surface area due to their unique tubular structure, which can reduce the recombination rate of photogenerated electron–hole pairs and provide directional channels for electrons, enabling the device to have a fast response.

We tested the response spectra of the devices using continuous calibrated monochromatic light. As shown in Figure 7a, the PEC UV detector based on the TOTQ structure responds in the 240–400 nm range, with the response peak (25.49 mA/W) appearing at 320 nm, which is 69% higher than previously reported devices based on Ag NW electrodes. As a comparison sample, the device based on FTO and TiO_2 P25 active layer only detects UV light above 300 nm. Figure 7b shows the UV light is irradiated onto the active layer of TiO_2 -NTs through quartz glass and generates electron–hole pairs. The electrons are transmitted along the Ti mesh to the outer circuit, and the holes diffuse to the electrolyte interface to undergo an oxidation reaction with iodine ions.

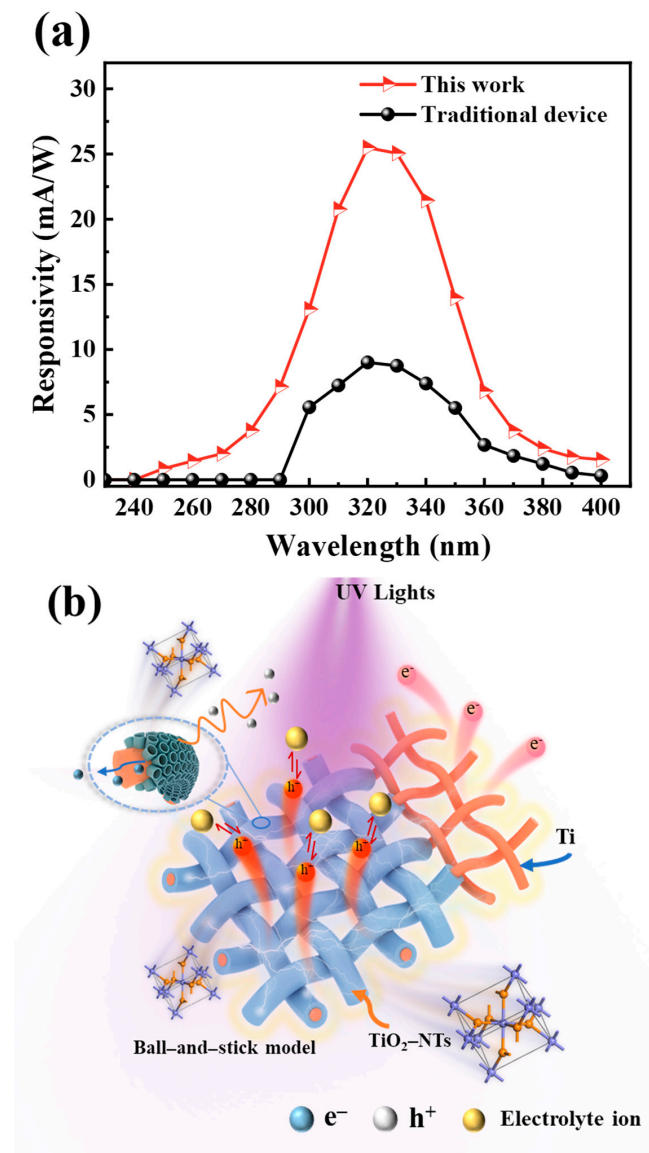


Figure 7. (a) Comparison of response spectra between traditional FTO/P₂₅ device and the TOTQ PEC UV detector. (b) Schematic diagram of generation and transfer of photogenerated electron–hole pairs in TOTQ system.

4. Conclusions

In order to solve the problem of the narrow response range of conventional PEC UV detectors, the idea of placing the collector inside the active layer is proposed in this work. A TiO₂-NTs@Ti core-shell structure was prepared by the anodizing method using a commercially available Ti mesh, together with the use of quartz with high UV transmittance as the substrate to obtain a special TOTQ photoanode structure. The TOTQ photoanode allows UV light of any wavelength to reach the active material directly while shortening the diffusion distance of photogenerated electrons. The one-step-synthesized all-Ti-based structure has better mechanical and chemical stability in iodine-based electrolytes. We precisely controlled the synthesis conditions and determined the optimal oxidation parameters as 60 V and 90 min, and the mechanism of the material structure's influence on the device performance is clarified by the analysis of electrochemical impedance spectra. The UV test results show good switching performance and high sensitivity, with a response time of 10²–10³ ms. Compared with conventional devices, the TOTQ PEC UV detector extends the detection range from 300–400 nm to 240–400 nm.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano14050439/s1>, Figure S1: SEM morphology of Ti mesh after oxidation at 15/30/45/60/75/90 V for 60 min; Figure S2: Curve of oxidation current density over time.

Author Contributions: Conceptualization, Y.W.; Data curation, M.Z.; Funding acquisition, Y.W.; Investigation, Y.W., M.Z., W.W., T.Y. and R.; Methodology, Y.W., M.Z. and Z.W.; Software, M.Z. and M.L.; Writing—original draft, M.Z. and W.W.; Writing—review and editing, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China (No. 61804092).

Data Availability Statement: The data presented in this study are available on request.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Xu, Z.; Sadler, B.M. Ultraviolet communications: Potential and state-of-the-art. *IEEE Commun. Mag.* **2008**, *46*, 67–73.
2. Cai, S.; Zuo, C.; Zhang, J.; Liu, H.; Fang, X. A paper-based wearable photodetector for simultaneous UV intensity and dosage measurement. *Adv. Funct. Mater.* **2021**, *31*, 2100026. [\[CrossRef\]](#)
3. Bai, Z.; Zhang, Y. Self-powered UV-visible photodetectors based on ZnO/Cu₂O nanowire/electrolyte heterojunctions. *J. Alloys Compd.* **2016**, *675*, 325–330. [\[CrossRef\]](#)
4. Yang, D.; Ma, D. Development of Organic Semiconductor Photodetectors: From Mechanism to Applications. *Adv. Opt. Mater.* **2019**, *7*, 1800522. [\[CrossRef\]](#)
5. Dastkhoon, M.; Ghaedi, M.; Asfaram, A.; Arabi, M.; Ostovan, A.; Goudarzi, A. Cu@SnS/SnO₂ nanoparticles as novel sorbent for dispersive micro solid phase extraction of atorvastatin in human plasma and urine samples by high-performance liquid chromatography with UV detection: Application of central composite design (CCD). *Ultrason. Sonochem.* **2017**, *36*, 42–49. [\[CrossRef\]](#)
6. Chen, J.; Ouyang, W.; Yang, W.; He, J.H.; Fang, X. Recent Progress of Heterojunction Ultraviolet Photodetectors: Materials, Integrations, and Applications. *Adv. Funct. Mater.* **2020**, *30*, 1909909. [\[CrossRef\]](#)
7. Guo, D.; Su, Y.; Shi, H.; Li, P.; Zhao, N.; Ye, J.; Wang, S.; Liu, A.; Chen, Z.; Li, C.; et al. Self-Powered Ultraviolet Photodetector with Superhigh Photoresponsivity (3.05 A/W) Based on the GaN/Sn:Ga₂O₃ pn Junction. *ACS Nano* **2018**, *12*, 12827–12835. [\[CrossRef\]](#)
8. Razeghi, M.; Rogalski, A. Semiconductor ultraviolet detectors. *J. Appl. Phys.* **1996**, *79*, 7433–7473. [\[CrossRef\]](#)
9. Omnès, F.; Monroy, E.; Muñoz, E.; Reverchon, J.-L. Wide bandgap UV photodetectors: A short review of devices and applications. *Gallium Nitride Mater. Devices* **2007**, *6473*, 111–125.
10. Ouyang, W.; Chen, J.; Shi, Z.; Fang, X. Self-powered UV photodetectors based on ZnO nanomaterials. *Appl. Phys. Rev.* **2021**, *8*, 031315. [\[CrossRef\]](#)
11. Wang, X.; Ding, K.; Huang, L.; Li, X.; Ye, L.; Luo, J.; Jiang, J.; Li, H.; Xiong, Y.; Ye, L.J.A.S.S. Enhancing the performance of Self-Powered Deep-Ultraviolet photoelectrochemical photodetectors by constructing α-Ga₂O₃@α-Al₂O₃ Core-Shell nanorod arrays for Solar-Blind imaging. *Appl. Surf. Sci.* **2024**, *648*, 159022. [\[CrossRef\]](#)
12. Zhang, M.; Yu, H.; Li, H.; Jiang, Y.; Qu, L.; Wang, Y.; Gao, F.; Feng, W. Ultrathin In₂O₃ Nanosheets toward High Responsivity and Rejection Ratio Visible-Blind UV Photodetection. *Small* **2023**, *19*, 2205623. [\[CrossRef\]](#)

13. Ni, S.; Guo, F.; Wang, D.; Liu, G.; Xu, Z.; Kong, L.; Wang, J.; Jiao, S.; Zhang, Y.; Yu, Q.; et al. Effect of MgO Surface Modification on the TiO₂ Nanowires Electrode for Self-Powered UV Photodetectors. *ACS Sustain. Chem. Eng.* **2018**, *6*, 7265–7272. [\[CrossRef\]](#)
14. Wei, K.; Li, B.; Gong, C.; Zhu, Z.; Zhang, Y.; Liu, M.; Ren, P.; Pan, X.; Wang, Y.; Zhou, J. Full near-ultraviolet response photoelectrochemical ultraviolet detector based on TiO₂ nanocrystalline coated stainless steel mesh photoanode. *Nanotechnology* **2021**, *32*, 475503. [\[CrossRef\]](#)
15. Wang, Y.; Li, B.; Ren, P.; Liu, M.; Gong, Z.; Zhang, M.; Zhao, H.; Zhang, Y.; Zhang, Y.; Liu, J. Expansion of the response range of photoelectrochemical UV detector using an ITO/Ag-nanowire/quartz UV-visible transparent conductive electrode. *J. Mater. Chem. C* **2022**, *10*, 4157–4165. [\[CrossRef\]](#)
16. Zhou, J.; Chen, L.; Wang, Y.; He, Y.; Pan, X.; Xie, E. An overview on emerging photoelectrochemical self-powered ultraviolet photodetectors. *Nanoscale* **2016**, *8*, 50–73. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Chen, Q.; Xu, D.; Wu, Z.; Liu, Z. Free-standing TiO₂ nanotube arrays made by anodic oxidation and ultrasonic splitting. *Nanotechnology* **2008**, *19*, 365708. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Lee, J.; Moon, S.; Patil, S.S.; Lee, K. Visible photoresponse of TiO₂ nanotubes in comparison to that of nanoparticles and anodic thin film. *Catal. Today* **2022**, *403*, 39–46. [\[CrossRef\]](#)
19. Mohammadi, N.; Abrego-Martinez, J.C.; Mohamedi, M. Three-Dimensional Pinecone-like Binder-Free Pt-TiO₂ Nanorods on Ti Mesh Structures: Synthesis, Characterization and Electroactivity towards Ethanol Oxidation. *Molecules* **2022**, *27*, 1921. [\[CrossRef\]](#) [\[PubMed\]](#)
20. Roy, P.; Berger, S.; Schmuki, P. TiO₂ nanotubes: Synthesis and applications. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 2904–2939. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Zhang, W.; Liu, Y.; Guo, F.; Liu, J.; Yang, F. Kinetic analysis of the anodic growth of TiO₂ nanotubes: Effects of voltage and temperature. *J. Mater. Chem. C* **2019**, *7*, 14098–14108. [\[CrossRef\]](#)
22. Xiao, F.X. Construction of highly ordered ZnO-TiO₂ nanotube arrays (ZnO/TNTs) heterostructure for photocatalytic application. *ACS Appl. Mater. Interfaces* **2012**, *4*, 7055–7063. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Wang, J.; Lin, Z. Anodic formation of ordered TiO₂ nanotube arrays: Effects of electrolyte temperature and anodization potential. *J. Phys. Chem. C* **2009**, *113*, 4026–4030. [\[CrossRef\]](#)
24. Hou, X.; Wang, X.; Liu, B.; Wang, Q.; Wang, Z.; Chen, D.; Shen, G. SnO₂@TiO₂ Heterojunction Nanostructures for Lithium-Ion Batteries and Self-Powered UV Photodetectors with Improved Performances. *ChemElectroChem* **2014**, *1*, 108–115. [\[CrossRef\]](#)
25. Liu, Z.; Subramania, V.; Misra, M.J.T.J.O.P.C.C. Vertically oriented TiO₂ nanotube arrays grown on Ti meshes for flexible dye-sensitized solar cells. *J. Phys. Chem. C* **2009**, *113*, 14028–14033. [\[CrossRef\]](#)
26. Liao, J.; Lin, S.; Zhang, L.; Pan, N.; Cao, X.; Li, J. Photocatalytic degradation of methyl orange using a TiO₂/Ti mesh electrode with 3D nanotube arrays. *ACS Appl. Mater. Interfaces* **2012**, *4*, 171–177. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Rustomji, C.S.; Frandsen, C.J.; Jin, S.; Tauber, M.J. Dye-sensitized solar cell constructed with titanium mesh and 3-D array of TiO₂ nanotubes. *J. Phys. Chem. B* **2010**, *114*, 14537–14543. [\[CrossRef\]](#)
28. Kuang, D.; Brillet, J.; Chen, P.; Takata, M.; Uchida, S.; Miura, H.; Sumioka, K.; Zakeeruddin, S.M.; Grätzel, M.J.A. Application of highly ordered TiO₂ nanotube arrays in flexible dye-sensitized solar cells. *ACS Nano* **2008**, *2*, 1113–1116. [\[CrossRef\]](#)
29. Varghese, O.K.; Gong, D.; Paulose, M.; Grimes, C.A.; Dickey, E.C. Crystallization and high-temperature structural stability of titanium oxide nanotube arrays. *J. Mater. Res.* **2011**, *18*, 156–165. [\[CrossRef\]](#)
30. Wang, Z.-B.; Aldalbahi, A.; Ahamad, T.; Alshehri, S.M.; Feng, P.X. Preparation of BiFeO₃ and its photoelectric performance as photoanode of DSSC. *Ceram. Int.* **2021**, *47*, 27565–27570. [\[CrossRef\]](#)
31. Zare, A.; Behaein, S.; Moradi, M.; Hosseini, Z. Application of a dual functional blocking layer for improvement of the responsivity in a self-powered UV photodetector based on TiO₂ nanotubes. *RSC Adv.* **2022**, *12*, 9909–9916. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Nayak, J.; Prabakar, K.; Park, J.W.; Kim, H. Effect of synthesis temperature on structure, optical and photovoltaic properties of TiO₂ nanorod thin films. *Electrochim. Acta* **2012**, *65*, 44–49. [\[CrossRef\]](#)
33. Bisquert, J. Theory of the impedance of electron diffusion and recombination in a thin layer. *J. Phys. Chem. B* **2002**, *106*, 325–333. [\[CrossRef\]](#)
34. Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. Decoupling of transport, charge storage, and interfacial charge transfer in the nanocrystalline TiO₂/electrolyte system by impedance methods. *J. Phys. Chem. B* **2002**, *106*, 334–339. [\[CrossRef\]](#)
35. Fu, A.; Chen, X.; Tong, L.; Wang, D.; Liu, L.; Ye, J. Remarkable Visible-Light Photocatalytic Activity Enhancement over Au/p-type TiO₂ Promoted by Efficient Interfacial Charge Transfer. *ACS Appl. Mater. Interfaces* **2019**, *11*, 24154–24163. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.