



High responsivity of ultraviolet sensor-based rutile-phased TiO₂ nanorod arrays using different bias voltage

S. M. Mokhtar¹ · M. K. Ahmad¹ · N. Nafarizal¹ · C. F. Soon¹ · M. H. Mamat² · N. M. A. N. Ismail³ · A. S. Ameruddin⁴ · A. B. Suriani⁵ · M. Shimomura⁶ · K. Murakami⁶

Received: 22 October 2018 / Revised: 19 February 2019 / Accepted: 19 March 2019
© Australian Ceramic Society 2019

Abstract

Highly oriented rutile titanium dioxide (TiO₂) nanorod arrays were grown on fluorine-doped tin oxide (FTO) substrate using a hydrothermal method. X-ray diffraction, Raman spectra, field emission-scanning electron microscopy, and ultraviolet-visible spectroscopy were conducted to determine the structural, morphological, and optical properties of the sample. The synthesized TiO₂ nanorod arrays exhibited tetragonal rutile structure. The photocurrent analysis was done by using photoelectrochemical method where different bias voltage (0 V to 0.9 V) was applied. The photocurrent value shows acceptable difference with increasing bias voltage. The TiO₂ nanorod array (TNAs) UV sensors show high responsivity as indicated by the fast rise and decay time of the photocurrent of less than 1 s with every bias voltage applied.

Keywords TiO₂ nanorod array · Rutile · Ultraviolet sensor

Introduction

Titanium dioxide (TiO₂) is one of the frequently used metal oxide materials in various fields due to its wide band gap (3.2 eV) such as photocatalysis [1], photovoltaics [2], and

photosensors [3]. It is attractive due to its high sensitivity, simple signal processing, low-cost production, and small size [4]. Titanium dioxide, or titania, can be found in three crystalline phases that are anatase, rutile, and brookite. Among these phases, TiO₂ nanoparticles of the rutile phase are the most thermodynamically stable. Frequent studies have revealed that the performances, as well as physical and chemical characteristics of nanostructure TiO₂, are strongly influenced by crystallite structure, morphology, and dimension [5–7]. The TNAs were fabricated using the hydrothermal method. Hydrothermal processing has been extensively used in the preparation of TiO₂ nanomaterials; thus, their textures can be controlled by various elements, for example precursor, amount of hydrochloric acid, reaction temperature, and reaction time. Long et al. has reported the effects of time and temperature to hydrothermal growth of the nanorods [8]. At 6 h reaction times, there is only a seed layer on top of the glass substrate. However, when the reaction times increase to 20 h, the seed layers have grown into nanorods without orientation in a certain direction. This is because the glass substrate used has an amorphous structure with very different lattice mismatch. Meanwhile, in this experiment, the substrate used is FTO substrate where there is only slight lattice mismatch of FTO and rutile structure that is $a = 4.737$, $c = 3.185$ and $a = 4.594$, $c = 2.958$, respectively. Phan et al. used hydrothermal method to be studied on the influence of concentrated HCl on TiO₂ morphology. Depending on the acid medium and ratio,

✉ M. K. Ahmad
akhairul@uthm.edu.my

¹ Microelectronic and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC) Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor, Malaysia

² Nano-Electronic Centre, Faculty of Electrical Engineering, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia

³ Department of Electronic Engineering, Faculty of Electric and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor, Malaysia

⁴ Department of Science, Faculty of Science, Technology, and Human Development, Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor, Malaysia

⁵ Nanotechnology Research Centre, Department of Physics, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia

⁶ Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, Hamamatsu, Shizuoka 432-8011, Japan

several morphologies can be obtained. They showed the role of HCl in creating the oriented organization of the crystalline phase and morphology-controlled TiO₂ nanomaterials.

Flame detections, space communications, ozone layer monitoring, and UV astronomy are among the technology that are using UV photoconductive sensor. Nowadays, fabrication of UV photosensor is gaining attention due to its applications in different fields. Among the materials that are being utilized in fabricating UV sensor are silicon (Si), gallium nitride (GaN), zinc selenide (ZnSe), silicon carbide (SiC), and diamond. Using Si materials as a UV sensor have caused several problems. First, Si has a low bandgap, which is 1.1 eV, causing low responsivity towards ultraviolet radiation and requiring a visible light filter if applied in the device structure. Si is also not suitable to be used as it has limitation in harsh environmental conditions, for example UV detection at high temperature. Meanwhile, GaN, SiC, and diamond show a decent performance under high-temperature conditions. However, the materials are not cost effective as they have high fabrication cost making it not fitting for large-scale production [9]. A number of materials, including TiO₂ nanostructured, have been proposed and studied intensively in order to fabricate a UV sensor with good stability and reliability at a reasonable price. The aims of this study are to prepare and study the effect of different bias voltage towards sensing properties of the TNAs thin films to ultraviolet light using photoelectrochemical (PEC) method. Among various UV photodetectors made of 1D nanostructures, PEC-based photodetectors show promising potential due to their low cost, simple fabrication process, and fast response. Moreover, PEC-based photodetectors work in 'self-powered' mode, which does not require batteries as external power source.

Experimental details

Growth of TiO₂ nanorod arrays by hydrothermal method

The single-crystalline rutile nanorod used for this study was grown vertically on FTO substrate using hydrothermal method. A diluted hydrochloric acid solution was prepared by mixing 120 mL of deionized water with 130 mL of concentrated hydrochloric acid and was stirred at ambient temperature for 5 min, and then 3.5 mL of titanium butoxide was added to the mixture and stirred for 10 min. After that, the mixture was poured into a stainless steel autoclave with a Teflon container cartridge. The FTO substrates were ultrasonically cleaned and were placed at an angle against the Teflon container with the conducting side facing down. Hydrothermal synthesis was conducted at 150 °C for 16 h. After synthesis, the autoclave was cooled down to room

temperature, and the FTO substrate was taken out and rinsed thoroughly with deionized water.

Characterization of TiO₂ nanorod samples and the UV photodetector

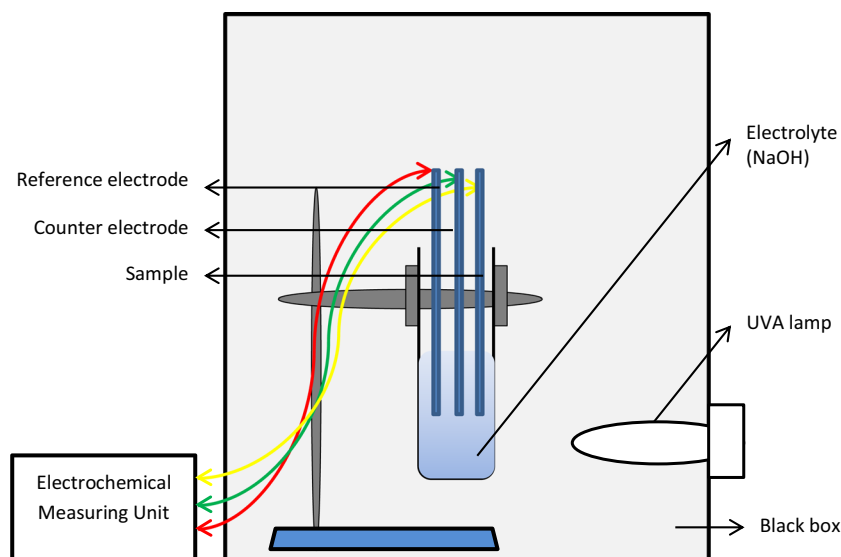
The crystal structure and crystallite size are defined by an X-ray diffractometer (XRD) PANalytical X-Pert3 Powder model. The scan axis used was 2 θ with range of 20°–60°, and the type of slit used was fixed divergence slit. Raman spectra were obtained using a Micro-Raman Spectroscope (Renishaw InVia microRaman System) operated with 514 nm wavelength of argon (Ar⁺) laser. The morphology and thickness of the TNAs were characterized by using a field emission scanning electron microscope (FESEM) JEOL JSM-7600F model operated at 15 kV. Finally, the photoresponse switching behavior measurement, a UV lamp with a wavelength of 365 nm, was used as light source, and the photocurrent was obtained by photoelectrochemical workstation using Solartron 1280C electrochemical measuring unit as the source of bias voltage. The schematic structure of the TiO₂ nanorod using photoelectrochemical workstation is shown in Fig. 1. Performance of the UV sensor was distinguished from photocurrent which is generated using a photo-electrochemical method using 1280C electrochemical measuring unit as the source of bias voltage. The UV light source used in this setup was a 365-nm UVA lamp. It is easily available in the market and is used widely in applications such as photo-catalyst and gas sensor. The measurement takes place in a dark condition to prevent unnecessary light illumination from other sources. Ag/KCl and platinum (Pt) is used in this experiment as reference and counter electrode, respectively. Meanwhile, the TiO₂ nanorods act as a working electrode and the electrolyte used in this experiment was from sodium (Na). Conductive side of the FTO substrate is placed facing the UVA lamp. The UVA lamp was turned ON and OFF every 5 s during the testing to see reaction of the nanorod thin film towards the UV lamp.

Results and discussion

Structural characterizations

The well-aligned TNAs with pure rutile phase are verified by the XRD pattern in Fig. 2. The scanning Bragg angle was within the range of θ -2 θ . A dominant sharp peak at 37.4° was observed within this range. The presence of this peak confirmed the growth of a (101) plane. Seven diffraction peaks were observed corresponded to the peaks of TiO₂ and FTO. Three of these peaks corresponded to the (101), (111), and (211) planes of TiO₂. The TiO₂ nanorod was polycrystalline. These nanorods can be indexed as a tetragonal rutile phase based on their XRD patterns [10, 11]. The reason that

Fig. 1 Photo-electrochemical instrument setup for measuring photocurrent



the hydrothermal method contributed to rutile phase instead of anatase and brookite could be accredited to the small lattice mismatch between FTO and rutile phase. Rutile-phase TiO_2 and FTO have near-identical lattice parameters of $a = 4.594$, $c = 2.958$ Å and $a = 4.737$, $c = 3.185$ Å for TiO_2 and SnO_2 , respectively, making the epitaxial growth of rutile TiO_2 on FTO film possible. Meanwhile, anatase and brookite have lattice parameters of $a = 3.784$, $c = 9.514$ Å and $a = 5.455$ and $c = 5.142$ Å, respectively. The production of these phases is unfavorable due to a high activation energy barrier which is hard to overcome at the low temperature used in this hydrothermal reaction [12]. Figure 3 shows the Raman spectra of TiO_2 nanorod thin film. The sample exhibits dominant peaks of rutile TiO_2 that is at 121 cm^{-1} , 444 cm^{-1} , and 611 cm^{-1} and a second-order scattering featured at 244 cm^{-1} which also

considered as a characteristic of rutile TiO_2 [13]. This supports the XRD data on Fig. 2 that the nanorod produced was pure rutile-phase TiO_2 .

Surface morphology

Figure 4 shows the micrograph of an as-grown TiO_2 nanorod arrays taken at (a) 10 k, (b) 50 k, and (c) cross section by a field emission scanning electron microscope at top and tilted views, respectively. The images at different magnification (10 K and 50 K) and different locations revealed that the entire surface of the FTO substrate is uniformly covered with ordered TiO_2 nanorod. Further analysis indicates that the nanorod is typically 110 to 140 nm in diameter and is in tetragonal shapes with square top facets consisting of many small grids. The thickness of the TNAs was $1.25\text{ }\mu\text{m}$.

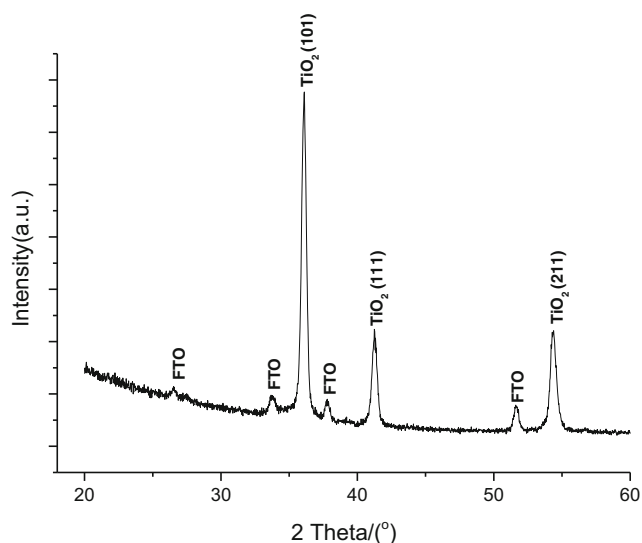


Fig. 2 X-ray diffraction pattern of the TiO_2 nanorod arrays grown on FTO substrate

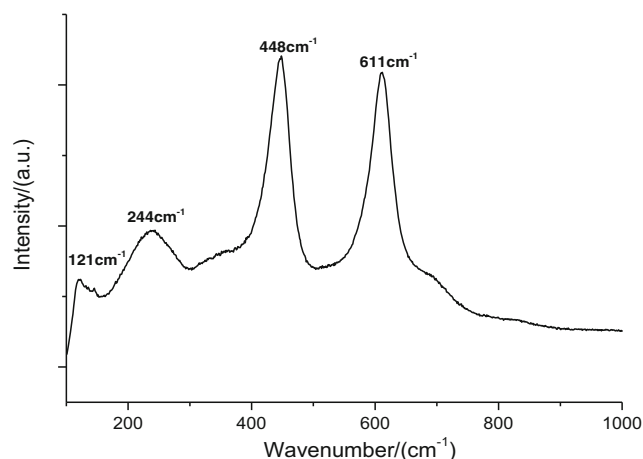
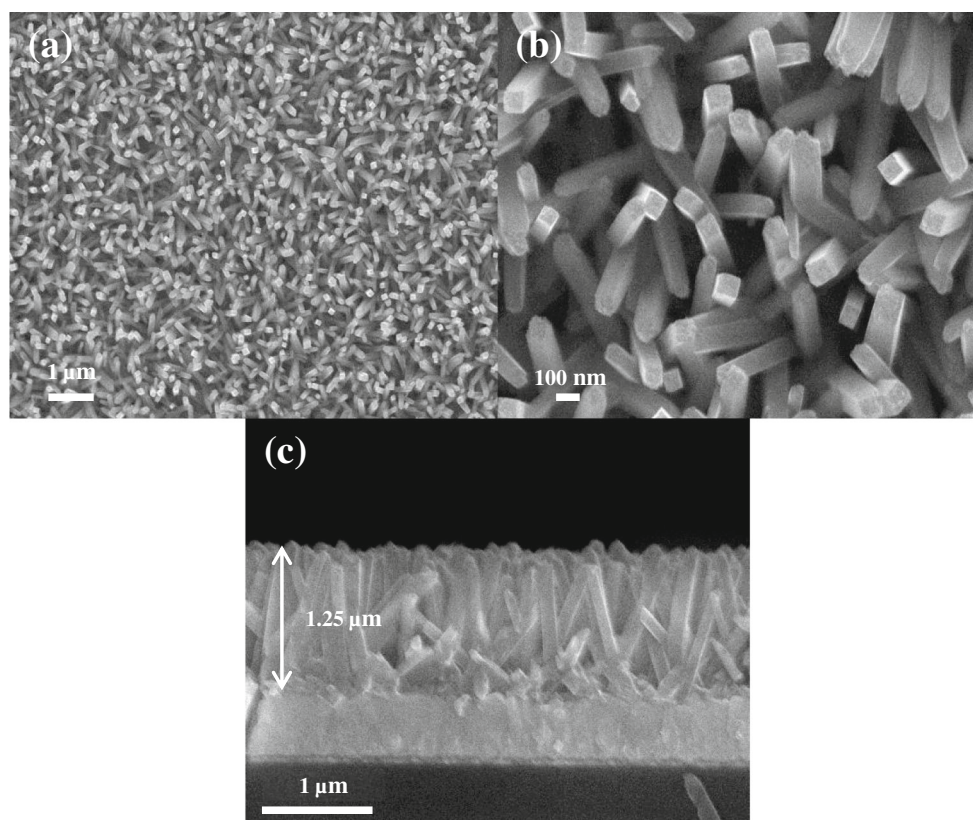


Fig. 3 Raman spectra of the TiO_2 nanorod arrays grown on FTO substrate

Fig. 4 **a** 10 k magnification, **b** 50 k magnification, and **c** cross-section FESEM image of the TiO₂ nanorod arrays grown on FTO substrate



Optical properties

The transmittance and absorption of the optimized sample are shown in Fig. 5a,b, respectively. Figure 5a shows the transmittance spectra of the TiO₂ nanorod in the wavelength region between 300 and 800 nm [14, 15]. The TiO₂ nanorod shows good transmittance in visible region with wavelength that is more than 400 nm [14, 15]. Meanwhile, for Fig. 5b, the absorbance spectra indicate that the TiO₂ nanorod exhibits high absorbance properties for wavelength below 400 nm which is in the ultra-violet region, and this correlates with its large bandgap [16–18].

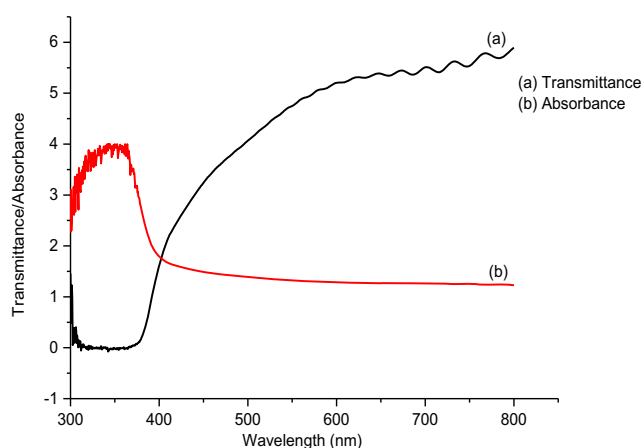


Fig. 5 The **a** transmittance and **b** absorbance spectra of the TiO₂ nanorod arrays

From these two spectra, it can be concluded that only light with the wavelength from 300 to 400 nm can reach the TiO₂ nanorod and thus contribute to the UV photoresponsivity. For these TNAs, the bandgap is indirect bandgap with energy of 3.0 eV as shown in Fig. 6. The determination of the optical bandgap is obtained by using Tauc's equation:

$$\alpha h\nu = A (h\nu - E_g)^n \quad (1)$$

where A is the constant, $h\nu$ is the photon energy, E_g is the bandgap energy, $n = 1/2$ for allowed direct transition, and $n = 2$

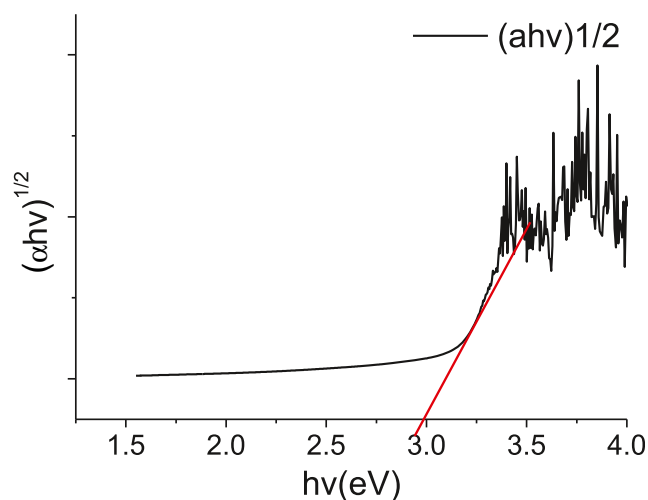


Fig. 6 Bandgap energy of from Tauc's plot

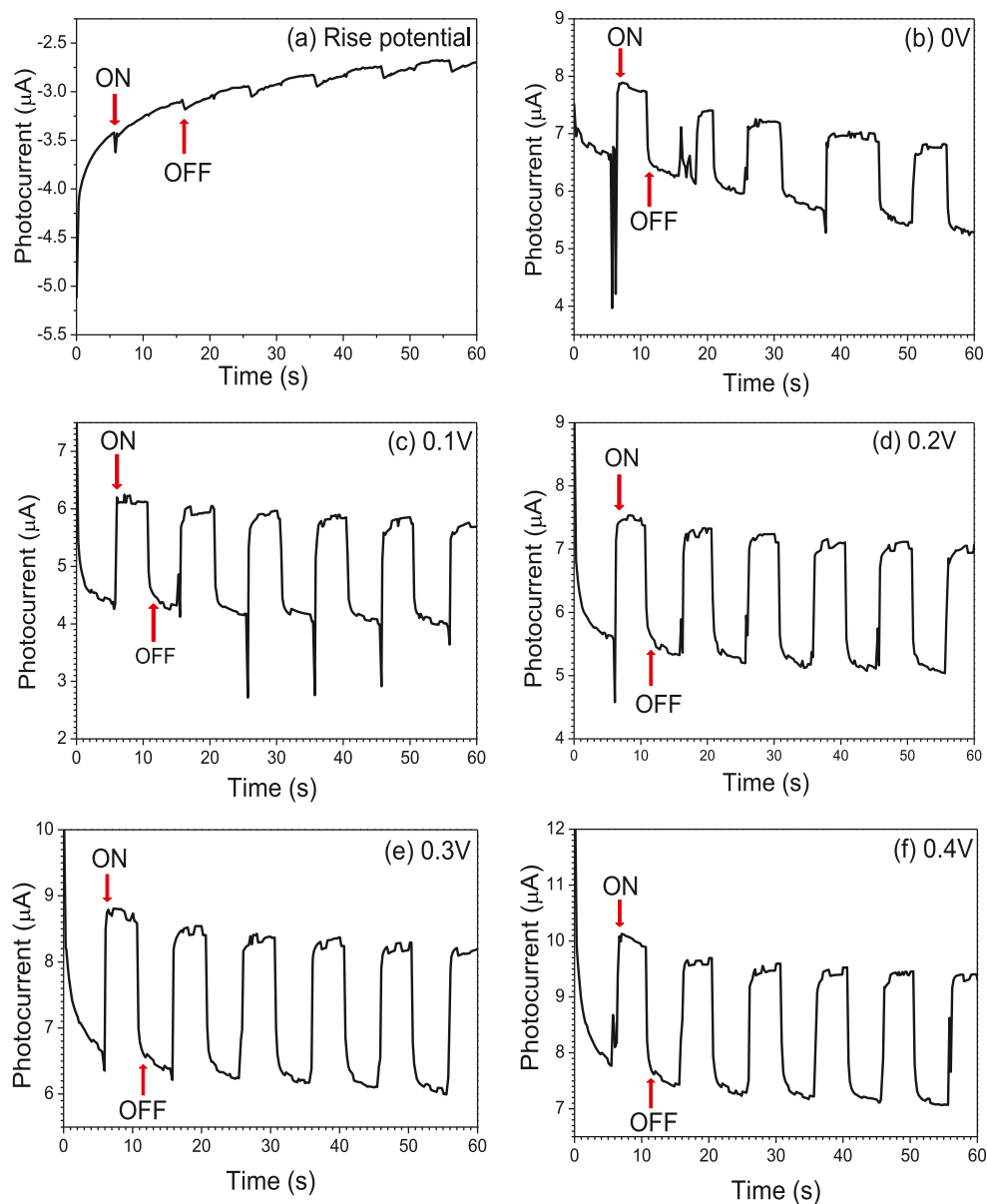
for allowed indirect transition. Thus, straight line segments in $(\alpha E)^2$ indicated direct bandgap and $(\alpha E)^{1/2}$ indicated indirect bandgap.

Photocurrent characteristics

Photocurrent of the optimized sample with different bias voltage from rise potential to 0.9 V (with 0.1 intervals) is shown in Fig. 7a–k. The rise potential of the optimized TiO₂ thin film was at -0.5 V. In terms of semiconductor physics, the energy can excite the electrons from valence to conduction bands, leaving hole in valence band, when energy provided by the irradiation is higher than the bandgap of TiO₂ [17]. It can be seen that the TNAs give acceptable differences in

photocurrent with different bias voltage supplied while the UV light was repeatedly switched on and off. However, at 0.9 V of bias voltage, the photocurrent has started to become saturated. This is because, by using the same sample, excited electrons from TiO₂ thin film undergo a redox reaction with OH⁺ from the electrolyte for a several times [18]. As the redox reaction occurs with a suitable acceptor and donor, electrons and hole from the thin film were prevented from recombined [19]. The values of the photocurrent for every on/off cycle were steady and repeatable. From the graph, the sudden rise and decay of the photocurrent that is called the surge current can be seen [20]. A surge current is an abrupt increase in current usually caused by a voltage imbalance. In general terms, surge is

Fig. 7 a Photocurrent of TNAs of rise potential and b–k photocurrent of the sample with 0–0.9 V bias voltage, respectively



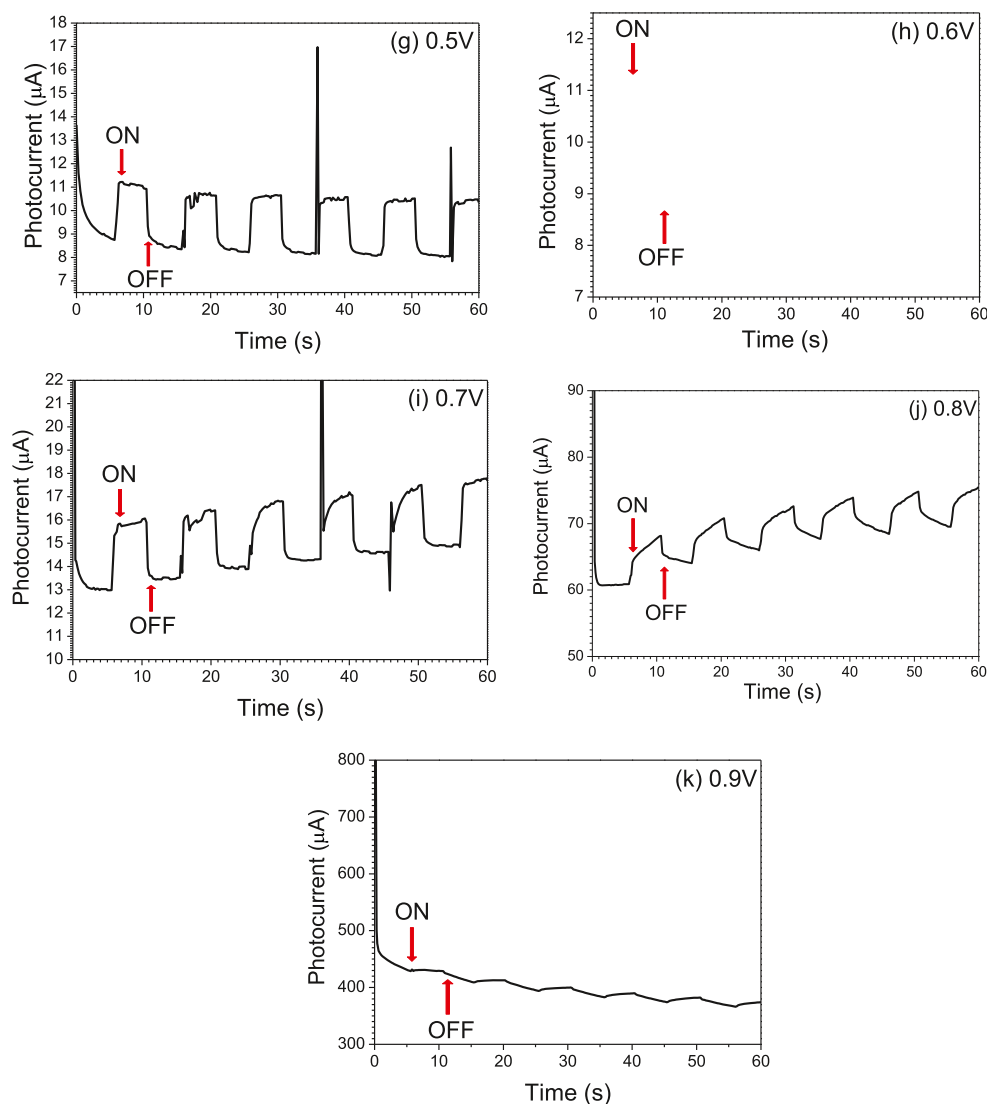


Fig. 7 (continued)

a sudden increase and electrical current is the rate of charge flows. In this study, the current surge was produced when the UV lamp is either turned ON or turned OFF. The electron experienced sudden transfer when UV light shone to the TiO_2 thin films. A UV lamp with a wavelength of 365 nm was used as light source as a study shows that radiations from light with higher wavelength are too small compared to radiation of 365 nm light [21].

Table 1 shows the photocurrent value, as well as the rise time and decay time of the photocurrent. Values for all photocurrent show acceptable differences with time [22]. Rise time and decay time also depict low value that is less than 1 s, indicating a rapid photoresponse characteristics [23]. Figure 8 shows the enlarged rising and decaying edges of the photocurrent. From Table 1, it can be observed that the photocurrent shows a value even in 0 V bias voltage. The optimized sample produced is an n-type semiconductor

confirmed by the photocurrent characteristics. The working principle of the UV photosensors, of n-type semiconductor material using PEC method, is simply discussed and shown in Fig. 9 [24]. When UV light (365 nm) shone on the nanorod/electrolyte UV detector, the incident photons that pass through the FTO glass into the nanorod, and electrons in TiO_2 are excited from the valence band to the conduction band, generating electron-hole pairs in the nanorod. The built-in potential produced by solid-liquid heterojunction separates the UV light-generated electron-hole pairs. The separated holes move from the valence band of the nanorod into the interface of the nanorod/electrolyte, subsequently seizing the holes from the water OH^- anions ($h^+ + \text{OH}^- \rightarrow \text{HO}$). Considering the quite large nanorod/electrolyte surface area, the small diameter of the nanorod, and the built-in interface potential, a fast removal of holes from the surface can be expected. On the other hand, the separated electrons transport into the TiO_2 conduction

Table 1 Photocurrent value, as well as the rise time and decay time of the photocurrent

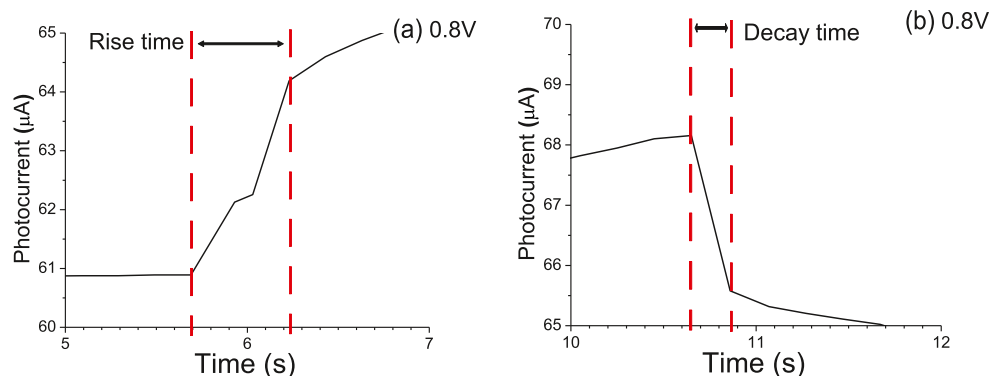
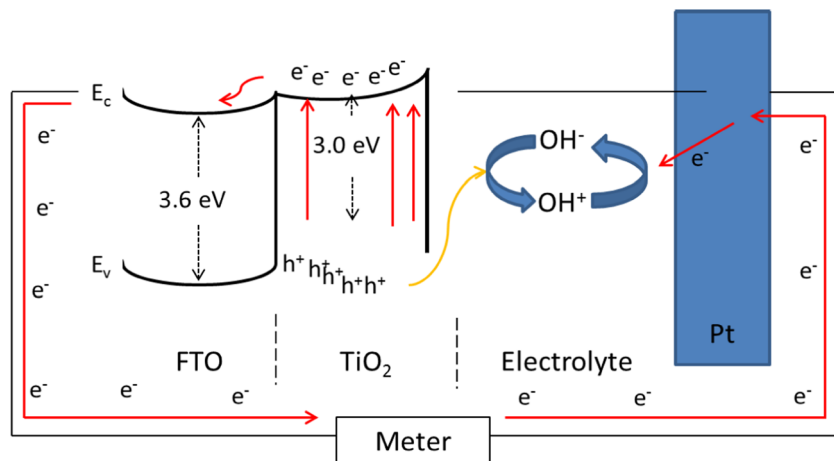
Voltage (v)	Photocurrent (μA)	Rise time (s)	Decay time (s)
Rise potential	3.5	0.3	0.6
0.1	3.0	0.6	0.4
0.2	2.6	0.4	0.4
0.3	2.5	0.4	0.2
0.4	3.4	0.7	0.5
0.5	2.4	0.7	0.4
0.6	2.2	0.4	0.5
0.7	1.9	0.4	0.4
0.8	1.6	0.5	0.3
0.9	—	—	—

band and are collected easily by the FTO contact. Those electrons move into the external circuit and then come back to the platinum (Pt) layer of the detector, thereupon returning the electrons to HO radicals ($e^- + \text{HO} \rightarrow \text{OH}^-$) at the interface of water/Pt. This way, the built-in potential makes the UV sensor generate photocurrent without any external bias

voltage. Even though 0 V bias is applied, the UV sensor still exhibits photosensitivity [23]. Bandgap bending of the TiO_2 nanorod does not change with different bias voltage as the photocurrent characteristics show the same behavior.

Conclusions

In conclusion, a photoelectrochemical cell-structured UV photodetector was developed using NaOH as the electrolyte and a rutile TNAs as the active photoelectrode. This device exhibits a distinguished performance for UV light detection. Under ambient environment, the photocurrent responds rapidly with UV light on/off switching irradiation. This photodetector also shows self-powered characteristics where it generates photocurrent without any external bias voltage. Different bias voltage applied gives acceptable differences on the photoresponse. Furthermore, this TiO_2 nanorod UV detector demonstrates high photosensitivity. All of these results indicate that this novel UV detector can be a promising candidate as a low-cost UV photodetector for commercially integrated photoelectronic applications.

Fig. 8 Response time of the TNA-based UV sensor**Fig. 9** Schematic energy band diagram and working principle of the UV photodetector [19]

Funding information Financial support was provided by the Ministry of Education (MOE) Malaysia (Vot 1213), Microelectronic and Nanotechnology-Shamsuddin Research Centre (MiNT-SRC), and Universiti Tun Hussein Onn Malaysia (UTHM) using Vot STG U347.

References

- Buzby, S., et al.: Visible light photocatalysis with nitrogen-doped titanium dioxide nanoparticles prepared by plasma assisted chemical vapor deposition. *J Vac Sci Technol B Microelectron Nanom Struct.* **24**(3), 1210–1214 (2006)
- Xiong, J., et al.: Efficient organic photovoltaics using solution-processed, annealing-free TiO₂ nanocrystalline particles as an interface modification layer. *Org. Electron.* **17**, 253–261 (2015)
- Okuya, M., et al.: Porous TiO₂ thin films prepared by spray pyrolysis deposition (SPD) technique and their application to UV sensors. *Solid State Ionics.* **172**(1–4 SPEC. ISS.), 527–531 (2004)
- Perillo, P.M., Rodríguez, D.F.: Sensors and actuators B: chemical short communication A room temperature chloroform sensor using TiO₂ nanotubes. *Sensors Actuators B Chem.* **193**, 263–266 (2014)
- Burda, C., Chen, X., Narayanan, R., El-sayed, M.A.: Chemistry and properties of nanocrystals of different shapes. *Chem. Rev.* **105**(4), 1025–1102 (2005)
- Chen, X., Mao, S.S.: Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chem. Rev.* **107**, 2891–2959 (2007)
- Lidija, M.T., Bojan, M.A., Paula, J.M., Olivera, B., Fernando, R.: Precursor particle size as the key parameter for isothermal tuning of morphology from nanofibers to nanotubes in the Na₂-xHxTinO_{2n+1} system through hydrothermal alkali treatment of rutile mineral sand. *Am. Chem. Soc.* **9**(5), 2152–2158 (2009)
- Zhou, W., Liu, X., Cui, J., Liu, D., Li, J., Jiang, H., Wang, J., Liu, H.: Control synthesis of rutile TiO₂ microspheres, nanoflowers, nanotrees and nanobelts via acidhydrothermal method and their optical properties. *CrystEngComm*, **13**(14), 4557–4565 (2011)
- Selman, A.M., Hassan, Z.: Highly sensitive fast-response UV photodiode fabricated from rutile TiO₂ nanorod array on silicon substrate. *Sensors Actuators A Phys.* **221**, 15–21 (Jan. 2015)
- Zu, X., et al.: Self-powered UV photodetector based on heterostructured TiO₂ nanowire arrays and polyaniline nanoflower arrays. *Synth. Met.* **200**, 58–65 (2015)
- Ahmad, M.K., et al.: Raman investigation of rutile-phased TiO₂ nanorods/nanoflowers with various reaction times using one step hydrothermal method. *J. Mater. Sci. Mater. Electron.* **27**(8), 7920–7926 (2016)
- Kim, J. et al.: Ga-doped ZnO transparent electrodes with TiO₂ blocking layer/nanoparticles for dye-sensitized solar cells, pp. 2–5, 2012
- Zhou, J.J., Wang, S.Y., Gunasekaran, S.: Preparation and characterization of whey protein film incorporated with TiO₂ nanoparticles. *J. Food Sci.* **74**(7), 50–56 (2009)
- Kuriechen, S.K., Murugesan, S., Raj, S.P.: Mineralization of azo dye using combined photo-Fenton and photocatalytic processes under visible light. *J. Catal.* **2013**, 1–6 (2013)
- Yang, G., Jiang, Z., Shi, H., Xiao, T., Yan, Z.: Preparation of highly visible-light active N-doped TiO₂ photocatalyst. *J. Mater. Chem.* **20**(25), 5301–5309 (2010)
- Tian, J., et al.: Enhanced photocatalytic performances of CeO₂/TiO₂ nanobelt heterostructures. *Small.* **9**(22), 3864–3872 (2013)
- Cao, C., Hu, C., Wang, X., Wang, S., Tian, Y., Zhang, H.: UV sensor based on TiO₂ nanorod arrays on FTO thin film. *Sensors Actuators B Chem.* **156**(1), 114–119 (Aug. 2011)
- R. van de Krol and Michael Grätzel, *Principles of Photoelectrochemical Cells*, vol. 102. Springer US, 2012
- Bard, A.J.: Design of semiconductor photoelectrochemical systems for solar energy conversion. *J. Phys. Chem. C.* **86**(May), 172–177 (1982)
- Li, H., Zheng, L., Shu, S., Cheng, H., Yang, Y.: Morphology control of anodic TiO₂ nanomaterials via cold work pretreatment of Ti foils. *J. Electrochem. Soc.* **158**(10), 346–351 (2011)
- Tian, Y., Hu, C., He, X., Cao, C., Huang, G., Zhang, K.: Chemical titania nanotube arrays for light sensor and UV photometer. *Sensors Actuators B Chem.* **144**, 203–207 (2010)
- Selman, A.M., Hassan, Z.: Effects of variations in precursor concentration on the growth of rutile TiO₂ nanorods on Si substrate with fabricated fast-response metal–semiconductor–metal UV detector. *Opt Mater (Amst).* **44**, 37–47 (Jun. 2015)
- Xie, Y., et al.: A self-powered UV photodetector based on TiO₂ nanorod arrays. *Nanoscale Res. Lett.* **8**(188), 1–6 (2013)
- Cao, C., Hu, C., Shen, W., Wang, S., Song, S., Wang, M.: Improving photoelectrochemical performance by building Fe₂O₃ heterostructure on TiO₂ nanorod arrays. *Mater. Res. Bull.* **70**(3), 155–162 (2015)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.