Blue TiO$_2$ nanotube arrays as semimetallic materials with enhanced photoelectrochemical activity towards water splitting

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Abstract: In the past years there has been a great interest in self-doped TiO$_2$ nanotubes (blue TiO$_2$ nanotubes) compared to undoped ones owing to their high carrier density and conductivity. In this study, blue TiO$_2$ nanotubes are investigated as photoanode materials for photoelectrochemical water splitting. Blue TiO$_2$ nanotubes were fabricated with enhanced photoresponse behavior through electrochemical cathodic polarization on undoped and annealed TiO$_2$ nanotubes. The annealing temperature of undoped TiO$_2$ nanotubes was tuned before cathodic polarization, revealing that annealing at 500 °C improved the photoresponse of the nanotubes significantly. Further optimization of the blue TiO$_2$ nanotubes was achieved by adjusting the cathodic polarization parameters. Blue TiO$_2$ nanotubes obtained at the potential of −1.4 V (vs. SCE) with a duration of 10 min exhibited twice more photocurrent response (0.39 mA cm$^{-2}$) compared to the undoped TiO$_2$ nanotube arrays (0.19 mA cm$^{-2}$). Oxygen vacancies formed through the cathodic polarization decreased charge recombination and enhanced charge transfer rate; therefore, a high photoelectrochemical activity under visible light irradiation could be achieved.

Key words: Blue TiO$_2$ nanotubes, cathodic polarization, self-doping, photoelectrochemical properties, water splitting

1. Introduction

Recent research activities on water splitting have focused on photocatalyst (PC) and photoelectrochemical (PEC) systems. Due to the fact that in PC systems the generated oxygen and hydrogen are not immediately separated, the PEC system has attracted significant interest. Illumination to a conductive electrode like TiO$_2$ leads to the generation of electron and hole pairs [1,2].

Photoelectrochemical (PEC) water splitting for H$_2$ generation has been used extensively to prevent environmental pollution [3–5]. PEC systems effectively separate the charge pairs into an anode and a cathode via absorbing light, and photochemical conversions can be achieved through the reduction of water to hydrogen [6,7]. TiO$_2$ is one of the most attractive materials for storage and conversion of energy exemplified as a photoanode for PEC water splitting [8–10], CO$_2$ reduction [11], and Li-ion battery [12] due to its nontoxicity, low cost, chemical stability, strong optical absorption, and photocorrosion resistance.

Among the different morphologies of TiO$_2$ nanostructures, a lot of effort has been devoted to TiO$_2$ nanotubes prepared by electrochemical anodization as efficient photoanodes for PEC cells due to simple fabrication, high surface area, one-dimensional nanostructure, and high orientation [13–15]. The well-ordered TiO$_2$ nanotubes provide enhanced charge separation and effective charge carrier transportation by decreasing the distance of charge carrier to electrolyte and increasing the electrode-electrolyte interfaces [16].

However, TiO$_2$ has been undesirable due to its weak electroconductivity and high levels of trap states [17,18]. The photocatalytic efficiency of TiO$_2$ is substantially restricted by its large bandgap energy and fast electron-hole recombination. The large bandgap of TiO$_2$ leads to the utilization of only the UV portion of light (only 4% of light). Therefore, bare TiO$_2$ suffers from weak light-harvesting and strong surface reflection [19–21].

To enhance light absorption, a lot of research activities have been focused on, for example, composite with semiconductors with a small bandgap [22], surface plasmon resonance of noble metal [23,24], dopant-free bandgap narrowing by improving TiO$_2$ morphology and electronic structure [25,26], and intercalation of doping elements [27–30].

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There are many efforts on modifying the valance band of TiO$_2$ by using nonmetals like N [31], S [32], and C [33]. The P states of these ions create impurity states above the valance band, therefore it shifts the valance band edge to higher levels and narrows the bandgap for harvesting the visible light [34]. On the other hand, in metal doping, cations fill the Ti sites and they introduce midgap electronic states inside the bandgap of TiO$_2$ [35,36].

Although metallic and nonmetallic element doping creates donor or acceptor states in the bandgap, dopants act as carrier recombination centers and decrease the efficiency of PEC [37]. Since the dopants introduce impurity states inside the TiO$_2$ bandgap, they lead to crystal instability and increase of charge carrier trapping [38]. To overcome these limitations, self-doping (reductive doping) has been introduced as a new strategy for increasing PEC efficiency. Several methods have been introduced to develop self-doped TiO$_2$, such as hydrogenation [39] and chemical and electrochemical reduction of TiO$_2$ [40]. As a result of reductive doping, the intrinsic defect concentrations are changed in the semiconductor. During the self-doping process, oxygen vacancies and Ti$^{4+}$ are formed, which can strongly enhance the PEC properties [41].

Narrowing the bandgap by means of oxygen vacancy states leads to an enhancement of light absorption followed by a color change to blue [42,43]. TiO$_2$ nanotubes exhibit an electrochromism process under a reduction environment and it could be turned to blue or black. The creation of Ti$^{4+}$ centers is accompanied by proton intercalation in the nanotubes [44].

Oxygen vacancies, as shallow donors, play a significant role in TiO$_2$ electronic properties [45]. Oxygen vacancies and Ti$^{4+}$ improve the light absorption of TiO$_2$ by separation of charge carriers. In fact, oxygen vacancies introduce impurity levels of 0.5–0.7 eV beneath the conduction band, therefore the electronic states could be generated inside the TiO$_2$ band gap [41,46]. This results in enhanced charge transport behavior and light absorption. In fact, via self-doping, TiO$_2$ semiconductor behavior of TiO$_2$ could be turned into an almost semimetallic behavior [47].

It is worth noting that during the reduction, the voltage should be optimized to prevent the evolution of excessive hydrogen [48] in this system. After all, developing a strategy to synthesize TiO$_2$ nanotubes with narrowing bandgap and high photoelectrochemical application is still a great challenge.

In this study, self-doped TiO$_2$ nanotube arrays (NTAs) are fabricated by using a facile cathodic polarization method producing an effective photocurrent for water splitting applications.

2. Materials and methods

An electrochemical anodization process was used to produce TiO$_2$ nanotube arrays. A commercial pure titanium sheet (grade 2, 0.6 mm) was prepared for this purpose as the anode material in the anodization process. Titanium samples were cut in dimensions of 1 × 2 cm$^2$ and ground step by step up to 1200 grid. For more smoothing, mechanical polishing with Al$_2$O$_3$ slurry (0.05 µm powder) was applied. The samples were then cleaned in acetone and ethanol for 15 min in an ultrasonic bath. The electrochemical anodization was carried out in two steps. In both steps, anodization was performed at the voltage of 60 V (high power DC power supply KXN6010D) for 4 h at 30 °C and in ethylene glycol (EG), 0.15 M NH$_4$F, and 3 vol.% DI water solution. Cylindrical stainless steel was used as the cathode material. During anodization, the electrolyte was agitated by using a magnetic stirrer.

The TiO$_2$ nanotube layer formed at the first step was ultrasonically removed in distilled water to expose the fresh surface of Ti. Then, the second anodization step was performed on this fresh surface. As-anodized samples were annealed at three different temperatures of 480, 500, and 520 °C by heating at the rate of 1.5 °C/min for 4 h. Subsequently, they were left in the furnace to cool down.

Blue TiO$_2$ nanotubes were produced by using cathodic electrochemical polarization in a three-electrode system with a workstation (AUTOLAB). The TiO$_2$ nanotube samples annealed at 500 °C were placed as a working electrode in the supporting electrolyte of 0.5 M Na$_2$SO$_4$. A platinum sheet (1.5 × 3 cm$^2$) and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The cathodic polarization process was performed at −1.2, −1.4, and −1.6 V for durations of 5, 10, and 20 min. After cathodic polarization, the blue TiO$_2$ nanotubes were dried in an oven at 80 °C for 30 min.

The surface morphology characterization of TiO$_2$ NTAs was performed by field emission scanning electron microscopy (FE-SEM; MIRA3FEG-SEM, TESCAN USA, Inc.,Warrendale, PA, USA). An X-ray diffraction technique [X’Pert PRO MPD (Malvern Panalytical Inc., Westborough, MA, USA)] employing Cu Ka radiation was used to characterize the phases and their purities. The chemical composition of metal oxide samples was characterized by X-ray photoemission spectroscopy (XPS) (SPECS EA 300 equipped with Al monochromatic anode). To examine the electrochemical response of TiO$_2$ NTAs before and after doping, cyclic voltammetry (CV) (AUTOLAB) was utilized in the dark and at a scan rate of 100 mV s$^{-1}$.

The PEC performances of the undoped and doped TiO$_2$ NTAs were evaluated in a three-electrode configuration consisting of TiO$_2$ NTAs as the working photoelectrode, Ag/AgCl as the reference, and Pt rod as the counter electrode. The
measurements were conducted in the supporting electrolyte of 0.5 M \( \text{Na}_2\text{SO}_4 \) using potentiostat/galvanostat (AUTOLAB) under solar-like irradiation of Xe lamp at AM 1.5 (100 mW·cm\(^{-2}\)). Linear sweep voltammetry (LSV) was performed at a scan rate of 100 mV·s\(^{-1}\). The chronoamperometric study was also carried out under chopped light irradiation (light on–off cycles: 20 s) at applied fixed bias of +0.5 V. Mott–Schottky measurements were performed at different applied DC potentials between −0.1 to 0.9 V and a frequency of 1000 Hz with a step potential of 0.05 V.

The electrochemical response of the pristine and blue TiO\(_2\) NTAs was investigated by electrochemical impedance spectroscopy (EIS) studies in a conventional three-electrode cell employing an electrochemical workstation (AUTOLAB) under a supporting medium of 0.5 M \( \text{Na}_2\text{SO}_4 \). All EIS tests were performed at an open-circuit voltage and the frequency window differed from 100 kHz to 0.01 Hz with a 10 mV rms sinusoidal modulation.

3. Results and discussion
3.1. Morphology characterization
Figure 1 presents the process schematic, the macro photograph of surface colors, and FESEM images of the TiO\(_2\) NTAs. As shown in Figure 1a, the as-anodized TiO\(_2\) NTAs were grey and after annealing at 500 °C turned to yellowish-grey. As seen

Figure 1. a) Macrophotograph of surface colors and process schematic of as-anodized, annealed (pristine) and blue TiO\(_2\) NTAs and FESEM images of b) pristine and c) blue TiO\(_2\) NTAs (the insets show the cross-section view of the nanotubes).
from the process schematic in Figure 1a, to produce blue TiO₂ NTAs, the annealed TiO₂ NTAs (as called pristine) were reduced under the cathodic polarization process. The reduction process has occurred during the cathodic polarization and blue coloration of the annealed TiO₂ NTAs was observed due to electrochromism similarly found in transition metal oxides such as TiO₂ [49]. In fact, the electrochromic effect has occurred owing to the reduction of Ti⁴⁺ to Ti³⁺ together with proton intercalation. During the cathodic polarization in Na₂SO₄ supporting electrolyte, Ti⁴⁺ is reduced to Ti³⁺ after applying a negative potential. The accumulation of electrons has occurred on the semiconductor film and charge compensation was achieved by a proton as follows [50]:

\[ \text{Ti}^{4+} + e^- + \text{H}^+ = \text{Ti}^{3+} + \text{H}^+ \]

The Ti³⁺ defects (or oxygen vacancy states) are formed because of injected electrons below the conduction band. Introducing the oxygen vacancy states leads the semiconductor pristine TiO₂ NTAs to transform into semimetallic blue TiO₂ nanotubes [26]. Figures 1b and 1c show FESEM images of the surface and also cross-sections (the insets) of pristine and blue TiO₂ NTAs, respectively. As shown in the figures, there is no difference between the surface morphologies of pristine and blue TiO₂ NTAs. The reason is that both have the same anodizing time and annealing process. Furthermore, the electrochemical reductive process only changes electronic and defect levels of blue TiO₂ NTAs, which has no obvious effect on the shape and length of the tubes.

Figures 2a and 2b show XRD and XPS patterns of the pristine and blue TiO₂ NTAs. Based on the XRD patterns (Figure 2a), the strong peak at 25.31 demonstrates that both the pristine and the blue TiO₂ NTAs are completely crystalized and consist of mostly pure anatase phase. Furthermore, there are no clear differences between the XRD patterns of pristine and blue TiO₂ NTAs, as their peaks positions are the same. Therefore, the phase structure is not affected by reductive doping and electrochromism. To investigate surface bonding, XPS spectrums of TiO₂ NTAs are shown in Figures 2b–2d. From high-resolution XPS spectra for the Ti2p and O 1s regions shown in Figures 2c and 2d, it can be concluded that the binding energies of Ti2p and O 1s are shifted to lower energies. These negative shifts are due to the presence of Ti3p and oxygen vacancies compared to the pristine one. For pristine TiO₂ NTAs, the binding energies of Ti2p3/2 and 2p1/2 XPS

![Figure 2. a) XRD patterns (anatase TiO₂ JCPDS card no. 21-1272) and b) XPS spectra, c and d) high-resolution XPS spectra of pristine and blue TiO₂ NTAs.](image-url)
Peaks are around 460 and 465 eV, respectively. These energies are typical for the Ti\(^{4+}\)–O bonds of TiO\(_2\) [26,51]. On the other hand, from Figure 2c it can be clearly seen that in blue TiO\(_2\)NTA, the Ti2p3/2 and 2p1/2 peak positions are shifted to lower energies. In blue TiO\(_2\)NTAs, the Ti2p3/2 and 2p1/2 peaks are centered at about 455 and 462 eV, respectively. This negative shift indicates the presence of oxygen vacancies and confirms the 2p3/2 and 2p1/2 peaks of Ti\(^{3+}\) [52]. The O 1s XPS spectra also display the same negative shift with a single peak at about 532 and 527 eV for pristine and blue TiO\(_2\)NTAs, respectively (Figure 2d). The XPS characterization findings offer oxygen vacancies that are intercalated into the TiO\(_2\) lattice during the cathodic polarization process.

To optimize the annealing temperature of pristine TiO\(_2\)NTA, the annealing process was performed at three different temperatures of 480, 500, and 520 °C. Based on our previous work [53], the XRD patterns of the TiO\(_2\)NTA annealed at 480, 500, and 520 °C showed only the anatase crystalline phase without detecting a rutile phase. Also, the XRD patterns revealed that pristine TiO\(_2\)NTA annealed at 500 °C has a much stronger intensity ratio of the anatase (101) peak than those of pristine TiO\(_2\)NTA annealed at 480 and 520 °C.

### 3.2. Photoelectrochemical measurements

#### 3.2.1. Annealing temperature

The cyclic voltammetry (CV) test was performed in the dark on various annealed pristine TiO\(_2\)NTAs in order to scan all possible redox reactions on the surface and find the proper potential for the next photoelectrochemical investigations. Therefore, CV tests were performed in three electrode systems in 0.5 M Na\(_2\)SO\(_4\) solution at a scan rate of 100 mV s\(^{-1}\). Figure 3a shows the related voltammograms. As seen from Figure 3a, with increasing the applied bias, the current density

![Figure 3](image-url)

**Figure 3.** a) CV curves at a scan rate of 100 mV s\(^{-1}\) in the absence of light source, b) linear sweep voltammograms collected under 100 mW cm\(^{-2}\) illumination at a scan rate of 100 mV s\(^{-1}\), and c) photoresponse vs. time under chopped light irradiation at fixed +0.5 V applied bias of the pristine TiO\(_2\)NTA annealed at different temperatures of 480, 500, and 520 °C.
is enhanced because of water oxidation. In contrast, decreasing the applied bias reduces the current density owing to water reduction. The applied bias of chronoamperometry tests should be selected far enough from redox potentials. Figure 3a shows that +0.5 V could be the proper potential for photoelectrochemical investigations. It is worth noting that as shown in Figure 3a, the pristine TiO$_2$ NTA annealed at 500 °C possesses significantly higher current density due to anatase structure and generally anatase is much more conductive than amorphous TiO$_2$.

To investigate the photoelectrochemical properties, the photocurrent densities of different pristine samples were measured by linear sweep voltammetry (LSV) in a three-electrode electrochemical system at a scan rate of 100 mV s$^{-1}$ in the dark and under 100 mW cm$^{-2}$ illumination. As shown in Figure 3b, all pristine samples revealed a very low dark current. No electrocatalytic water splitting occurs in the dark. Obviously, under illumination, the current density is enhanced and the pristine annealed at 500 °C shows higher photocurrent density indicating more effective charge separation. Figure 3c shows the chronoamperometry plots of pristine samples annealed at different temperatures under chopped irradiation and applied voltage of +0.5 V. A good photoresponse can be seen in chopped light cycles in all samples. In the dark mode, the current values are almost zero, whereas upon illumination, the photocurrent rapidly increases to a steady-state value and significant photoactivity can be observed. This manner is repeated for all on/off cycles. From Figure 3c, the steady-state photocurrent of the pristine annealed at 500 °C (0.19 mA cm$^{-2}$) is nearly 2 times higher than of pristine annealed at 480 °C (0.11 mA cm$^{-2}$) and also nearly 1.2 times higher than of pristine annealed at 520 °C (0.16 mA cm$^{-2}$), indicating a higher photocactivity of the pristine annealed at 500 °C. Therefore, the annealing temperature of 500 °C was selected for further investigation of the blue TiO$_2$ NTAs.

### 3.2.2. Cathodic polarization voltage

The photocatalytic properties of blue TiO$_2$ NTAs were evaluated by optimizing cathodic polarization parameters. For this purpose, cathodic polarization was performed at three different voltages of –1.2, –1.4, and –1.6 V to determine the proper synthesis voltage for photocatalytic application. Before recording the photoresponse of the samples, CV tests were performed in 0.5 M Na$_2$SO$_4$ solution at a scan rate of 100 mV s$^{-1}$ in the dark to find a safe potential for the next photoelectrochemical investigations. Figure 4a shows the CV curves of blue TiO$_2$ NTAs synthesized at different voltages. From Figure 4a, the CV curves of blue TiO$_2$ NTAs have a rectangular shape characteristic, indicating a weak dependence of current density on potential because blue TiO$_2$ NTA reveals semimetallic behavior. In contrast, a strong dependence of current density on potential and consequently a triangular shape of the voltammogram indicate semiconducting behavior (Figure 3a). As seen from Figure 4a, the blue TiO$_2$ synthesized at –1.3 V reveals low current density and it still slightly retains the semiconducting feature due to the low density of Ti$^{3+}$ states. Obviously, among the voltagrams in Figure 4a, the blue TiO$_2$ at –1.4 V has higher current density owing to a higher level of Ti$^{3+}$ states, indicating more efficient charge separation and transport in the sample with a high level of Ti$^{3+}$ states. Also, increasing the negative voltage up to –1.6 V leads to more reduction and evolution of H$_2$, therefore the current is declined [26]. Figure 4b shows LSV curves of the blue TiO$_2$ NTAs synthesized at different voltages. From Figure 4b, it is obvious that unlike the pristine TiO$_2$ NTAs, the blue ones have a remarkable current response in the dark. The blue TiO$_2$ NTAs have greatly enhanced electrical conductivity because of the high content of Ti$^{3+}$ states, therefore it reveals an increased dark current. Also, the blue TiO$_2$ NTAs synthesized at –1.4 V has a high photocurrent compared to that of others due to its high content of Ti$^{3+}$ states. According to the chronoamperometry plots of the blue TiO$_2$ NTAs (Figure 4c) at an applied bias of +0.5 V and under chopped irradiation, it is clear that the steady-state photocurrent of blue TiO$_2$ NTA synthesized at –1.4 V (0.39 mA cm$^{-2}$) is nearly 1.5 times higher than of the blue TiO$_2$ NTAs at –1.2 V (0.25 mA cm$^{-2}$) and nearly 1.2 times higher than of the blue TiO$_2$ NTAs at –1.6 V (0.31 mA cm$^{-2}$). The Mott–Schottky method was used to estimate the Ti$^{3+}$ states densities. Figure 4d shows Mott–Schottky plots of the blue TiO$_2$ NTAs synthesized at different voltages. By calculating the slope of the Mott–Schottky plot, the donor density of blue TiO$_2$ NTAs could be obtained. The Mott–Schottky plot is based on the square of capacitance $(1/C^2)$ against applying potential. The space charge capacitance $C_{sc}$ of a semiconductor is expressed as follows:

$$
\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon \varepsilon_0 \varepsilon N_D} (E - E_{fb} - \frac{K_BT}{e})
$$

where $N_D$ is the donor density, $\varepsilon_0$ is the dielectric permittivity of the vacuum $(8.854 \times 10^{-14}$ F cm$^{-1}$), $\varepsilon$ is the dielectric constant of the semiconductor $(31$ for TiO$_2$ anatase$)$, $e$ is the elementary electric charge, and $K_BT$ is the Boltzmann constant. Based on the Mott–Schottky equation and the slopes of the plots in Figure 4d, the donor densities of the blue TiO$_2$ NTA synthesized at –1.2, –1.4, and –1.6 V are $1.71 \times 10^{13}$, $4.89 \times 10^{13}$, and $4.19 \times 10^{12}$ cm$^{-3}$, respectively. This indicates that the blue TiO$_2$ NTA at –1.2 V has a lower donor density than the blue samples at –1.4 and –1.6 V and there are slight differences between the donor densities of the blue TiO$_2$ NTAs at –1.4 and –1.6 V.
3.2.3. Cathodic polarization time

The duration of the cathodic polarization process for acquiring optimized blue TiO$_2$ NTAs was also investigated. Figure 5a shows CV curves of blue TiO$_2$ NTAs synthesized in 5, 10, and 20 min. As seen from the figure, the blue TiO$_2$ NTAs synthesized in 5 and 10 min have the same current density, whereas the blue TiO$_2$ NTAs synthesized in 20 min reveal lower current density. It is clear that increasing the reduction time of TiO$_2$ NTAs up to 20 min enhances sample resistance and decreases conductivity due to the instability of oxygen vacancies and the destruction of TiO$_2$ NTAs. To evaluate the photoelectrochemical properties, an LSV study was performed on blue TiO$_2$ NTAs synthesized in different times of 5, 10, and 15 min; the results are shown in Figure 5b. As shown in Figure 5b, the blue TiO$_2$ NTA synthesized in 10 min has a higher photocurrent compared to that of NTA synthesized in 5 and 20 min, owing to its high content of Ti$^{3+}$ states. In fact, more efficient charge separation and transport could have occurred in the high density of Ti$^{3+}$ states. The chronoamperometry plots of the blue TiO$_2$ NTAs synthesized at different times are also shown in Figure 5c. As seen from Figure 5c, the steady-state photocurrent of blue TiO$_2$ NTAs synthesized in 10 min (0.39 mA cm$^{-2}$) is nearly 1.3 times higher than of blue TiO$_2$ NTAs synthesized in 20 min (0.3 mA cm$^{-2}$) and nearly 1.2 times higher than of blue TiO$_2$ NTAs synthesized in 5 min (0.34 mA cm$^{-2}$). Obviously, the photoresponse of blue TiO$_2$ NTAs was found to be weakened as the cathodic polarization time exceeds 10 min. The Mott–Schottky plots of blue TiO$_2$ NTAs synthesized at different times are shown in Figure 5d. Based on the Mott–Schottky plots, the donor densities of the blue TiO$_2$ NTA synthesized in 5, 10, and 20 min are $3.35 \times 10^{22}$, $4.59 \times 10^{22}$, and $1.82 \times 10^{21}$ cm$^{-3}$, respectively. It can be clearly seen that when the cathodic polarization time extends to 20 min, the donor densities of the blue TiO$_2$ NTA decline.
3.2.4. Optimized undoped and self-doped

To evaluate the self-doping process of a photoelectrochemical property, the photoactivity of pristine (undoped TiO$_2$ NTAs annealed at 500 °C) and blue (annealed TiO$_2$ NTAs reduced at –1.4 V for 10 min) TiO$_2$ NTAs is compared in Figure 6. The LSV in the dark and under illumination is shown in Figure 6a. Unlike the pristine TiO$_2$NTA with very low dark current, the dark current of blue TiO$_2$NTA is greatly enhanced owing to increased carrier density and massive defects in the blue TiO$_2$NTA. Also, clearly, the photocurrent of blue TiO$_2$NTAs under illumination is distinctly higher than that of the pristine, indicating more efficient charge separation and transport in the blue TiO$_2$NTA owing to the high density of Ti$^{3+}$ states.

The photoresponses of the pristine and blue TiO$_2$NTAs measured by chronoamperometry are shown in Figure 6b. The photocurrent of blue TiO$_2$NTA is about 2 times larger than that of pristine TiO$_2$NTA because the blue TiO$_2$NTAs have a high amount of oxygen vacancy or Ti$^{3+}$ donor sites, which leads to an increase in visible light absorption, charge separation, and transport of the sample. The results are comparable with similar studies in the literature [40,43,54,55]. Furthermore, as seen from Figure 6b, when the illumination changes to off, an apparent gradual decay of current (shown with arrow) could be seen in the pristine TiO$_2$NTA, suggesting an onset of recombination in the semiconductor pristine TiO$_2$NTAs. In contrast, the blue TiO$_2$NTA did not show this character and the photocurrent drastically decreased, confirming that the oxygen vacancies in the blue TiO$_2$NTAs act as charge carrier traps and hamper the electron-hole recombination [56].

To interpret the photoelectrochemical mechanism of the blue TiO$_2$NTA, OCP and EIS measurements were carried out after inducing stable conditions via the supporting electrolyte of 0.5 M Na$_2$SO$_4$. Based on the results, open-circuit voltages of 42 and 65 mV were separately obtained for the pristine and blue TiO$_2$NTA. Figure 7 depicts the Nyquist plot and the related equivalent circuit when the pristine and blue TiO$_2$NTAwas placed in contact with the electrolyte. Rs is the
resistance of the solution between the working and reference electrodes. Also, a serial combination of Faraday resistance and Warburg impedance is considered inside the nanotubes due to the diffusion-controlling nature of the process. In blue $\text{TiO}_2$ NTA, an RC pore connection was added in series to the equivalent circuit due to its capacitive behavior [26].

The straight line at 45° in Nyquist plots indicates diffusion processes in the system. The effect of blue $\text{TiO}_2$ NTA on the kinetics of the electrochemical processes can be interpreted from the data using ZView software. The ZView fitting results have been listed in Table 1. As seen from Table 1, the Rct resistance of the blue $\text{TiO}_2$ NTA was reduced to a negligible content of 0.000109 $\Omega \text{ cm}^{-2}$. This phenomenon is interpreted by reducing the bandgap owing to the oxygen vacancy levels, so the diffusion becomes completely capacitive. DRS measurements on the blue $\text{TiO}_2$ nanotubes revealed a significant reduction in bandgap energy. The results showed a narrowing band gap while doping manifesting a reduction of the bandgap from 3.16 eV for the pristine to 2.7 eV for the blue $\text{TiO}_2$ NTAs. Therefore, the absorption wavelength shifted from 390 nm to around 460 nm, which is a shift to the inset of the visible region [26]. Flatband potentials from the Mott–Schottky curves can be estimated as 40 mV for the pristine $\text{TiO}_2$ NTA. A positive slope of the samples indicates the semiconducting behavior of the n-type electrodes. Pristine $\text{TiO}_2$ NTA displayed a strong capacity dependence on the voltage that is normal.
for the space charge layer-controlled capacity of an n-type semiconductor. In contrast, the blue TiO$_2$NTA sample exhibited a weak dependence of capacitance on the applied voltage, meaning that the blue sample has metallic behavior. In metallic behavior, a capacitance is solely determined by the Helmholtz layer at the solid-liquid interface, hence a flatband potential cannot be expected [26]. Therefore, the oxygen vacancy levels significantly improved the electron transport of the blue TiO$_2$NTAs. Previous studies stated that by decreasing the resistance, an electron is easy to be transferred to the underlying TiO$_2$, hence electron injection is enhanced and photo application of the electrode is improved [57].

### 4. Conclusion

Self-doped (blue) TiO$_2$ NTAs can be produced through a simple cathodic polarization method. Tuning the annealing temperature of TiO$_2$ NTAs shows the high photoelectrochemical activity of TiO$_2$ NTAs annealed at 500 °C. The photoelectrochemical activity of the blue TiO$_2$ NTAs depends on the cathodic polarization parameters. Blue TiO$_2$ NTAs synthesized at –1.4 V with a duration of 10 min exhibit twice more photocurrent response (0.39 mA cm$^{-2}$) compared to the undoped TiO$_2$ NTAs (0.19 mA cm$^{-2}$). For blue TiO$_2$ NTAs, oxygen vacancies decrease the charge recombination and enhance the charge transfer rate, consequently leading to high photoelectrochemical activity needed for water splitting applications.

### Conflicts of interest

The authors declare no conflict of interest.

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