Comprehension of the Synergistic Effect between m&t-BiVO$_4$/TiO$_2$-NTAs Nano-Heterostructures and Oxygen Vacancy for Elevated Charge Transfer and Enhanced Photoelectrochemical Performances

Zhufeng Shao $^{1,*}$, Jianyong Cheng $^1$, Yonglong Zhang $^1$, Yajing Peng $^1$, Libin Shi $^1$ and Min Zhong $^2$

$^1$ College of Physical Science and Technology, Bohai University, Jinzhou 121000, China
$^2$ College of Chemistry and Materials Engineering, Bohai University, Jinzhou 121000, China
* Correspondence: jinhaiyuan@126.com

Abstract: Through the utilization of a facile procedure combined with anodization and hydrothermal synthesis, highly ordered alignment TiO$_2$ nanotube arrays (TiO$_2$-NTAs) were decorated with BiVO$_4$ with distinctive crystallization phases of monoclinic scheelite (m-BiVO$_4$) and tetragonal zircon (t-BiVO$_4$), favorably constructing different molar ratios and concentrations of oxygen vacancies (V$_o$) for m&t-BiVO$_4$/TiO$_2$-NTAs heterostructured nanohybrids. Simultaneously, the m&t-BiVO$_4$/TiO$_2$-NTAs nanocomposites significantly promoted photoelectrochemical (PEC) activity, tested under UV–visible light irradiation, through photocurrent density testing and electrochemical impedance spectra, which were derived from the positive synergistic effect between nanohetero-interfaces and V$_o$ defects induced energetic charge transfer (CT). In addition, a proposed self-consistent interfacial CT mechanism and a convincing quantitative dynamic process (i.e., rate constant of CT) for m&t-BiVO$_4$/TiO$_2$-NTAs nanoheterojunctions are supported by time-resolved photoluminescence and nanosecond time-resolved transient photoluminescence spectra, respectively. Based on the scheme, the m&t-BiVO$_4$/TiO$_2$-NTAs-10 nanohybrids exhibited a photodegradation rate of 97% toward degradation of methyl orange irradiated by UV–visible light, 1.14- and 1.04-fold that of m&t-BiVO$_4$/TiO$_2$-NTAs-5 and m&t-BiVO$_4$/TiO$_2$-NTAs-20, respectively. Furthermore, the m&t-BiVO$_4$/TiO$_2$-NTAs-10 nanohybrids showed excellent PEC biosensing performance with a detection limit of 2.6 µM and a sensitivity of 960 mA cm$^{-2}$ M$^{-1}$ for the detection of glutathione. Additionally, the gas-sensing performance of m&t-BiVO$_4$/TiO$_2$-NTAs-10 is distinctly superior to that of m&t-BiVO$_4$/TiO$_2$-NTAs-5 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 in terms of sensitivity and response speed.

Keywords: m&t-BiVO$_4$/TiO$_2$-NTAs nanoheterojunctions; oxygen vacancy defects; charge transfer; photodegradation; biosensing and gas-sensing application

1. Introduction

With the continuous development of globalization and the spread of infectious viruses (such as COVID-19) encroaching on human health, the sustainable utilization of energy and the protection of the natural environment have become issues of substantial concern worldwide. A promising avenue is photoelectrochemicals (PEC), which, due to the pioneering work of Fujishima and Honda, have received a great deal of attention for a variety of potential applications, including water-splitting hydrogen generation, rechargeable solar cells, photocatalytic fuel cells, organic pollutant photodegradation, and biosensing [1–3]. TiO$_2$ is credited as among the most promising and well-documented PEC materials, as it possesses an appropriate energy-band position towards the redox reaction of water splitting, has excellent chemical stability, is abundantly available, and is environmentally friendly. At present, powder suspensions and thin films are the two representative types of TiO$_2$-related photocatalysts [4]. Notably, powdered TiO$_2$-based PEC materials have been
adopted because they have a fully available surface area, lower requirements in terms of cleaning, and they can be conveniently manipulated [5]. Nevertheless, the practical application of TiO\(_2\)-related powdered photocatalysts is still under restrictions due to the poor PEC performance, low reusability, and low recyclability [6]. Compared with the PEC nanomaterials of particulates, thin-film TiO\(_2\)-related photocatalysts have gained more attention owing to the following reasons: (i) with valid and appropriate light absorption, abundant free electrons are generated; (ii) the thin-film form demonstrates maximum activity, with the activity up to an order of magnitude higher compared with the powder form; (iii) the operating cost and recycling reuse of thin-film-based panels are expected to be substantially lower compared with powder-like samples without mechanical stirring; (iv) more efficient electron transfer occurs in thin-film PEC nanosystems through the underlying conductive layer, and therefore, the thin-film system can substantially improve the PEC activity compared with powder suspension processes; (v) they are well suited to efficient large-scale applications [7,8]. Furthermore, the self-organized TiO\(_2\) nanotube array films (NTAs) prepared by the Ti foil anodic oxidation process and vertically oriented on Ti-metal substrates are outstanding nanoscale thin-film architectures for boosting the PEC and biosensing performances [9,10]. TiO\(_2\) NTAs with highly ordered nanoporous surfaces possess unique characteristics, which are summarized as follows: (i) an enhanced active adsorption area for redox target compounds [11]; (ii) ordered-array architectures, which not only enable charge transfer (CT) along the axial direction, but also enable the segregation of the photoexcited charge carriers [12]; (iii) band modification to improve the light absorption and reduce the charge recombination [13]. Although the profitable properties of TiO\(_2\) NTAs are evident, the intrinsic features of TiO\(_2\) remain, which mainly include the UV-activated wide band-gap energy (E\(_g\) ~3.2 eV), and the rapid charge recombination rate that results in a sluggish rate of charge separation [14], which inherently conflicts with the aim of PEC-related practical applications under visible-light irradiation. To circumvent the abovementioned obstacles, researchers have demonstrated that doping with metals (e.g., Au, Ag, and Cu) or nonmetals (e.g., C, N, and S) is a valid route for elevating the visible-light-harvesting capacity of TiO\(_2\) NTAs [15]. Metallic elements, when deposited on TiO\(_2\) NTAs, can induce a suitable band-gap shift and act as light gatherers, prolonging the wavelength absorption scope and enhancing the PEC activity in the visible-light region. Nevertheless, the method is hampered by several drawbacks, as noble-metal nanoparticles (NPs) are quite toxic in nature, the reaction setup is costly and cumbersome, and photocorrosion is inevitable during the PEC process. Likewise, using nonmetal ions instead of metals to dope TiO\(_2\)-NTAs photoanode materials is an alternative viable approach for exploring visible-light-active photocatalysts. Nonmetallic element doping could introduce mid-gap energy levels above the valence band (VB) of TiO\(_2\) NTAs and act as a trapping center for the photoexcited electrons, which achieve the expected purposes for the photoresponse of the narrow band gap and suppress the recombination of photogenerated species. The decrease in the electronegativity of PEC materials that leads to a reduced PEC-related capacity due to the introduction of new energy states is an unavoidable issue [16]. Considering the trend of practical application, visible-light-active PEC nanosystems with striking CT abilities are more advantageous because a smaller percentage (5%) of the solar spectrum is emitted in the UV region. Within this frame, the construction of TiO\(_2\)-NTAs-based nano-heterojunctions not only substantially broadens the light-harvesting window, but it can also help increase the speed of the charge carrier separation.

Bismuth vanadate (BiVO\(_4\)) is an intrinsic n-type direct band-gap ternary oxide semiconductor, and it has been proposed as a promising alternative to visible-light-active PEC materials owing to its high stability, nontoxicity, and appropriate band position [17]. The PEC performances of BiVO\(_4\) are intensely affected by the prepared morphology and crystallographic structure. BiVO\(_4\) appears in three main crystalline phases based on different synthesized methods: monoclinic scheelite (ms-BiVO\(_4\)), tetragonal scheelite (ts-BiVO\(_4\)), and tetragonal zircon (tz-BiVO\(_4\)), with E\(_g\) values of 2.4 eV, 2.4 eV, and 2.9 eV [18,19], re-
spectively. Among them, state-of-the-art ms-BiVO₄ is the most stable and has the best photocatalytic activity, delivering a remarkable stability above 1000 h. The theoretical photocurrent density was 7.5 mA cm⁻² with a solar-to-hydrogen conversion efficiency of 9.2% under AM 1.5 G illumination [20], which is mainly attributed to the transition from the VB to the conduction band (CB) caused by the orbital mixing of Bi 6s and O 2p, which leads to the narrowed band gap and the sufficient oxidation potential of the VB (ca. +2.79 eV vs. NHE) to oxidize various organic compounds [21]. Moreover, ts-BiVO₄ also possesses strong surface adsorption properties [24], which stemmed from the more negative oxidation potential of the VB (~70 nm), and sluggish electron transfer kinetics are the intrinsic drawbacks of the pristine ms-BiVO₄, which have rarely been studied, while the crystal phase of tz-BiVO₄ exhibits the lowest photocatalytic performance owing to its wide bandgap, which restricts the widespread photodegradation and water-splitting application in visible-light regions. Based on conclusive experiments [22], researchers have verified that an inferior carrier mobility (0.044 cm² V⁻¹ s⁻¹), short carrier diffusion length (~70 nm), and sluggish electron transfer kinetics are the intrinsic drawbacks of the pristine ms-BiVO₄, which result in unsatisfactory photocurrent densities. Moreover, Wang et al. [23] stressed that the reduction in the capability of electrons on the CB of pure ms-BiVO₄ (+0.04 eV vs. NHE) was weak, even though the holes on the VB of BiVO₄ possessed strong oxidation capability, which resulted in its inability to reduce the oxygen molecule (O₂) to a superoxide radical (O₂⁻), −0.33 eV vs. NHE) by trapping the electrons on the CB, as well as weak surface adsorption properties [24], which stemmed from the more negative O₂/O₂⁻ potential than the CB of ms-BiVO₄, and incurring a disappointing PEC conversion efficiency. In the single ms-BiVO₄ phototrigger system, the tradeoff between an adequate redox potential and the generation of plenty of energetic photoexcited carriers according to the bandgap limits improves the PEC performances. The redox reaction on a photoelectrode is an integral whole, and it only takes place when there is an excess of photogenerated e⁻ and h⁺ on the surface. Too many free movable phototriggered carriers accumulated on the surface of the semiconductor causes deficiency in the powerful in-built electric field for efficacious delivery, which is inevitably unfavorable for PEC reactions, and the carriers are more inclined to recombine in the interiors of photocatalysts. The construction of ms-BiVO₄/tz-BiVO₄ (m/t-BiVO₄) hetero- nanostructures is an alternative strategy to ameliorate the charge kinetics of ms-BiVO₄ alone, and in particular, to facilitate the charge separation, as researchers have recently demonstrated [25]. However, the m/t-BiVO₄ heterogeneous PEC materials are not only under harsh synthesis conditions, but they are also incapable of presenting an improvement in the energy-band-matching level to speed up the photoinduced charge segregation compared with ms-BiVO₄/TiO₂ and tz-BiVO₄/TiO₂ (m&t-BiVO₄/TiO₂) nano-heterostructures. Energy-band-matching m&t-BiVO₄/TiO₂-NTAs nano-heterojunctions with rich intrinsic oxygen vacancy (Vₒ) defects exhibit an impressive catalytic activity owing to the synergistic effect between the heterojunction interface effect and vacancy effect [26]. Furthermore, researchers have extensively unveiled the intrinsic correlation between the boosted PEC-related performances and the expedited CT dynamic process associated with the Vₒ in m&t-BiVO₄/TiO₂-NTAs nanocomplexes. The details of the contributions of the Vₒ defects are summarized as follows [23,27–29]: (I) Vₒ defects can function as electron donors that increase the majority carrier density and photovoltage; (II) Vₒ could provide shallow trapping sites to promote electron–hole (e⁻–h⁺) pair segregation and restrain the recombination of the charge carrier; (III) the electronic structure can be overlapped and delocalized by Vₒ defects, which leads to an enlarged light-absorption edge; (IV) the abundant surface Vₒ defects, which are positively charged, can serve as PEC reaction centers to adsorb adequate photodegradable active group species, including O₂⁻ and hydroxyl radicals (OH); (V) Vₒ sites contribute to the upward shift (more negative) in the Fermi level (E_F) and the CB of BiVO₄, and they can act as active sites to elevate the charge injection efficiency, benefitting from the favorable band-energy offset between the m&t-BiVO₄/TiO₂-NTAs nano-heterojunctions, which is instigated to enhance the frustrating reduction kinetics.

Contrasted with other preparation methods, hydrothermal synthesis is a preferable approach for the formation of nano-heteroarchitectures between the m&t-BiVO₄ and TiO₂.
NTAs. Its suitability for large-scale industrial production is due to the simple process, environmental friendliness, and low cost [30]. The pH value of the precursor solution has a substantial impact on the molar ratios of the crystalline phase and the concentration of the surface defect states for ms-BiVO$_4$ and tz-BiVO$_4$ [25,31], which could also have a striking impact on the energy band position and the efficiency of the interfacial CT in the heterojunction. According to the relevant research, the timescale for the interfacial CT and recombination ultrafast kinetic process of m&t-BiVO$_4$/TiO$_2$-NTAs nanohybrids is of a nanosecond (ns) magnitude [32], involving the rate-determining step of the surface redox reactions and making it exceedingly challenging to comprehend. The timescale is much greater than the timescale of the photoexcited $e^{-}-h^{+}$ pair transition from VB to CB (viz., the femtosecond (fs) level) [33]. Simultaneously, it is possible to integrate the probing technique of an ultrafast fs laser triggered with time-resolved photoluminescence (PL) spectroscopy into an instrument that is capable of measuring transient PL on nanosecond timescales, providing the verifiable quantitative and qualitative information on the charge carrier dynamics in the intermediate states in nano-heterostructures associated with the $V_o$ intrinsic defects, including the transient PL intensity of the time-dependent photoexcited carrier lifetime, and the rate constant of the CT [34,35], which plays a decisive role in improving the PEC-related performances. Logically, by utilizing the positive synergetic effects between m&t-BiVO$_4$ and TiO$_2$ NTAs, we can obtain an improved PEC efficiency and highly sensitive PEC aptasensor [36,37]. However, to the best of our knowledge, the qualitative interfacial CT mechanism and quantitative charge injection dynamic process associated with $V_o$ defects by taking advantage of transient-PL kinetics probing have not been comprehensively explored. Moreover, the inherent physical connection between the pH values of the precursor solution, different crystalline-phase molar ratios, and the expected concentration of $V_o$ defects are rarely referred to.

First, we fabricated tidy and smooth TiO$_2$ NTAs with highly ordered alignment top surfaces through the anodization approach, facilitating easy access for the uniform deposition of m&t-BiVO$_4$ NPs via a convenient hydrothermal method, which we used to construct m&t-BiVO$_4$/TiO$_2$ NTA type-II heterostructure nanohybrids with different crystalline-phase molar ratios and the expected concentration of $V_o$ defects. Moreover, the photoinduced carriers are dramatically separated and transferred at the interface between the m&t-BiVO$_4$ and TiO$_2$ NTAs, benefitting from the synergistic effects between the elevated band offset in staggered heterostructures and the increased exposed reaction active sites induced by the $V_o$ defects, which are responsible for the boosted PEC-related performances. Additionally, we can use the unique combination of nanosecond-time-resolved transient PL (NTRT-PL) and time-resolved PL (TRPL) spectroscopy to independently track the charge carrier dynamics between the donor and acceptor energy levels, qualitative and quantitative extrapolating the CT process at the interfaces between the m&t-BiVO$_4$ and TiO$_2$ NTAs, which allows for the acquisition of the CT rate coefficient and charge carrier lifetime. Moreover, the established correlations between the PEC degradation performance, biosensing and gas-sensing sensitivity, and the crystalline structural feature of the m&t-BiVO$_4$/TiO$_2$ NTA nano-heterostructures provide insight into the expected interfacial energy band alignment related to the $V_o$ defect concentration, which elevates the ultrafast injection of the free carriers from BiVO$_4$ into TiO$_2$ NTAs. Furthermore, the research highlights the importance and novelty of probing interfacial CT kinetic processes modulated by $V_o$ surface defects for understanding the mechanisms of PEC conversion in m&t-BiVO$_4$/TiO$_2$-NTAs nanocomplexes. We hope that the investigation can provide practical experiences and in-depth comprehension for the design of PEC-related devices with substantially superior performances.

2. Experimental Section

2.1. Preparation of TiO$_2$-NTAs Substrates via Anodization

We bought all the reagents and solvents from commercial sources, and we used them without any further purification. We prepared the TiO$_2$ NTAs by anodizing Ti foils in an
electrolyte containing NH$_4$F (0.45 wt.%) and ethanediol (98 vol.%). This process resulted in the formation of TiO$_2$ NTAs on the surface of the Ti foils, which researchers described in a previous report [35].

2.2. Fabrication of m&t-BiVO$_4$/TiO$_2$-NTAs Heterostructure Nanohybrids

The BiVO$_4$ NPs were deposited onto the surface of the fabricated TiO$_2$ NTAs via a facile low-temperature hydrothermal method. In brief, we sequentially dissolved a 2 mL concentration of 0.1 M of Bi(NO$_3$)$_3$ 5H$_2$O and a 2 mL concentration of 0.1 M of NH$_4$VO$_3$ in 19 mL of ethylene glycol, and we then added a 1 mL concentration of 2.0 M of HNO$_3$ to form a precursor solution. Adding HNO$_3$ aqueous solution can help dissolve other reagents and render the resulting solution more acidic. We adjusted the mixture to a certain pH value (2, 5, or 8) by slowly adding ammonia with a magnetic stirrer to obtain different crystalline-phase molar ratios of m&t-BiVO$_4$. We transferred the orange transparent precursor into a Teflon-lined stainless-steel autoclave (50 mL) after vigorous stirring for 30 min, and we maintained it at 100 °C with different hydrothermal deposition times (5 h, 10 h, and 20 h). We vertically placed the preprepared highly ordered TiO$_2$ NTAs in the autoclave in advance though a home-built Teflon sample holder.

As a reference for characterizing the optical and PEC performances, we prepared the pristine BiVO$_4$ films by the hydrothermal route. Briefly, we methodically dissolved 0.2 mmol of Bi(NO$_3$)$_3$ 5H$_2$O, 0.2 mmol of NH$_4$VO$_3$, and 1 mL of 2.0 M HNO$_3$ in 19 mL of ethylene glycol. We adjusted the pH value of the sample suspension to 5 with ammonia, and then vertically placed the prearranged clean FTO conductive glass substrate into the mixed solution and maintained it at 100 °C for 10 h.

After we rinsed the as-prepared specimens with deionized water, we dried them with a nitrogen gas flow. For facilitating the generation of intrinsic defects and the expected crystalline phases, we annealed the as-obtained specimens in a furnace in dry air. The annealing temperature was 450 °C, and the time was 30 min. The heating rate was 10 °C/min, and the cooling rate was 10 °C/min. The choice of the annealing temperature was deliberate to avoid the transformation of the crystal structure of t-BiVO$_4$ into m-BiVO$_4$ during the annealing process (annealing temperature > 500 °C) [38]. We present the details on the process of incorporating modified BiVO$_4$ NPs onto FTO and TiO$_2$ NTA surfaces with the same area size (1 cm × 1.5 cm) in Scheme 1.

![Scheme 1](image-url)

**Scheme 1.** Preparation process of m&t-BiVO$_4$/TiO$_2$-NTAs nanocomplex (a), and pristine BiVO$_4$ films (b).

2.3. Characterization

We characterized the microstructures of the as-prepared nano-heterostructures by scanning electron microscopy (SEM) (Hitachi S4200) and transmission electron microscopy (TEM) (JEOL JEM-2100). We performed the UV–visible diffuse reflectance spectrometry (UV–vis DRS) measurements using a UV–vis spectrophotometer (UV-1800, Shimadzu). We characterized the phase purity of the prepared specimens by an X-ray diffractometer (XRD) (Shimadzu XRD-600). We used micro-Raman spectroscopy to investigate the crystal structure and chemical bonding states of the nanocomposites, equipped with a confocal microscope with an Ar$^+$ laser operating at 532 nm (Horiba JY-HR800). We investigated
the oxidation states of the as-formed samples by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250). We determined the instrument’s resolution to be 1.0 eV from the Ag 3d$_{5/2}$ peak’s full width at half maximum. We calibrated the XPS energy scale by aligning the Ag 3d$_{5/2}$ line on clean silver with the $E_F$, which we set at 368.3 eV. The XPS spectra energy axis shifted due to the specimen charging that takes place during X-ray irradiation. Consequently, we set the C1s binding energy line to 285.0 eV, which is the standard hydrocarbon energy used to reference the charging effect.

We used CHI660E equipment (Chenhua) to perform the PEC-related performance tests. We performed the transient photocurrent density curve (transient I–t curve) measurements via frontside illumination under AM 1.5G (SS150A, ZOLIX) at a constant applied potential of 0 V in a 0.1 M Na$_2$SO$_4$ solution. The 0.2 M Na$_2$SO$_4$ solution acted as the electrolyte for the electrochemical impedance spectra (EIS) analysis. We constructed Mott–Schottky plots at 1 kHz to examine the relationship between the voltage and capacitance in the 0.5 M Na$_2$SO$_4$ solution. We adopted the following equation for the NHE potentials: $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.1976$ V, where $E_{\text{Ag/AgCl}}$ is the Ag/AgCl electrode.

We excited the NTRT-PL using a Ti:sapphire femtosecond (fs) laser system (Spectra-Physics). We present the schematic diagram of the experimental setup in Figure 1. We collected the data for the TRPL using a custom-built single-photon-counting system, and the excitation source wavelength was 375 nm. We dispersed the signals of the PL emission for Vo defects ($\lambda_{\text{em}} = 2.9$ eV) by means of a grating spectrometer, and we detected them by a high-speed photomultiplier tube conjunction with a single-photon-counting card.

![Figure 1. Schematic of experiment setup for NTRT-PL measurements.](image)

### 2.4. Performance of MO Photodegradation, PEC Biosensing, and Gas-Sensing Measurements

We assessed the photocatalytic activities of the as-prepared nano-heterojunctions using the photodegradation of MO under UV–visible light irradiation. We used the UV–vis spectrophotometer to assess the concentration of the MO solution (10 mg/L) every 20 min. We monitored the intensity change in the characteristic absorption peak at 465 nm in order to determine the concentration of the MO solution. We used a concentration of 2 mM methanol solution, isopropanol (IPA) as holes ($h^+$), and hydroxyl radicals (OH) scavengers to detect the reactive species [39].

We measured the PEC biosensing performance by the electrochemical workstation (CHI660E). Simultaneously, the supporting electrolyte was a 0.1 M solution of phosphate-buffered saline (PBS) (pH $= 7.0$) We determined the detection limit to be 0.5 V by observing the lowest value that could be distinguished from the background signal. We investigated the gas-sensing properties of the as-synthesized nanohybrids by a home-built test chamber (1 L). We used a nanoamperemeter (GT8230) to document the measuring current as a function of the exposure time by applying a sweep voltage (5V) under 100 ppm of NH$_3$.

### 3. Results and Discussions

We used SEM and TEM to characterize the surface morphology and cross-sectional arrangement of the pure TiO$_2$ NTAs, referenced pristine BiVO$_4$ films, and binary BiVO$_4$/TiO$_2$-NTAs nanohybrids with different BiVO$_4$ NP hydrothermal synthesis times (5 h, 10 h, and 20 h), as displayed in Figure 2. We prepared the BiVO$_4$ NPs with uniform size and reg-
ular spherical-shaped distribution on the FTO conductive surface by the hydrothermal method, and the average particle size of the BiVO$_4$ NPs was about 50 nm. Moreover, we found spherical-form BiVO$_4$ NPs with agglomeration in some places, which enhance the specific surface area, which increases the active surface area for the redox reactions [40]. Simultaneously, we manufactured the TiO$_2$ NTAs with smooth and uniform top surfaces on the Ti substrate, and the average pore diameter and wall thickness are about 100 nm and 10 nm, respectively, as depicted in Figure 2b. The inset in Figure 2b is the TEM image of a single nanotube, illustrating that the outer diameter and length are separately ca. 100 nm and 5 µm, respectively, which accord well with the top-view SEM observation. We present the typical SEM images for the vertical-view morphologies of the BiVO$_4$/TiO$_2$-NTAs nanohybrids for increasing the BiVO$_4$ NP hydrodeposition times from 5 h to 20 h with a precursor solution with pH values successively equal to 2, 5, and 8 after annealing at 450 °C in Figure 2c–e. We observed distinctly different nanotopographies (from dispersed or aggregated spherical-shaped NPs to clustered nanosheets) after the decoration of BiVO$_4$ onto the surfaces of the TiO$_2$ NTAs. We present the SEM image for the BiVO$_4$/TiO$_2$-NTAs nanocomposites with a BiVO$_4$ NP hydrothermal preparation time of 5 h (BiVO$_4$/TiO$_2$-NTAs-5) in Figure 2c, which we could use to precisely examine the discrete distribution of BiVO$_4$ NPs with an average size of nearly 30 nm, which embrace upon opening and infill the interstices of TiO$_2$ NTAs. Furthermore, we present the overhead-view SEM image of BiVO$_4$/TiO$_2$-NTA-10 in Figure 2d. The BiVO$_4$ NPs with a mean size of ca. 50 nm are evenly distributed on the top surface of the nanotube, as well as in the intertube space, and they also fill the interior of the nanotubes, connecting them together. The skeleton of the TiO$_2$ NTAs remains unchanged. BiVO$_4$ nanosheets (NSs) formed in some areas on the surfaces of the TiO$_2$ NTAs. The top-view SEM image of the BiVO$_4$/TiO$_2$-NTAs nanocomposites with a BiVO$_4$ hydrothermal reaction time of 20 h, labeled as BiVO$_4$/TiO$_2$-NTAs-20, are exhibited in Figure 2e. The result further verified that the synthetic reaction time and pH value for the preparation of BiVO$_4$ are essential factors, as they have a tendency to aggregate together by forming NS clusters, randomly distributed on the top surfaces of the nanotubes, with a length and width of approximately 120 nm and 100 nm, respectively, which are in good agreement with the published article in terms of the occurrence of the introduction of foreign species at the surface, which usually block the nanotube openings [41].

**Figure 2.** SEM pictures of (a,b) top-view for as-formed pristine BiVO$_4$ films and pure TiO$_2$-NTAs, and low-resolution TEM picture for individual nanotube of TiO$_2$ inset in figure (b). (c–e) Top-view SEM images of BiVO$_4$/TiO$_2$-NTAs with BiVO$_4$ hydrothermal-deposition times of 5 h, 10 h, and 20 h, respectively. (f) SEM picture with cross-section for as-obtained BiVO$_4$/TiO$_2$-NTAs nanoheterostructures with BiVO$_4$ nanoparticles (NPs) deposited time 10 h.
To definitively illustrate the formation of BiVO$_4$/TiO$_2$-NTAs nano-heterostructures, we performed a cross-sectional SEM characterization on a representative specimen of BiVO$_4$/TiO$_2$-NTAs-10, as presented in Figure 2f. The incorporation of BiVO$_4$ NPs led to an increase in the surface roughness of the BiVO$_4$/TiO$_2$-NTAs-10 nanohybrids, which indicated that the particle size of the BiVO$_4$ and the outer diameter of the individual TiO$_2$ nanotube were about 50 nm and 100 nm, respectively, which coincide with the results of Figure 2b,d. Most notably, the deposited BiVO$_4$ NPs screened the entrances of the TiO$_2$ NTAs, successfully preparing the BiVO$_4$/TiO$_2$-NTAs nano-heterostructures.

We examined the crystalline structures and phase compositions of the as-prepared films in depth by XRD. We present the XRD patterns of the pristine TiO$_2$ NTAs, pure BiVO$_4$ films, and BiVO$_4$/TiO$_2$-NTAs binary nano-heterojunctions in Figure 3. The BiVO$_4$/TiO$_2$-NTAs dual nano-heterostructures with various thermal depositing times (5 h, 10 h, and 20 h) correlate with the different pH values (2, 5, and 8, respectively) of the precursor solutions. Evidently, all the specimens had narrowed and sharpened peaks under the hydrothermal crystallization conditions, proving that the as-fabricated products were crystalline, as expected, which is consistent with a previous report [42]. As shown in Figure 3a, there are five diffraction peaks of the untampered TiO$_2$ NTAs (labeled with a ‘▼’ mark), with diffraction 2$\theta$ angles located at 37.88°, 48.12°, 53.97°, 55.10°, and 62.74°, which are indexed to the (004), (200), (105), (211), and (204) diffraction planes, respectively. These results suggest that the sample is anatase TiO$_2$ (Card No. 21-1272). The anatase TiO$_2$, in particular, has a better PEC performance than the other crystal phases, resulting from the smaller effective mass and longer carrier lifetime, which result in a faster migration rate and higher generation of active species for PEC reactions [43]. We present the XRD patterns of the as-obtained BiVO$_4$ films with pH values equal to 5 of the precursor solution annealing at 450 °C in Figure 3b, in which it can be seen that the locations of the diffraction peaks coincide with the tz-BiVO$_4$ and ms-BiVO$_4$ phases, according to the standard JCPDS files, which proves the successful fabrication of the m/t-BiVO$_4$ isotype crystal-phase heterojunctions. Specifically, the prominent peaks sited at 18.3°, 24.4°, 32.7°, 34.7°, 43.8°, and 50.7° typically correspond to the (101), (200), (112), (220), (103), and (213) crystal planes (labeled with a ‘■’ mark) of the tz-BiVO$_4$ (Card No. 14-0133), respectively. Simultaneously, the ms-BiVO$_4$ sample displays the characteristic diffraction profiles at 28.8°, 30.5°, 35.2°, 39.7°, 42.5°, 46.7°, 58.0°, and 59.2° (denoted by ‘♦’ mark), corresponding to the (121), (040), (002), (211), (051), (240), (170), and (123) crystal planes, which is in good accordance with Card No. 14-0688. We probed the crystallinities of the hydrothermally precipitated BiVO$_4$ NPs decorated on the TiO$_2$ NTAs with various deposition amounts (from 5 h to 20 h) in different pH values (from 2 to 8) of the precursor solution by XRD, as presented in Figure 3c–e.

![Figure 3](image-url)

**Figure 3.** XRD of pristine TiO$_2$-NTAs (a,b) pure BiVO$_4$ films, and (c–e) BiVO$_4$/TiO$_2$-NTAs nanohybrids with different hydrothermal deposited amounts, respectively.
Compared with the diffraction peak positions of Figure 3a,b, the XRD patterns for Figure 3c-e vividly imply the lack of impurity peaks, except in the crystal phases of the TiO$_2$ NTAs, ms-BiVO$_4$, and tz-BiVO$_4$ in the BiVO$_4$/$\text{TiO}_2$-NTAs samples, demonstrating the high purity of the hydrothermal treatment and the prospective achievement of binary m&t-BiVO$_4$/$\text{TiO}_2$-NTAs heterostructure nanocomposites (i.e., ms-BiVO$_4$/$\text{TiO}_2$-NTAs and tz-BiVO$_4$/$\text{TiO}_2$-NTAs nano-heterojunctions). Simultaneously, the XRD patterns of the m&t-BiVO$_4$/$\text{TiO}_2$-NTAs nanohybrids show all the diffraction peaks of the anatase phase TiO$_2$, which means that the original structure of the TiO$_2$-NTAs was maintained during the BiVO$_4$ coating process. The intensities of the diffraction profiles for the TiO$_2$-NTAs in the patterns of pristine TiO$_2$-NTAs and m&t-BiVO$_4$/$\text{TiO}_2$-NTAs nano-heterojunctions decreased with the increasing hydrothermal BiVO$_4$ deposition times from 0 h to 20 h, mainly owing to the blocking effect of the heterogeneous interface between the m&t-BiVO$_4$ and TiO$_2$-NTAs [44], which gradually weakens the XRD signal strength of the anatase TiO$_2$-NTAs substrates with the increasing deposition amount of BiVO$_4$. For the as-prepared samples of the BiVO$_4$/$\text{TiO}_2$-NTAs activated at 450 °C, we probed the mixed heterogeneous phases of the m&t-BiVO$_4$/$\text{TiO}_2$-NTAs, and the research data are in agreement with the achievement reported by Parida et al., who demonstrated the coexistence of m&t-BiVO$_4$, as the samples were annealed from 300 °C to 600 °C [45]. More notably, when the pH values for the precursor solution increased successively from 2 to 8, the diffraction peak intensities of (121) and (040) progressively increased for the ms-BiVO$_4$/$\text{TiO}_2$-NTAs nano-heterostructures, while those of (101) and (200) gradually declined for the tz-BiVO$_4$/$\text{TiO}_2$-NTAs nano-heterojunctions, as plotted in Figure 3c-e. To quantitatively evaluate the proportions of tz-BiVO$_4$ ($\eta_{\text{tz-B/T}}$) and ms-BiVO$_4$ ($\eta_{\text{ms-B/T}}$) in the specimens of pristine BiVO$_4$, BiVO$_4$/$\text{TiO}_2$-NTAs-5, BiVO$_4$/$\text{TiO}_2$-NTAs-10, and BiVO$_4$/$\text{TiO}_2$-NTAs-20, we made the estimates using Equations (1) and (2) [46,47]. $I_{\text{tz-B/T}}$ and $I_{\text{ms-B/T}}$ refer to the relative intensities of the diffraction profiles for the tetragonal phase (i.e., (101) and (200)) and monoclinic phase (i.e., (121) and (040)), respectively. We present the details on the percentage compositions of the $\eta_{\text{tz-B/T}}$ and $\eta_{\text{ms-B/T}}$ in the single and dual nano-semiconductors in Table 1.

\begin{align}
\eta_{\text{tz-B/T}} (%) = (I_{\text{tz-B/T}} \times 100%) / (I_{\text{tz-B/T}} + I_{\text{ms-B/T}}) \\
\eta_{\text{ms-B/T}} (%) = (I_{\text{ms-B/T}} \times 100%) / (I_{\text{tz-B/T}} + I_{\text{ms-B/T}})
\end{align}

Table 1. The percentage composition of tetragonal and monoclinic phases of BiVO$_4$ in pure BiVO$_4$ and m&t-BiVO$_4$/$\text{TiO}_2$-NTAs nanoheterojunctions (determined by Equations (1) and (2)) under different pH values of precursor.

| as-Formed Samples | pH Value of Precursor | ms-BiVO$_4$ ($\eta_{\text{ms-B/T}}$, %) | tz-BiVO$_4$ ($\eta_{\text{tz-B/T}}$, %) |
|-------------------|----------------------|----------------------------------------|----------------------------------------|
| pristine BiVO$_4$ films | 5                    | 46.7                                   | 53.3                                   |
| BiVO$_4$/$\text{TiO}_2$-NTAs-5 | 2                    | 36.8                                   | 63.2                                   |
| BiVO$_4$/$\text{TiO}_2$-NTAs-10 | 5                    | 48.4                                   | 51.6                                   |
| BiVO$_4$/$\text{TiO}_2$-NTAs-20 | 8                    | 71.9                                   | 28.1                                   |

Table 1 indicates that the fractions of $\eta_{\text{ms-B/T}}$ (or $\eta_{\text{tz-B/T}}$) in the m&t-BiVO$_4$/$\text{TiO}_2$-NTAs binary nano-heterojunction samples increased (or decreased) with the increasing pH values of the precursor solution, and vice versa, manifesting the efficacious construction of the different ratios of m&t-BiVO$_4$/$\text{TiO}_2$-NTAs nanohybrids, which was achieved by controlling the pH values, which was entirely in agreement with the results reported by Huang et al. [25]. We believe that the increased pH values for the precursor inhibit the crystal growth of the tz-BiVO$_4$ due to the enlargement of ms-BiVO$_4$. The proportion composition of ms-BiVO$_4$ and tz-BiVO$_4$ in the individual BiVO$_4$ films is approximately equal to that in the BiVO$_4$/$\text{TiO}_2$-NTAs-10 specimen, which verifies the formation of ms/tz-BiVO$_4$ heterojunctions in BiVO$_4$ films alone, and further validates the crucial role of the pH value in mediating the heterostructure ratio for m&t-BiVO$_4$/$\text{TiO}_2$-NTAs nanocomplexes under the determined annealing temperature.
As represented in Figure 4, we performed UV–vis DRS measurements and derived Tauc plots to evaluate the optical absorption intrinsic properties and bandgap values of the as-obtained specimens for unitary and binary semiconductors, respectively, which are indispensable characterization instruments for constructing superior photoresponse nanohybrids. We present the UV–vis DRS detection by a wavelength-dependent absorbance between 350 nm and 700 nm for the pristine TiO$_2$-NTAs, pure BiVO$_4$ films, and m&t-BiVO$_4$/TiO$_2$-NTAs binary nano-heterojunctions with varying BiVO$_4$ NP hydrothermal preparation times (5 h, 10 h, and 20 h) in Figure 4a. The absorption edges of the TiO$_2$-NTAs alone are nearly identical at 393 nm, which is due to the transition of the near band edge (NBE) [48]. The UV–vis DRS spectrum pattern for the pristine BiVO$_4$ films is perceptibly redshifted compared with that of the single TiO$_2$-NTAs in Figure 4a, exhibiting the characteristic spectrum related to 496 nm, which is between the intrinsic absorption band edges of ms-BiVO$_4$ (517 nm) and tz-BiVO$_4$ (428 nm). Furthermore, as illustrated in the traces of UV–vis DRS for m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterostructures, the absorption edges of the dual nanohybrids are substantially transparent to longer wavelength regions in comparison with the pure TiO$_2$ NTAs, which indicates that the incorporation of BiVO$_4$ elevates the absorption ability and facilitates the transport of photogenerated electrons, which is the result of the synergistic effect of the heterostructure between m&t-BiVO$_4$ and TiO$_2$ NTAs. Evidently, with the increase in the hydrothermal times from m&t-BiVO$_4$/TiO$_2$-NTAs-5 to m&t-BiVO$_4$/TiO$_2$-NTAs-20, there is a gradual shift of the absorbance boundary to a larger wavelength, which indicates that the bandgap is reducing, and the material is becoming more sensitive to visible light. Simultaneously, all the absorption patterns of the m&t-BiVO$_4$/TiO$_2$ NTAs with various amount of BiVO$_4$, and especially for m&t-BiVO$_4$/TiO$_2$-NTAs-10, present conspicuous forward saddle-backing shapes in the visible region (i.e., labeled as area I), which are probably traceable to the increased average atomic distance induced by the V$_{O}$ defects in BiVO$_4$ [27]. Additionally, the absorption peaks located at 497 nm, labeled as area II, are ascribed to the absorption of the V$_{O}$ defects in TiO$_2$ NTAs [49]. The corresponding $E_g$ values of the as-prepared specimens can subsequently be determined using Tauc plots, as exhibited in Figure 4b. The $(\alpha h\nu)^{1/n}$ against the photon energy ($h\nu$) curves are plotted basing on the following classic Tauc equation [50]:

$$ (\alpha h\nu)^{1/n} = A(h\nu - E_g) $$

The absorption coefficient, Planck’s constant, incident light frequency, proportionality constant, bandgap energy, and characteristic integer are denoted by $\alpha$, $h$, $\nu$, $A$, $E_g$, and $n$, respectively. The $n$ value depends on the nature of the optical transition, and because of the characteristic direct transitions of BiVO$_4$ and TiO$_2$, the value of $n$ is 1/2 [51]. Logically,
by extrapolating the linear portion of $\alpha h \nu$ to zero, we can estimate the $E_g$ for the as-formed samples. The predicted $E_g$ values for the pristine TiO$_2$ NTAs, bare BiVO$_4$ films, m&t-BiVO$_4$ /TiO$_2$-NTAs-5, m&t-BiVO$_4$ /TiO$_2$-NTAs-10, and m&t-BiVO$_4$ /TiO$_2$-NTAs-20 are about 3.15 eV, 2.50 eV, 2.65 eV, 2.58 eV, and 2.52 eV, respectively. In order to further evaluate the validity of the calculated $E_g$ values for the m&t-BiVO$_4$ /TiO$_2$-NTAs under different hydrothermal-synthesis conditions, we can use the alternative bandgap prediction method associated with the weighting of the m&t-BiVO$_4$ content, as follows:

$$E_{g-W} = E_{g-ms} \times \eta_{ms-B/T} (%) + E_{g-tz} \times \eta_{tz-B/T} (%)$$  \hspace{1cm} (4)

where $E_{g-W}$, $E_{g-ms}$, $E_{g-tz}$, $\eta_{ms-B/T}$, and $\eta_{tz-B/T}$ are the bandgap energies for the weighted contents. The $E_g$ for ms-BiVO$_4$ is 2.4 eV, while the $E_g$ for tz-BiVO$_4$ is 2.9 eV, which are the percentages of the monoclinic and tetragonal phases of BiVO$_4$ in m&t-BiVO$_4$ /TiO$_2$-NTAs nano-heterojunctions, respectively. For convenience, we list the detailed comparison results in Table 2. By stripping out the impact of the TiO$_2$-NTAs substrates for the energy-band structures of the m&t-BiVO$_4$ /TiO$_2$-NTAs with different preparation conditions, the obtained $E_g$ from the Tauc formula and evaluated $E_{g-W}$ are essentially consistent, as expected, which reinforces the assumption that the presence of BiVO$_4$ associated with V$_o$ provides a synergistic enhancement in the visible-light absorption, which, in turn, promotes the energy coupling between photons and excitons. The difference in the $E_g$ values between pristine BiVO$_4$ and m&t-BiVO$_4$ /TiO$_2$-NTAs-10 under the same hydrothermal manufactured environment probably derives from the discrepancy in the thickness of the photoactive layer between them [52].

**Table 2.** Comparative data of $E_g$ for Tauc and $E_{g-W}$ for weighted contents towards m&t-BiVO$_4$ /TiO$_2$-NTAs dual nano-hybrids with different fabrication conditions.

| as-Prepared Samples | Calculated $E_g$ for Tauc (eV) | Predicted $E_{g-W}$ (eV) |
|---------------------|-------------------------------|-------------------------|
| m&t-BiVO$_4$ /TiO$_2$-NTAs-5 | 2.65 | 2.66 |
| m&t-BiVO$_4$ /TiO$_2$-NTAs-10 | 2.58 | 2.59 |
| m&t-BiVO$_4$ /TiO$_2$-NTAs-20 | 2.52 | 2.54 |

In order to further intuitively unveil the synergistic effect of BiVO$_4$ and TiO$_2$ NTAs on the surface defects, which profoundly influence the CT process and the performance of PECs, we analyzed the chemical components and bonding configurations of the as-prepared nano-heterojunctions using XPS, as exhibited in Figure 5.

**Figure 5.** High-resolution X-ray photoelectron spectroscopy characterizations of (a) Ti 2p, (b) Bi 4f, and (c) V 2p core level for pure TiO$_2$-NTAs, pristine BiVO$_4$ films, and m&t-BiVO$_4$ /TiO$_2$-NTA-10, respectively.
Specifically, in Figure 5a, we plot the high-resolution XPS spectra (HR-XPS) of the Ti 2p core level for the pristine TiO$_2$-NTAs and BiVO$_4$/TiO$_2$-NTAs-10 dual nanocomposites. We fit the experimental data points (black and green dots) with a curve (red solid line) using a mixed Gaussian–Lorentzian function. We chose this function because it provided the optimized fit to the data points, as determined by the nonlinear least-squares fitting algorithm, including Ti$^{3+}$2p$_{3/2}$, Ti$^{4+}$2p$_{3/2}$, Ti$^{3+}$2p$_{1/2}$, and Ti$^{4+}$2p$_{1/2}$, which originated from the core levels of Ti$^{3+}$ and Ti$^{4+}$. The two intense peaks in the pure TiO$_2$ NTAs at the binding energies (BEs) sited at 458.5 eV and 464.2 eV represent Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ [53], respectively. Moreover, the BE of the Ti 2p core level for the referenced BiVO$_4$/TiO$_2$-NTAs-10 centered at 458.2 eV and 463.8 eV are assigned to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ [54], respectively. Additionally, the BE values of the different oxidation states of the Ti atoms are distinct. The BE peaks located at 458.7 eV, 464.5 eV, 458.5 eV, and 464.3 eV are attributed to the Ti$^{4+}$ valence state [35], and the BE peaks positioned at 458.1 eV, 463.6 eV, 458.2 eV, and 463.9 eV are attributed to the Ti$^{3+}$ valence state and V$_6$ defects in the TiO$_2$ NTAs [54,56,57]. We present the surface atomic Ti$^{3+}$/Ti$^{4+}$ ratios of the pristine TiO$_2$-NTAs specimens and binary m&t-BiVO$_4$/TiO$_2$-NTAs-10 nano-heterojunctions in Table 3, which we obtained by calculating the integral fitting of the peak areas for the concentration of the spin-orbit-splitting Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ core levels in the Ti 2p XPS spectra, which directly correspond to the concentrations of the V$_6$ defects (Ti$^{3+}$) and Ti$^{4+}$ [58]. We found an explicit shift of 0.3–0.4 eV to a low BE (redshift) in the peak positions of Ti 2p for m&t-BiVO$_4$/TiO$_2$-NTAs-10 compared with the pristine TiO$_2$ NTAs, which mainly derived from the CT from the BiVO$_4$ to TiO$_2$ after the formation of the heterostructures [59], which increased the electron density and V$_6$ defect concentration in the TiO$_2$ NTAs [60].

| as-Prepared Samples | Assignment | Binding Energy (eV) | Surface Atomic Ratio Ti$^{3+}$/Ti$^{4+}$ |
|---------------------|------------|---------------------|----------------------------------------|
| pristine TiO$_2$-NTAs | Ti 2p$_{3/2}$ | 458.5 | 0.543 |
|                     | Ti$^{3+}$ 2p$_{3/2}$ | 458.2 | |
|                     | Ti$^{4+}$ 2p$_{3/2}$ | 458.7 | |
|                     | Ti 2p$_{1/2}$ | 464.2 | |
|                     | Ti$^{3+}$ 2p$_{1/2}$ | 463.9 | |
|                     | Ti$^{4+}$ 2p$_{1/2}$ | 464.5 | |
|                     | Ti 2p$_{3/2}$ | 458.2 | |
|                     | Ti$^{3+}$ 2p$_{3/2}$ | 458.1 | |
|                     | Ti$^{4+}$ 2p$_{3/2}$ | 458.8 | |
| m&t-BiVO$_4$/TiO$_2$-NTAs-10 | Ti 2p$_{1/2}$ | 463.8 | |
|                     | Ti$^{3+}$ 2p$_{1/2}$ | 463.6 | 0.988 |
|                     | Ti$^{4+}$ 2p$_{1/2}$ | 464.8 | |

As can be observed in Figure 5b, the HR-XPS of the Bi 4f core level in the pure BiVO$_4$ films reveals two peaks at 158.3 eV and 163.6 eV, which index to the orbits of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ [61], respectively. In contrast, the spin-orbit splitting of Bi 4f (158.6 eV and 163.9 eV) for BiVO$_4$/TiO$_2$-NTAs-10 shift to a higher BE by approximately 0.3 eV, relative to its values for pristine BiVO$_4$ films. The separation between the splitting of the two spin orbits of Bi 4f is 5.3 eV for both the BiVO$_4$ films alone and BiVO$_4$/TiO$_2$-NTAs-10, which is attributed to the expected oxidation state of Bi$^{3+}$ in BiVO$_4$ [62]. As plotted in Figure 5c, two spin-orbit-splitting peaks of V 2p are centered at 515.9 eV and 523.4 eV for the pure BiVO$_4$ films, assigned to V 2p$_{3/2}$ and V 2p$_{1/2}$, respectively, and certifying the existence of the V$^{5+}$ oxidation state in BiVO$_4$ [63]. Compared with that of bare BiVO$_4$, the V 2p spin-orbit peaks of BiVO$_4$/TiO$_2$-NTA-10 (i.e., V 2p$_{3/2}$ and V 2p$_{1/2}$) shifted to the higher BE at around 0.3 eV of 516.2 eV and 523.7 eV, respectively. The phenomenon of the BE shift to greater values for the Bi 4f and V 2p core levels for BiVO$_4$/TiO$_2$-NTAs-10 than pure BiVO$_4$ are indicative of the electron migration from BiVO$_4$ to TiO$_2$ between the different components in the interface of the nanocomposites, which suggests the weakened electron
screening effect because of the decrease in the electron density for the BiVO$_4$ [64], which is consistent with the aforementioned XPS analysis of Ti 2p for BiVO$_4$/TiO$_2$-NTAs-10.

We applied XPS detection to further certify the influence of the various pH values of the precursor (2, 5, 8) on the surface valence states and $V_o$ defect concentration of the interface in the as-prepared nano-heterostructures of m&t-BiVO$_4$/TiO$_2$-NTAs with different hydrodeposition times (5 h, 10 h, and 20 h). We present the Bi 4f-core-level high-resolution XPS spectra of the m&t-BiVO$_4$/TiO$_2$-NTA heterojunctions with precipitation times of 5 h, 10 h, and 20 h in Figure 6a. The split BE peaks of Bi 4f appear at 158.6 eV–158.9 eV and 163.9 eV–164.3 eV for Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively, which are characteristics of the trivalent oxidation state of Bi element species [61,65,66]. Compared with the m&t-BiVO$_4$/TiO$_2$-NTAs-5 sample (158.9 eV and 164.3 eV for Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively), the spin-orbit splitting of the Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ signals for BiVO$_4$/TiO$_2$-NTA-20 (158.7 eV and 164.1 eV, respectively), and BiVO$_4$/TiO$_2$-NTAs-10 (158.6 eV and 163.9 eV, respectively) slightly shift towards lower BE values by 0.2 eV and 0.3 eV, respectively, sufficiently attesting to the interfacial interaction that is formed in a typical m&t-BiVO$_4$/TiO$_2$-NTAs heterojunction sample. We present the core level XPS spectra of the V 2p for m&t-BiVO$_4$/TiO$_2$-NTAs nanohybrids with deposition times of 5 h, 10 h, and 20 h in Figure 6b. Two asymmetric BE peaks are centered at 516.5 eV and 524.2 eV for the V 2p of m&t-BiVO$_4$/TiO$_2$-NTAs-5, which are ascribed to the characteristic spin-orbit signals of V 2p$_{3/2}$ and V 2p$_{1/2}$ [67], respectively, while the broad V 2p XPS spectra of m&t-BiVO$_4$/TiO$_2$-NTAs-10 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 exhibited characteristic splitting BE peaks at 516.2–516.3 eV and 523.7–524.0 eV, respectively, which can be assigned to the V 2p$_{3/2}$ and V 2p$_{1/2}$ spin-orbit signals [68,69], respectively. Coincidentally, besides the core level XPS spectra of Bi 4f, we distinctly observed a slight shift to the lower BE values in the core-level signals of V 2p for the m&t-BiVO$_4$/TiO$_2$-NTAs-10 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 samples compared with that of m&t-BiVO$_4$/TiO$_2$-NTAs-5, which is evidence of the existence of $V^{4+}$ in BiVO$_4$/TiO$_2$-NTAs nano-heterostructures. Based on previous research reports [59,70], we are inclined to accept that the lower shift in the BE value for the XPS peak has an inevitable relationship with the presence of $V_o$ defects, which is due to the changes in their local coordination environments and the increase in the electron density of the Bi and V atoms after introducing the $V_o$. The further deconvolution of each asymmetric V 2p-core-level peak of all the specimens using Gaussian distribution peaks produces two doublets: the high-intensity doublet observed at the higher BE values, which was assigned to the $V^{5+}$ state, and the low-intensity doublet at lower BE values, which indicated the presence of $V^{4+}$ related to $V_o$ defects in BiVO$_4$ [71]. As demonstrated in Figure 6b, for the m&t-BiVO$_4$/TiO$_2$-NTAs-5 sample, besides the signals at 516.5 eV and 524.1 eV that index to the V 2p$_{3/2}$ and V 2p$_{1/2}$ peaks of $V^{5+}$ [32], the signals sited at 516.2 eV and 523.4 eV confirm the presence of the $V^{4+}$ valence state [72]. To further deconvolute the V 2p lines of the m&t-BiVO$_4$/TiO$_2$-NTAs-10 sample, the profiles of the V 2p$_{3/2}$ doublet at the BE values of 515.5 eV and 516.3 eV can be assigned to the $V^{4+}$ 2p$_{3/2}$ and $V^{5+}$ 2p$_{3/2}$, respectively, and the peak of the V 2p$_{1/2}$ core level has two components: $V^{5+}$ 2p$_{1/2}$ and $V^{4+}$ 2p$_{1/2}$, with the latter appearing at lower BE values, located at 523.8 eV and 523.1 eV [73,74], respectively. Eventually, each V 2p core-level signal for the m&t-BiVO$_4$/TiO$_2$-NTAs-20 sample is decomposed into $V^{4+}$ and $V^{5+}$ doublet peaks, exhibiting the $V^{4+}$ 2p$_{3/2}$ and $V^{4+}$ 2p$_{1/2}$ peaks centered at the BE values of 515.8 eV and 523.3 eV, respectively, and showing the $V^{5+}$ 2p$_{3/2}$ and $V^{5+}$ 2p$_{1/2}$ peaks at the BE values of 516.4 eV and 524.0 eV, respectively, which correspond to the $V^{4+}$ and $V^{5+}$ cations in BiVO$_4$ [75,76], respectively. Additionally, the m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions are oxygen-deficient through the electroneutrality principle, and the $V^{4+}$/ $V^{5+}$ molar ratios dictate the amount of nonstoichiometric oxygen, which is proportional to the ratio of the peak area of $V^{4+}$/$V^{5+}$ [77]. As depicted in Table 4, the calculated surface molar ratio of m&t-BiVO$_4$/TiO$_2$-NTA-10 had a higher ratio of $V^{4+}$/ $V^{5+}$ (0.587) then that for BiVO$_4$/TiO$_2$-NTA-20 (0.491), and the lowest ratio was for BiVO$_4$/TiO$_2$-NTA-5 (0.436).
Figure 6. HR-XPS spectroscopy characterizations of (a) Bi 4f, (b) V 2p, and (c) O 1s core levels for m&t-BiVO$_4$/TiO$_2$-NTAs heterojunctions nanohybrids with different hydrothermal-synthesis times 5 h, 10 h, and 20 h, respectively.

Table 4. Surface molar ratios V$^{4+}$/V$^{5+}$ of V 2p XPS spectra for spin-orbit splitting doublets V 2p$^{1/2}$ and V 2p$^{3/2}$ as to the specimens of m&t-BiVO$_4$/TiO$_2$-NTAs with different hydrothermal synthesis times, respectively.

| as-Prepared Samples | Assignment | Binding Energy (eV) | Surface Atomic Ratio V$^{4+}$/V$^{5+}$ |
|---------------------|------------|--------------------|---------------------------------------|
|                     |            | V$^{4+}$ 2p$^{3/2}$ | 516.2                                 |
|                     |            | V$^{5+}$ 2p$^{3/2}$ | 516.5                                 |
| m&t-BiVO$_4$/TiO$_2$-NTAs-5 | V$^{4+}$ 2p$^{1/2}$ | 523.4                     | 0.436                                 |
|                     |            | V$^{5+}$ 2p$^{1/2}$ | 524.1                                 |
|                     |            | V$^{4+}$ 2p$^{3/2}$ | 515.5                                 |
| m&t-BiVO$_4$/TiO$_2$-NTAs-10 | V$^{5+}$ 2p$^{3/2}$ | 516.3                     | 0.587                                 |
|                     |            | V$^{4+}$ 2p$^{1/2}$ | 523.1                                 |
|                     |            | V$^{5+}$ 2p$^{1/2}$ | 523.8                                 |
|                     |            | V$^{4+}$ 2p$^{3/2}$ | 515.8                                 |
|                     |            | V$^{5+}$ 2p$^{3/2}$ | 516.4                                 |
| m&t-BiVO$_4$/TiO$_2$-NTAs-20 | V$^{4+}$ 2p$^{1/2}$ | 523.3                     | 0.491                                 |
|                     |            | V$^{5+}$ 2p$^{1/2}$ | 524.0                                 |

To further verify the existence of V$_o$ defects in the surface region of the as-prepared m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterostructures, we analyzed the HR-XPS spectra of the O 1s core-level signals, and we present the results in Figure 6c. We deconvoluted all of the specimens into three components by Gaussian function fitting, indexing to three oxygen species: lattice oxygen (L$_o$), V$_o$, and adsorbed oxygen (A$_o$), which was evidenced by the corresponding characteristic peaks at 529.9–530.0 eV, 530.5–531.1 eV, and 531.3–531.7 eV [78–81], respectively. In order to intuitively unveil the influence of the hydrothermal preparation environment on the number of V$_o$ defects, we summarize the estimated V$_o$/(L$_o$ + A$_o$) and A$_o$/(L$_o$ + V$_o$) molar ratios of the O 1s XPS spectra for the m&t-BiVO$_4$/TiO$_2$-NTAs specimens with various hydrothermal synthesis times (5 h, 10 h, and 20 h) in Table 5, with the ratios of the peak area decomposed into three components: V$_o$, L$_o$, and A$_o$. The maximal molar ratio value of V$_o$/(L$_o$ + A$_o$) for m&t-BiVO$_4$/TiO$_2$-NTAs-10 is 0.571, followed by 0.402 for m&t-BiVO$_4$/TiO$_2$-NTAs-20, and the minimal value of 0.361 for m&t-BiVO$_4$/TiO$_2$-NTAs-5. Simultaneously, the molar ratio values of A$_o$/(L$_o$ + V$_o$) evidenced a similar varied trend, with that of V$_o$/(L$_o$ + A$_o$) for the TiO$_2$-NTAs hydrothermal precipitation BiVO$_4$ NPs with times of 5 h, 10 h, and 20 h equaling 0.336, 0.423, and 0.396, respectively, which substantiates the amount of A$_o$ species directly proportional to the V$_o$ levels. According to a synthetic comparison of the above results, the higher surface V$^{4+}$/V$^{5+}$ molar ratio for the as-formed m&t-BiVO$_4$/TiO$_2$-NTAs samples contain a higher amount of V$_o$ defects,
and we observed a greater lower shift in the XPS peak, which was also confirmed by the molar ratio of \( \text{A}_0/(\text{L}_0 + \text{V}_0) \) for the as-prepared samples, which mainly resulted from the chemisorption of the \( \text{A}_0 \) species at the surface \( \text{V}_0 \) defects of \( \text{BiVO}_4 \) \[81\]. As expected, the concentration of \( \text{V}_0 \) defects in the dual m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs} \) heterostructure nanosystem was mediated by the synergistic effect of the precipitating time and pH value of the precursor. With the increase in the hydrothermal reaction time from 5 h to 20 h, the number of \( \text{V}_0 \) defects gradually increased and then decreased, instead of showing nonlinear variation, and we found the maximal content of \( \text{V}_0 \) defects in m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs}-10. Hence, we conclude that the pH value of the precursor primarily controls the concentration of the \( \text{V}_0 \) defects in the m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs} \) heterostructure nanosystem.

Table 5. Surface \( \text{V}_0/(\text{L}_0 + \text{A}_0) \), and \( \text{A}_0/(\text{L}_0 + \text{V}_0) \) molar ratios of O 1s XPS spectra for the specimens of m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs} \) with different hydrothermal synthesis times (5 h, 10 h, and 20 h), respectively.

| as-Prepared Samples | Assignment | Binding Energy (eV) | \( \text{V}_0/(\text{L}_0 + \text{A}_0) \), and \( \text{A}_0/(\text{L}_0 + \text{V}_0) \) |
|---------------------|------------|--------------------|--------------------------------------------------|
| m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs}-5 | \( \text{L}_0 \)| 529.9 | 0.361 and 0.336 |
|                     | \( \text{V}_0 \)| 530.5 | |
|                     | \( \text{A}_0 \)| 531.3 | |
|                     | \( \text{L}_0 \)| 529.9 | |
| m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs}-10 | \( \text{L}_0 \)| 531.1 | 0.571 and 0.423 |
|                     | \( \text{V}_0 \)| 531.3 | |
|                     | \( \text{A}_0 \)| 531.3 | |
|                     | \( \text{L}_0 \)| 530.0 | |
| m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs}-20 | \( \text{V}_0 \)| 530.5 | 0.402 and 0.396 |
|                     | \( \text{A}_0 \)| 531.7 | |

Raman spectroscopy is a powerful technique that can detect vibrational transitions, the bounding states in crystals, and the local structure distortions of inorganic materials. Accordingly, we obtained Raman spectra to evaluate the detailed structural and composition insights for the m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs} \) nanohybrids synthesized by the hydrothermal-precipitation method with various reactive times using a green laser (532 nm), as sketched in Figure 7.

Figure 7. Raman spectra of (a) pristine \text{TiO}_2-\text{NTAs}, pure \text{BiVO}_4 \text{ films, and m\&t-\text{BiVO}_4/\text{TiO}_2-\text{NTAs} nanoheterostructures with different BiVO}_4 hydrothermal depositing contents; (b) magnified spectra of the 100–200 cm\(^{-1}\) region, and (c) enlarged view of the 760–900 cm\(^{-1}\) range, respectively.
In Figure 7a, we depict the Raman patterns of the selected samples, the peaks of which are located within the scope of 100–1000 cm$^{-1}$. In the given Raman spectrum of the pristine TiO$_2$-NTAs, we identified a dramatically strong Raman peak at 149.6 cm$^{-1}$, which corresponded to the E$_{1g}$ vibrational mode, and a lower intense peak around 197.7 cm$^{-1}$, which indexed to the main E$_{1g}$ active mode of TiO$_2$. We could assign the other three medium-intensity peaks located at 397.8 cm$^{-1}$, 513.8 cm$^{-1}$, and 639.0 cm$^{-1}$ to the B$_{1g}$ (A$_1g$ + E$_{1g}$) and E$_{1g}$ vibrational modes [82], respectively. Anatase phase TiO$_2$ was indicated by the presence of these Raman peaks, labeled by the symbol “▼”, which is consistent with the XRD analysis. The Raman spectrum analysis of the pure BiVO$_4$ film as a reference exhibited the presence of eight typical vibrational bands at 210.9 cm$^{-1}$; 248.6 cm$^{-1}$; 326.5 cm$^{-1}$; 367.3 cm$^{-1}$; 711.2 cm$^{-1}$; 758.3 cm$^{-1}$; 821.7 cm$^{-1}$; 855.6 cm$^{-1}$, which are characteristic of mixed BiVO$_4$ phases with ms-BiVO$_4$ (marked as “♦”) and tz-BiVO$_4$ (denoted with “■”), and which confirm the XRD results [83]. Specifically, we observed the external twisting vibrational modes in the pure BiVO$_4$ at 210.9 cm$^{-1}$ and 248.6 cm$^{-1}$, corresponding to the formation of monoclinic and tetragonal phases, respectively, which are assigned to the translation/rotation and the Bi–O stretching modes, respectively, while those at 326.5 cm$^{-1}$ and 367.3 cm$^{-1}$ could be ascribed to the asymmetric (B$_g$ symmetry mode) and symmetric (A$_g$ symmetry mode) bending modes of the V–O bond in the VO$_4$ units for the ms-BiVO$_4$ phase [37], respectively. Likewise, the pure BiVO$_4$ materials exhibited Raman bands at 711.2 cm$^{-1}$ and 821.7 cm$^{-1}$ and were assigned to antisymmetric stretching (B$_g$ symmetry mode) and symmetric stretching (A$_g$ symmetric mode) of the two sets of the V–O vibration of the monoclinic BiVO$_4$ phase, respectively. Furthermore, the B$_g$ stretching mode of V–O for the Raman peak sited at 711.2 cm$^{-1}$ is related to the V$_o$ defects [84], which is in good agreement with the UV–vis DRS test. The antisymmetric stretching vibration mode and symmetric bending vibration mode of the V–O bond in the tetragonal phase are indicated by the Raman bands at 758.3 cm$^{-1}$ and 855.6 cm$^{-1}$, respectively [83]. The Raman spectra of the hydrothermal-synthesized m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions adopted the TiO$_2$-NTAs decorated with various BiVO$_4$ deposition times (5 h, 10 h, and 20 h) (Figure 7), which can be distinctly observed in the differences in the Raman patterns between them, which we categorized into four main groups, as follows: (I) Besides the monoclinic and tetragonal phases of BiVO$_4$, we observed the Raman characteristic peaks of the anatase TiO$_2$-NTAs in all three selected specimens, validating the predictions for the m&t-BiVO$_4$/TiO$_2$-NTAs mixed-phase nano-heterostructures, which coincide with the UV–vis DRS and XRD experiments. However, the intensities of the Raman peaks for the anatase TiO$_2$ NTAs located at 149.6 cm$^{-1}$, 397.8 cm$^{-1}$, 513.8 cm$^{-1}$, and 639.0 cm$^{-1}$ gradually decreased when increasing the hydrothermal-reactive times from 5 h to 20 h, which is possibly because the deposited BiVO$_4$ NPs attenuated the Raman signal of the underlying TiO$_2$-NTAs [35]. (II) The peak intensities of the monoclinic phase (i.e., 210.9 cm$^{-1}$, 326.5 cm$^{-1}$, 367.3 cm$^{-1}$, and 821.7 cm$^{-1}$) increased with the increase in the pH values of the precursor from 2 to 8, while the intensities of the weak peaks for the tetragonal phase decreased with increasing pH values, which demonstrates that the content of m-BiVO$_4$ increases with the increase in the pH value, and the variation trend of that for t-BiVO$_4$ is the opposite, which corroborates that the pH value of the precursor has a substantial influence on the m-BiVO$_4$ and t-BiVO$_4$ contents in m&t-BiVO$_4$/TiO$_2$-NTAs nanocomposites, and which is in accordance with the results of the XRD detection. (III) As shown in Figure 7b, the enlarged view of the E$_{1g}$ active vibration peaks of the anatase TiO$_2$ (corresponding to Region I) centered at 147.2 cm$^{-1}$, 151.5 cm$^{-1}$, and 148.6 cm$^{-1}$ for the m&t-BiVO$_4$/TiO$_2$-NTAs-5, m&t-BiVO$_4$/TiO$_2$-NTAs-10, and m&t-BiVO$_4$/TiO$_2$-NTAs-20 specimens, respectively, allow us to discern that the increased deposition of BiVO$_4$ results in varied shift values to higher wavenumbers in comparison with m&t-BiVO$_4$/TiO$_2$-NTAs-5, and especially for the m&t-BiVO$_4$/TiO$_2$-NTAs-10 with the maximum value, which originates from the generation of V$_o$ defects in BiVO$_4$ caused by the deformation of the TiO$_2$ lattice after its modification following the introduction of BiVO$_4$ NPs [85]. (III) Additionally, Figure 7c is the magnified view of Region II in Figure 7a, and the range is between 760 cm$^{-1}$ and
900 cm\(^{-1}\). It explicitly portrays that the Raman peaks of the A\(_g\) symmetric stretching modes for the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10 and m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 specimens are broader and shift to lower wavenumbers in comparison with those of m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-5, and the shifts observed for m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10 are the most pronounced and are ascribed to the increase in the V–O bond length owing to the introduction of V\(_o\) in BiVO\(_4\) [86,87], which is completely consistent with the XPS experimental results.

To further evaluate the role of the m&t-BiVO\(_4\) decoration and V\(_o\) defects in the charge separation, migration, and recombination of the photoexcited e\(^-\)–h\(^+\) pairs at the heterointerface between the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs photoabsorber layer and electrolyte, we assessed the PEC characteristics, including the transient I–t curves and EIS of the primary and binary specimens, to explore the photocatalytic mechanism. We present the data in Figure 8a,b. A comparison of the transient photocurrent magnitude is thus a useful technique to demonstrate the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs heterojunction photoactivity in response to the hydrothermal treatment under different reactive times. We noted the product’s photoresponse switching behavior over the course of nine chopped photoswitching cycles at an interval of 10 s under simulated solar light irradiation, and we present the results in Figure 8a. The photocurrent values of the as-obtained specimens in the order of pristine TiO\(_2\)-NTAs < pure BiVO\(_4\) films < m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-5 < m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 < m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10 indicates the higher separation efficiency and longer charge carrier lifetime in the binary hetero-nanohybrids than in the single semiconductor. The pristine TiO\(_2\)-NTAs had a weak photocurrent intensity (ca. 0.146 \(\mu\)A cm\(^{-2}\)) owing to the wide E\(_g\), in which there was a limited photoresponse, while the pure BiVO\(_4\) revealed a higher photocurrent response (ca. 0.243 \(\mu\)A cm\(^{-2}\)) than the primary TiO\(_2\)-NTAs, with the on/off switch benefiting from the narrower E\(_g\) corresponding to greater visible-light absorption. The current density dramatically increased once the BiVO\(_4\) and TiO\(_2\) NTAs were fabricated into a heterojunction. The m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-5 and m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 samples had more sensitive photocurrent responses compared with the pure BiVO\(_4\) and TiO\(_2\)-NTAs, approximately equaling 0.349 \(\mu\)A cm\(^{-2}\) and 0.503 \(\mu\)A cm\(^{-2}\), respectively, which were about 2.4 and 3.4 times more than that of the pure TiO\(_2\)-NTAs sample, respectively. The m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10 sample expressed the highest photocurrent density, reaching about 0.646 \(\mu\)A cm\(^{-2}\), which was about 4.4 times that of the pure TiO\(_2\)-NTAs. Simultaneously, according to the study of m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10, the light caused a spike in the data, which was due to the transient accumulation of photoinduced charges, which suggests that many carriers are produced in the heterojunctions rather than recombination.

Figure 8. Transient I-t curves for (a,b) EIS of pure TiO\(_2\)-NTAs, solely BiVO\(_4\) films, and dual nano-sized m&t-BiVO\(_4\)/TiO\(_2\)-NTAs nanohybrids deposited BiVO\(_4\) under different prepared times 5 h, 10 h, and 20 h irradiated by AM 1.5G simulated solar light, respectively.
As exhibited in Figure 8b, the Nyquist plot for an EIS measurement typically consists of a series of semicircular arcs at high frequencies, and a linear portion at low frequencies. The resistance to charge separation is represented by the diameter of the semicircle, with a smaller arc radius signifying a greater efficiency of the photoinduced carrier separation. The pristine TiO$_2$-NTAs sample had the greatest impedance arc radius compared with the other specimens, which suggests the greatest charge transfer resistance in all the selected samples, which is probably due to the poor light sensitivity in the visible-wavelength region for the TiO$_2$-NTAs, which reduces the electron conduction rate. In comparison with the pure TiO$_2$-NTAs, the arc radius of the pure BiVO$_4$ films was further reduced, manifesting the more effective generation and separation of the photogenerated e$^-$$-$h$^+$ pairs within the scope of the simulated solar spectrum, which coincides quite well with the results of the UV–vis DRS and transient I–t analyses. The semicircular diameters of all these samples are ranked as follows: pristine TiO$_2$-NTAs > single BiVO$_4$ films > m&t-BiVO$_4$/TiO$_2$-NTAs-5 > m&t-BiVO$_4$ /TiO$_2$-NTAs-20 > m&t-BiVO$_4$ /TiO$_2$-NTAs-10, which is consistent with the variation trend of the abovementioned photocurrent density. The construction of an m&t-BiVO$_4$ /TiO$_2$-NTAs nano-heterojunction provides an effective way to transport electrons to the charge collector and separate charges at the electrode/electrolyte interfaces. Strikingly, for the m&t-BiVO$_4$ /TiO$_2$-NTAs nano-hybrids, the arc radii of the curves decreased as the amount of BiVO$_4$ increased (from 5 h to 10 h), and then began to increase when the BiVO$_4$ deposition time reached 20 h. The smallest radius is seen in the Nyquist curve for BiVO$_4$ /TiO$_2$-NTAs-10, which indicates the appropriate amount of BiVO$_4$ NPs required to improve the conductivity and interfacial CT. If too much BiVO$_4$ is deposited, then this will hinder the CT process for m&t-BiVO$_4$ /TiO$_2$-NTAs nanocomposites. Hence, the diverse enhancement of the PEC performances are dependent on the different concentrations of V$_o$ defects in m&t-BiVO$_4$ /TiO$_2$-NTAs nanohybrids, which increases the carrier concentration and the transport of electrons by these channels, which allows for the effective separation of electron–hole pairs, as well as the spontaneous reaction with electrolytes to serve as additional highly reactive sites [88].

Steady-state PL spectroscopy is a broadly acknowledged channel to obtain additional insights into the electronic structure and properties of the active sites on the surfaces or interfaces of BiVO$_4$ /TiO$_2$-NTAs nano-heterojunctions, whereby information such as the surface V$_o$ and other defects, as well as the efficiency of the charge carrier trapping, migration, and recombination, can be provided. Compared with the change in the absolute intensity for the PL, we focus more on the variations in the steady-state PL spectral weight and features. We present the steady-state PL spectra for the pristine TiO$_2$-NTAs, pure BiVO$_4$ films, and binary BiVO$_4$ /TiO$_2$-NTAs nano-heterojunctions with different BiVO$_4$ NPs deposition amounts from 5 h to 20 h, excited by a 266 nm fs pulse at an ambient temperature, in Figure 9a,b. When in a steady state, the PL spectrum for pure TiO$_2$ NTAs exhibits an asymmetric waveband emission plot, consisting of weak strength at 395 nm (3.1 eV) and an intense emission intensity at 489 nm (2.5 eV), which correspond to the NBE radiative transition [89] of the photogenerated carriers and the indirect radiative transition of the self-trapped electrons from V$_o$ defects to holes in the TiO$_2$-NTAs [90], respectively. Moreover, the steady-state PL pattern for the pure BiVO$_4$ films were between 300 nm and 800 nm, with two emitted contributions sited at 427 nm (2.9 eV) and 516 nm (2.4 eV). Various authors have associated double emission peaks with the direct radiative transition of the self-trapped electrons associated with the V$_o$ defects, surface vanadium vacancies (V$_v$), and V$_o$ defect states with the holes in the VB of m&t-BiVO$_4$ [86,93,94], respectively. Simultaneously, there are three other successive PL irradiation domains: Region I (from 536 nm to 585 nm), Region II (from 610 nm to 650 nm), and Region III (from 678 nm to 700 nm), which originate from the indirect transition of the self-trapped electrons associated with the V$_o$ defects, surface vanadium vacancies (V$_v$), and V$_o$ defect states with the holes in the VB of m&t-BiVO$_4$ [86,93,94], respectively. Additionally, the steady-state PL spectra for the BiVO$_4$ /TiO$_2$-NTAs binary nano-heterostructures with various BiVO$_4$ deposition amounts were characterized with an acquisition time of 100 ms, and they also exhibited broad spectral emissions in the scope
from 350 nm to 725 nm (Figure 9b). All the m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterosystems expressed three emission peaks located at 395 nm, 427 nm, and 516 nm, which originated from the direct recombination of the carriers between the CB and VB for TiO$_2$, t-BiVO$_4$ and m-BiVO$_4$, respectively, which are identical to the results in Figure 9a. Likewise, according to the differences in the origin of the PL spectra, the visible region can be divided into three parts: Region I (from 536 nm to 585 nm), Region II (from 603 nm to 650 nm), and Region III (from 678 nm to 700 nm), which originated from the indirect transition of the self-trapped carriers with the V$_o$ and V$_v$ defect states in m&t-BiVO$_4$. Beyond that, we can clearly observe the steady-state PL band in the range of from 447 nm to 509 nm, labeled as Region III, which resulted from the indirect radiative transition between the trapped electrons in the V$_o$ defect states and the holes in the VB of the TiO$_2$-NTAs [95,96]. The PL intensity associated with the V$_o$ defects in the m&t-BiVO$_4$ increased with the increase in the BiVO$_4$ deposition times from 5 h to 10 h, and then decreased when the BiVO$_4$ deposition times were 20 h in Regions I and III, which is in accordance with the characterized results of the concentration for the V$_o$ defects. As expected, the appearance of the PL intensity related to the V$_v$ defects under 450 °C atmospheric annealing conditions without vanadium sources for all the tested [97] specimens manifested the coherent variation trend of the PL intensity for V$_o$ defects, which is mainly attributed to the higher V$_o$ concentration, which leads to a greater carrier density and the promotion of the generation of surface V$_v$ defects (O$_2$ + 2V$^{5+}$ + 10e$^-$ → V$_v$ + VO$_2$) [98]. The additional V$_v$ defects formed a series of discrete shallow defect levels in the bandgap of the m&t-BiVO$_4$ photoelectrode, which can trap the photogenerated electrons and promote charge separation, which have positive effects on the PEC performance, as well as on the V$_o$ defects [93,99]. Meanwhile, there was a significant steady-state PL band between 447 nm and 509 nm (Region III) that pertained to the photoinduced electron radiative recombination related to the V$_o$ shallow trapping levels in the TiO$_2$-NTAs [95,96], which is sensitive to the deposition amount of m&t-BiVO$_4$.

![Figure 9](image_url)

**Figure 9.** Steady-state PL spectra of bare TiO$_2$-NTAs and pure BiVO$_4$ films (a,b) m&t-BiVO$_4$/TiO$_2$-NTAs nanoheterojunctions with different depositing times of BiVO$_4$ excited by 266 nm femtosecond pulse, respectively.

We present the NTRT-PL spectra for the pristine TiO$_2$-NTAs and pure BiVO$_4$ film specimens in Figure 10a,b. We irradiated these samples with a monochromatic fs laser wavelength at 266 nm under an atmospheric environment and normal temperature, with an interval time evolution of 1.5 ns.

The NTRT-PL patterns for the bare TiO$_2$-NTAs sample, as plotted in Figure 10a, express a comparatively low transient PL emitted peak near 395 nm from 0 ns to 3 ns, which is ascribed to the direct radiative transition of the photoinduced carriers between the CB and VB in the TiO$_2$ NTAs, as stated above [89]. The blueshift phenomenon for the transient PL emission peaks of the pure TiO$_2$ NTAs emerged at 509 nm, 499 nm, 488 nm, 463 nm, and 447 nm with the increase in the intensities, and then decreased for a time evolution of
0–6 ns, originating from the indirect radiative emissions from the $V_o$ defect levels within the VB of TiO$_2$, which is in accordance with the PL earlier reported by other researchers [100]. Simultaneously, we could observe seven transient PL radiative peaks in the pure m&t-BiVO$_4$ film sample, as revealed in Figure 10b, which were centered at 427 nm, 517 nm, 536 nm, 627 nm, 640 nm, 678 nm, and 700 nm, which is consistent with the results of the steady-state PL for the pristine BiVO$_4$ presented in Figure 9a. As described above, we believe that the transient PL emission peaks sited at 427 nm and 516 nm are connected to the NBE direct recombination of t-BiVO$_4$ and m-BiVO$_4$, respectively. Likewise, the other transient PL radiative peaks centered at 536 nm, 627 nm, 640 nm, 678 nm, and 700 nm could be attributed to the indirect transition of the trapping carriers related to the $V_o$ and $V_v$ defects in the pure t&m-BiVO$_4$ films.

![Figure 10. NTRT-PL spectra of the pure TiO$_2$-NTAs (a,b) pure BiVO$_4$ films irradiated by fs light with wavelength of 266 nm, respectively.](image-url)

Ultrafast time-resolved PL spectroscopy is an authoritative indicator tool to track the CT dynamics. Stronger PL intensities represent higher concentrations of defect levels and holes associated with indirect and direct radiative recombination processes, respectively. We present the NTRT-PL spectra of the m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions with various BiVO$_4$ NP hydrothermal preparation times (5 h, 10 h, and 20 h) in Figure 11a–c. For the convenience of discussion, the NTRT-PL-wavelength classified regions agree with the steady-state PL, as discussed above. With the evolution of the time spent recording the spectral, we observed transient PL emission peaks in four different wavelength regions: Region I (from 536 nm to 585 nm); Region II (from 603 nm to 650 nm); Region III (from 678 nm to 700 nm); Region IV (from 447 nm to 503 nm). The as-prepared specimens exhibited Regions I–IV emissions that were unambiguously related to the indirect radiative transitions between the trapped electrons at the $V_o$ and $V_v$ defects in m&t-BiVO$_4$, as well as to the indirect radiative emissions from the $V_o$ defects in the TiO$_2$ NTAs. These findings were consistent with the steady-state PL spectroscopy in Figure 9b. Additionally, the emitted PL peaks sited at 395 nm, 427 nm, and 518 nm can be assigned to the direct NBE transition of the m&t-BiVO$_4$/TiO$_2$-NTAs heterojunctions, which coincide with the results in Figure 10.

The information on the band-gap structure (i.e., CB, VB, and Fermi level ($E_F$)) is essential to unveiling the interfacial CT mechanism between the m&t-BiVO$_4$ and TiO$_2$-NTAs nano-heterojunctions. To further dive into this issue, we subsequently conducted a Mott–Schoktty (M–S) analysis on the deliberated pristine TiO$_2$ NTAs, pure m&t-BiVO$_4$
films, and m&t-BiVO$_4$/TiO$_2$-NTAs nanohybrids, as plotted in Figure 12. We used the M–S formula (i.e., $1/C^2 = (2/\varepsilon_0\varepsilon_rN_d)(E-E_{fb}-k_BT/e)$) [101] to assess the flat band potential ($E_{fb}$) and density of the donor carriers ($N_d$), where C and e are the differential capacitances of the Helmholtz layer and electron charge ($1.602 \times 10^{-19}$ C), respectively; $\varepsilon_0$ is the permittivity of the vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$); $\varepsilon_r$ is the relative permittivity (68 for BiVO$_4$ and 170 for TiO$_2$); $E_{fb}$ is the hypothetical potential at which the semiconductor bands are flat and the band bending is zero, which is extrapolated from the $1/C^2$ axis in M–S plots; E is the applied electrode potential; $k_B$ and $T$ are the Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$) and absolute temperature, respectively. Furthermore, we can calculate the $N_d$ value with the following equation [102]: $N_d = (2/e\varepsilon_r\varepsilon_0)\left[d(1/C^2)/dE\right]^{-1}$. The specimens were of the n type, with positive slopes for the M–S curves of $1/C^2$ versus the potential. We present the calculated values of the $N_d$, $E_{fb}$, and CB in Table 6.

![Figure 11](image1.png)

**Figure 11.** NTRT-PL spectra of the m&t-BiVO$_4$/TiO$_2$-NTAs nanoheterojunctions for BiVO$_4$ NPs with different hydrothermal deposited times: (a) 5 h, (b) 10 h, and (c) 20 h under wavelength of 266 nm irradiation at atmospheric environment, respectively.

![Figure 12](image2.png)

**Figure 12.** Mott-Schottky plots of the pristine TiO$_2$-NTAs, pure m&t-BiVO$_4$ films (inset), and as-obtained BiVO$_4$/TiO$_2$-NTAs nanocomposites with different BiVO$_4$ hydrothermal precipitation times, respectively.
which increases the degree of the band bending at the interface between BiVO$_4$ (5 h, 10 h, and 20 h) are approximately −0.275 eV, −0.528 eV, and −0.464 eV, respectively. This effect is caused by the alignment of the CB potential position (E$_{CB}$) for the pristine TiO$_2$ nanosheets, which is 0.1 eV higher than that of the E$_{CB}$ for the pristine TiO$_2$ nanosheets, which is 0.1 eV higher than that of the pristine TiO$_2$-NTAs hetero-nanophotoanodes. The number of active sites in BiVO$_4$ films, and m&$t$-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions with different BiVO$_4$ NPs, which sufficiently validates that the donor density can be improved by a more powerful built-in electric field in the nano-heterojunction. The change trend is also similar to the results of the photocurrent densities and EIS, which substantially reduce the carrier recombination. Furthermore, the N$_d$ values increased with the BiVO$_4$-NPs hydrothermal reaction times, increasing from 5 h to 10 h, and then decreasing when a more compact BiVO$_4$-NPs distribution deposition time was applied (20 h), validating that the V$_o$ defects could boost the charge carrier densities and electrical conductivities in the m&$t$-BiVO$_4$/TiO$_2$-NTAs hetero-nanophotoanodes. The exposure of the CB edge of m&$t$-BiVO$_4$ towards the VB, resulting in an increase in the bandgap. This effect is caused by the alignment of the E$_F$ between the m&$t$-BiVO$_4$ and TiO$_2$-NTAs, which increases the degree of the band bending at the interface between BiVO$_4$ and TiO$_2$-NTAs, which, in turn, facilitates the charge separation and transfer.

Table 6. The density of donor carriers (N$_d$), flat band potential (E$_{fb}$), and position of CB for pure TiO$_2$-NTAs, pristine m&$t$-BiVO$_4$ films, and m&$t$-BiVO$_4$/TiO$_2$-NTAs nanocomplex with BiVO$_4$ depositing times 5 h, 10 h, and 20 h, respectively.

| Samples                      | N$_d$ (cm$^{-3}$) | E$_{fb}$ (vs. NHE) | CB Position (vs. NHE) |
|------------------------------|------------------|--------------------|-----------------------|
| pristine TiO$_2$-NTAs        | 6.2 × 10$^{17}$  | −0.175             | −0.275                |
| Pure BiVO$_4$ films          | 3.3 × 10$^{18}$  | 0.377              | 0.277                 |
| m&$t$-BiVO$_4$/TiO$_2$-NTAs-5 | 4.5 × 10$^{18}$  | −0.329             | −0.429                |
| m&$t$-BiVO$_4$/TiO$_2$-NTAs-10| 7.6 × 10$^{18}$  | −0.428             | −0.528                |
| m&$t$-BiVO$_4$/TiO$_2$-NTAs-20| 6.6 × 10$^{18}$  | −0.364             | −0.464                |

As is evident, the values of the N$_d$ for the samples of bare TiO$_2$-NTAs, pure m&$t$-BiVO$_4$ films, and m&$t$-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions with different BiVO$_4$ amounts from 5 h to 20 h are 6.2 × 10$^{17}$ cm$^{-3}$, 3.3 × 10$^{18}$ cm$^{-3}$, 4.5 × 10$^{18}$ cm$^{-3}$, 7.6 × 10$^{18}$ cm$^{-3}$, and 6.6 × 10$^{18}$ cm$^{-3}$, respectively. The N$_d$ values for the bare TiO$_2$-NTAs and pure BiVO$_4$ films are lower than that of the hydrothermal decorated TiO$_2$-NTAs with BiVO$_4$ NPs, which sufficiently validates that the donor density can be improved by a more powerful built-in electric field in the nano-heterojunction. The change trend is also similar to the results of the photocurrent densities and EIS, which substantially reduce the carrier recombination. Furthermore, the N$_d$ values increased with the BiVO$_4$-NPs hydrothermal reaction times, increasing from 5 h to 10 h, and then decreasing when a more compact BiVO$_4$-NPs distribution deposition time was applied (20 h), validating that the V$_o$ defects could boost the charge carrier densities and electrical conductivities in the m&$t$-BiVO$_4$/TiO$_2$-NTAs hetero-nanophotoanodes. The number of active sites in BiVO$_4$ constantly increases as a result of the growing trend of vacancy-state active sites with the increment in the BiVO$_4$, and it decreases for the excess BiVO$_4$ deposition mediated by pH values from 2 to 8. Additionally, the E$_{fb}$ of the pristine TiO$_2$-NTAs, pure m&$t$-BiVO$_4$ films, and m&$t$-BiVO$_4$/TiO$_2$-NTAs nanohybrids with different BiVO$_4$ amounts from 5 h to 20 h are as follows: −0.375 eV, 0.180 eV, −0.529 eV, −0.628 eV, and −0.564 eV vs. Ag/AgCl, respectively. Based on the relationship expression E$_{CB}$ = E$_{CB}$ = E$_{CB}$ − 0.1976 (25 °C) [35], they are approximately −0.175 eV, 0.377 eV, −0.329 eV, −0.428 eV, and −0.364 eV vs. NHE, respectively. Because the CB potential position (E$_{CB}$) for the most n-type semiconductors is 0.1 eV higher than that of the E$_{fb}$ [103], the E$_{fb}$ value for the pristine TiO$_2$ NTAs was −0.175 eV vs. NHE using the M–S plot, which completely coincides with the previously published literature [104]. The calculated value of the E$_{CB}$ for the pure TiO$_2$ NTAs was −0.275 eV, which is almost consistent with the −0.250 eV of the E$_{CB}$ position reported by other researchers [105]. The V$_o$ defects are thought to function as electron donors, increasing the potential height of the E$_{CB}$ [106]. Moreover, the E$_{CB}$ positions of the m&$t$-BiVO$_4$/TiO$_2$-NTAs heterostructure nanohybrids with different BiVO$_4$ hydrothermal deposition times (5 h, 10 h, and 20 h) are approximately −0.429 eV, −0.528 eV, and −0.464 eV vs. NHE, respectively. The exposed surface V$_o$ defects in the m&$t$-BiVO$_4$ further strengthen the evidence that they act as electron donors, which could promote the electrical conductivity in BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions. The presence of V$_o$ defects is especially expected to shift the CB edge of m&$t$-BiVO$_4$ towards the VB, resulting in an increase in the bandgap. This effect is caused by the alignment of the E$_F$ between the m&$t$-BiVO$_4$ and TiO$_2$-NTAs, which increases the degree of the band bending at the interface between BiVO$_4$ and TiO$_2$-NTAs, which, in turn, facilitates the charge separation and transfer.

On the basis of the above obtained experimental results of the NTRT-PL spectra and M–S plots, we present the mechanisms proposed to interpret the transient CT process for pristine TiO$_2$ NTAs and pure m&$t$-BiVO$_4$ films under fs laser irradiation at a wavelength of 266 nm at room temperature in Figure 13. Due to the absence of CT behavior before the formation of the photoexcited charge carriers, it is likely that the O$_2$ was spontaneously attached on individual TiO$_2$ NTAs and m&$t$-BiVO$_4$, respectively. Additionally, the E$_g$ for the pristine TiO$_2$ NTAs is 3.15 eV, employing the aforementioned experimental results for the E$_g$ using the Tauc plots in Figure 4b, and the values of the E$_F$, E$_{CB}$, and VB potential...
positions (\(E_{VB}\)) for the TiO\(_2\) NTAs are \(-0.10\) eV, \(-0.25\) eV, and 2.9 eV versus the potential of normal hydrogen electrode (vs. NHE, \(E_{NHE}\)) \[105\], respectively, which agrees with the M–S analysis and is depicted in Figure 13a. Simultaneously, the values of the \(E_{CB}\) and \(E_F\) for the t-BiVO\(_4\) and m-BiVO\(_4\) are 0.24 eV, 1.44 eV, 0.34 eV, and 0.9 eV vs. NHE without photoirradiation conditions, respectively, according to the previously mentioned research \[105,107,108\], while the \(E_{VB}\) edges of the t-BiVO\(_4\) and m-BiVO\(_4\) are 3.14 eV and 2.74 eV vs. NHE, respectively, using the formula \(E_{VB} = E_g - E_{CB}\), and the \(E_g\) values for them are 2.9 eV and 2.4 eV, respectively (Figure 13c).

In Figure 13b,d, we illustrate the processes of the generation, transfer, and radiative recombination of the photoexcited charge carriers in the TiO\(_2\) NTAs alone and pristine m\&t-BiVO\(_4\) when exposed to 266 nm light. For the sample of undecorated TiO\(_2\) NTAs, the large number of electrons in the VB were excited to the CB by the incident photon energy, leaving behind holes in the VB of TiO\(_2\). This occurs when the photon energy (4.7 eV) is greater than the bandgap energy (3.15 eV) of TiO\(_2\)-NTAs. At the initial time of UVC photoexcitation (denoted as \(t = 0\) ns), the concentration of the \(e^-\)\(_{CB}\) in the CB achieved the maximum value because there was no more generation of charges until the next cycle of light irradiation. We detected two transient PL peaks at 395 nm and 509 nm, which originated from direct and indirect radiative recombination, respectively, as illustrated in Figure 10a. As we have previously investigated \[96,106\], the \(V_o\) defect energy levels consist of a series of discrete levels that act as shallow donor levels slightly below the CB of anatase TiO\(_2\). The transient PL intensities centered at 499 nm, 488 nm, 463 nm, and 447 nm gradually decreased with the recording time from 1.5 ns to 6 ns, which was accompanied by a similar variation trend for the PL emitted peak centered at 395 nm, which we mainly ascribed to the direct and indirect carrier radiative recombination between the CB, \(V_o\) defects, and VB in the TiO\(_2\) NTAs. Based on previous reports \[35\], we believe that the probability of radiation from a shallow defect level is much greater than from a deep-trapping defect level, resulting in a blueshift of the transient PL peaks, which accords with the gradually decreased amount of \(e^-\)\(_{CB}\), as exhibited in Figures 10a and 13b. The atmosphere’s oxygen content cannot
trap the CB from the TiO$_2$-NTAs to generate superoxide radical anions (O$_2^-$) because the E$_{CB}$ level positions are more positive (−0.25 eV vs. NHE) than the redox potential of O$_2$/O$_2^-$ (−0.33 eV vs. NHE) [24], which is an essential active oxygen species for impacting the PEC activity. The h$^+$$_{VB}$ in the VB can oxidize the OH$^-$ into hydroxyl radical (OH) in the atmosphere, which is because the h$^+$$_{VB}$ level positions (≥2.90 eV vs. NHE) are more positive than the redox potential of OH/OH$^-$ (≥1.99 eV vs. NHE) [109].

We present the energy-band diagram of the m-BiVO$_4$/t-BiVO$_4$ nano-heterojunction semiconductor after the thermodynamic equilibrium and irradiated by 266 nm fs light in Figure 13d. After the intimate contact between m-BiVO$_4$ and t-BiVO$_4$, the E$_F$ of t-BiVO$_4$ from 1.44 eV is 0.9 eV vs. NHE, and it was the same for the E$_F$ of m-BiVO$_4$. At the same time, the E$_{CB}$ and E$_{VB}$ of t-BiVO$_4$ decreases from 0.24 eV to −0.30 eV and from 3.14 eV to 2.60 eV, respectively, and the establishment of an n–n junction at the interface creates an equilibrium electric field, which, in turn, generates an internal electric field. The m-BiVO$_4$ energy band is decreased while the t-BiVO$_4$ energy band is increased, which creates an equilibrium state in the nano-system. Hence, the type-II nano-heterojunction bandgap results in a shift in the E$_{CB}$ and E$_{VB}$ of t-BiVO$_4$ beyond those of m-BiVO$_4$. The calculated CB offset (∆E$_c$) was 0.64 eV, and the VB offset (∆E$_v$) was 0.14 eV. When we irradiated the m-BiVO$_4$/t-BiVO$_4$ type-II nano-heterojunctions by 266 nm light, the electrons in the VB of the m&t-BiVO$_4$ were inevitably excited to the CB with simultaneous generated holes in the VB owing to the fact that the radiated photon energy was larger than both the E$_g$ values of the t-BiVO$_4$ and m-BiVO$_4$. At the end of fs light irradiation (t = 0 ns), the e$^-$$_{CB}$ concentration of the CB for the m&t-BiVO$_4$ reached the maximum, spontaneously bringing about the NBE direct radiation recombination processes of the e$^-$−h$^+$ pairs, which could be responsible for the transient PL peaks sited at 427 nm and 517 nm. Additionally, Dai and Wang et al. [110,111] previously reported that the average lifetime ($\tau$$_{ave}$) of charge carriers for t-BiVO$_4$ is shorter than that of m-BiVO$_4$, demonstrating $\tau$$_{ave}$ values for t-BiVO$_4$ and m-BiVO$_4$ of 5.49 ns and 11.22 ns, respectively. The relation between the $\tau$$_{ave}$ and the recombination probability is inversely proportional, and the direct radiative recombination probability for t-BiVO$_4$ is much greater than that of m-BiVO$_4$, which means that the NBE radiative PL intensity for t-BiVO$_4$ ($\lambda$$_{PL}$ = 427 nm) is higher than that of m-BiVO$_4$ ($\lambda$$_{PL}$ = 517 nm). With the evolution of the spectral recording time from 0 ns to 1.5 ns (t = 1.5 ns), the new transient radiative PL peaks emerged at 536 nm, 627 nm, 640 nm, 678 nm, and 700 nm, originating from the indirect radiative PL recombination between the e$^-$$_{CB}$ in the shallow trapping defect states and the VB of m&t-BiVO$_4$. The concentration of the e$^-$$_{CB}$ for t-BiVO$_4$ decreased when the irradiation time was increased from 1.5 ns to 3 ns (t = 3 ns). The ∆E$_c$ should provide a facilitated way for the photogenerated e$^-$$_{CB}$ injection from the CB of t-BiVO$_4$ to the CB of m-BiVO$_4$, and the ∆E$_v$ should promote the photogenerated h$^+$$_{VB}$ transfer from the VB of m-BiVO$_4$ to the VB of t-BiVO$_4$, resulting in an enhanced PL intensity of 536 nm and increased e$^-$$_{CB}$ concentration for m-BiVO$_4$, which are responsible for the boosted PL strengths of the emitted wavelength sited at 627 nm, 640 nm, 678 nm, and 700 nm. Afterwards, we observed the gradually decreased transient-PL intensities for all of them with the evolution of the spectral recording time from 4.5 ns to 6 ns (t = 4.5–6 ns), which were mainly attributed to the continuous consumption for the e$^-$$_{CB}$ concentration in t-BiVO$_4$ and m-BiVO$_4$. The h$^+$$_{VB}$ in the VB of m&t-BiVO$_4$ could convert the OH$^-$ into an OH radical, benefitting from its E$_{VB}$ potential positions that are sufficiently more positive (2.60 eV and 2.74 eV) than the redox potential of OH/OH$^-$ [109]. The trapped O$_2$ in the CB of m&t-BiVO$_4$ could not be transformed into O$_2^-$, which was because the E$_{CB}$-level positions were lower (−0.30 eV and 0.34 eV) than the redox potential of O$_2$/O$_2^-$, as displayed in Figure 13d.

We proposed the plausible kinetic process of interfacial CT in the binary BiVO$_4$/TiO$_2$-NTAs nano-heterostructures, which is dependent on the synergistic effect between the content ratio of the m&t-BiVO$_4$ related to the hydrothermal deposition time and the amount of V$_o$ defects mediated by the pH value, as we schematically illustrate in Figure 14.
Figure 14. Diagrammatic sketches of (a) CB, VB, and $E_F$ potential positions (vs. NHE) for individual BiVO$_4$ and TiO$_2$-NTAs before contact; (b,c,d) are band-gap structure, charge carriers photo-excited and transient CT for BiVO$_4$/TiO$_2$-NTAs nanohybrids with various BiVO$_4$ NPs hydrothermal-deposited amount before and after irradiated by UVC light, respectively.

We present the potential energy positions of the CB, VB, and $E_F$ for the TiO$_2$-NTAs and m&t-BiVO$_4$ against NHE in Figure 14a. The specific potential energy values for these materials are similar to those seen in Figure 13. There is no CT process before the individual m&t-BiVO$_4$ and pristine TiO$_2$-NTAs contact, resulting in rather flat energy bands for the BiVO$_4$ and TiO$_2$-NTAs. We present the band configurations and schematic diagram of the generation, separation, and transport processes for the photogenerated charge carrier assembling of the m&t-BiVO$_4$/TiO$_2$-NTAs-5 nano-heterojunction before and after irradiation by 266 nm fs light in Figure 14b. Before light irradiation, the detailed potential energy positions of the $E_F$ for the t-BiVO$_4$ alone and m-BiVO$_4$ were 1.27 eV and 0.73 eV (vs. NHE), respectively, which agrees with previous reports [25,112]. The CB positions of the single t-BiVO$_4$ and m-BiVO$_4$ are 0.24 eV and 0.34 eV, whereas the CB and $E_F$ values for the TiO$_2$ NTAs are $-0.25$ eV and $-0.1$ eV, respectively. Hence, we can deduce the VB potential positions for the t-BiVO$_4$, m-BiVO$_4$, and TiO$_2$-NTAs sited at 3.14 eV, 2.74 eV, and 2.9 eV, respectively, and the $E_F$ values of the t-BiVO$_4$, m-BiVO$_4$, and TiO$_2$ NTAs are 2.9 eV, 2.4 eV, and 3.15 eV, respectively. When the close contact between m&t-BiVO$_4$ with a preparation time of 5 h and TiO$_2$ NTAs, a t-BiVO$_4$/m-BiVO$_4$/TiO$_2$-NTAs integrated nano-heterojunction barrier is formed at the interface between the BiVO$_4$ and TiO$_2$, owing to the alignment of their different $E_F$ level positions, as stated above. When the thermodynamic equilibrium was established, the $E_F$ values for the t-BiVO$_4$ and m-BiVO$_4$ shifted to become $-0.1$ eV, which was identical to the $E_F$ level of the TiO$_2$. Furthermore, the $E_C$ and $E_V$ potential positions for the t-BiVO$_4$ increased from 0.24 eV to $-1.13$ eV and from 3.14 eV to 1.77 eV, respectively, while those for the m-BiVO$_4$ increased from 0.34 eV to $-0.49$ eV and from 2.74 eV to 1.91 eV, respectively. Logically, the maximal energy difference values of the CB and VB between the t-BiVO$_4$ and TiO$_2$-NTAs are 0.88 eV and 1.13 eV, respectively, denoted as $\Delta E_C$ and $\Delta E_V$, respectively, which suggests the formation of an enhanced built-in electric field force on the interfaces between the m&t-BiVO$_4$/TiO$_2$-NTAs-5 nano-heterojunctions compared with the isolated t-BiVO$_4$/m-BiVO$_4$ type-II nanoheterostructures. We present a schematic diagram of the energy-band potential position for the m&t-BiVO$_4$/TiO$_2$-NTAs-10 specimen under dark conditions in Figure 14c. After the
thermodynamic equilibrium, the \( E_F \) values for t-BiVO\(_4\) and m-BiVO\(_4\) were \(-0.1\) eV, which was the same as the \( E_F \) level of the TiO\(_2\). Simultaneously, the \( E_C \) and \( E_V \) of the t-BiVO\(_4\) increased from \(0.24\) eV to \(-1.3\) eV and from \(3.14\) eV to \(1.6\) eV, respectively, whereas those of the m-BiVO\(_4\) increased from \(0.34\) eV to \(-0.66\) eV and from \(2.74\) eV to \(1.74\) eV, respectively, resulting from the \( E_F \) values for the t-BiVO\(_4\) and m-BiVO\(_4\), which were \(1.44\) eV and \(0.9\) eV, respectively. The \( \Delta E_c \) and \( \Delta E_v \) values for m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-10 were \(1.05\) eV and \(1.3\) eV, respectively, which vividly demonstrates the construction of a powerful built-in electric field driven by the Coulomb repulsive force. Additionally, in Figure 14d, we exhibit the potential energy positions of the bandgap for the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 sample, tightly contacted and without light irradiation. The calculated \( E_c \) and \( E_v \) positions of the t-BiVO\(_4\) were \(-1.19\) eV and \(1.71\) eV, respectively, while those of the m-BiVO\(_4\) were \(-0.55\) eV and \(1.85\) eV, respectively, when the thermodynamic equilibrium was reached, originating from the \( E_F \) values of the t-BiVO\(_4\) and m-BiVO\(_4\), which were \(1.33\) eV and \(0.9\) eV moved towards \(-0.1\) eV, respectively, which is in good agreement with the previous description on the variation in the work function with the \( \nu_0 \) defect concentration [86]. As a consequence, the heterostructure alignment of m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 with the extreme \( \Delta E_c \) and \( \Delta E_v \) between the t-BiVO\(_4\) and TiO\(_2\)-NTAs are \(0.94\) eV and \(1.19\) eV, respectively. The \( \Delta E_c \) and \( \Delta E_v \) values increased with the increasing hydrothermally synthesized times of the BiVO\(_4\) NPs for the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs nanohybrids from \(5\) h to \(10\) h, and then decreased when the BiVO\(_4\) deposition time was \(20\) h. As expected, the m&t-BiVO\(_4\)/TiO\(_2\)-NTAs-20 specimen exhibited the maximum values for the \( \Delta E_c \) and \( \Delta E_v \) among the as-prepared samples, implying that it is the most forceful supplement of the CT driving force, which is completely consistent with the variation trend of the \( \nu_0 \) defect amount and the truth for the effective acceleration of the electron mobility. We illustrate and detail the typical CT pathway for t-BiVO\(_4\)/m-BiVO\(_4\)/TiO\(_2\)-NTAs nano-heterojunctions with different BiVO\(_4\) NP hydrothermal preparation times (\(5\) h, \(10\) h, and \(20\) h) under \(266\) nm light irradiation in ambient air in Figure 14b–d. In the circumstance that the exposed m&t-BiVO\(_4\)/TiO\(_2\)-NTAs nano-heterojunctions are irradiated by UVC light, the exposure of the t-BiVO\(_4\) in ambient air in Figure 14b–d. In the circumstance that the exposed m&t-BiVO\(_4\)/TiO\(_2\)-NTAs nano-heterojunctions with different BiVO\(_4\) concentrations and strong electronic perturbations around the vacancy defects [23,113], as depicted in Figure 11a–c, we can see that there were almost identical NP deposition amounts in Figure 11a–c, we can see that there were almost identical
When irradiated by UVC light, the staggered band offset consequently induces a built-in electric field in the m&t-BiVO$_4$ of 1.05 eV/1.30 eV, and 0.94 eV/1.19 eV for the different BiVO$_4$ nano-heterojunctions, which drive the photogenerated electron injection into the CBs of BiVO$_4$. Thus, the transient PL peak intensities located at 2.4 eV, Regions II and III, increased as the recording time increased from 0 ns to 3 ns. The increasing consumption of the photoinduced $e^-$$_{CB}$ in the CB of BiVO$_4$, which resulted from the direct and indirect radiative recombination between the CB, vacancy defects, and h$_{VB}^+$ in the VB during the last stage of the spectral recording time ($t = 4.5$ ns–6 ns), gave rise to the attenuated transient PL intensities sited at 2.9 eV and 2.4 eV, Regions I–III. Besides the $E_{CB}$ potential for t-BiVO$_4$, the $E_{CB}$ edge of m-BiVO$_4$ also had a superior potential to that of the TiO$_2$ NTAs, and hence, could supply minor electron resistance pathways compared with the single m&t-BiVO$_4$ nano-heterojunctions. At the end stage of the spectra recording ($t = 6$ ns), the transient PL peak emission centered at 3.1 eV and in Region IV gradually declined, mainly agreeing with the drastic decrease in the $e^-$$_{CB}$ concentration in the CB of the TiO$_2$ NTAs-10 specimen evinced the strongest transient PL intensity compared with those for all the other samples, which elucidates the concerted interaction between the deposited amount and the deposition time and V$_0$ defect content mediated by the prepared pH value, which induced the discrepancy in the $\Delta E_{CB}/\Delta E_{e^-}$ among the as-formed specimens, and which was identical to the 0.88 eV/1.13 eV, 1.05 eV/1.30 eV, and 0.94 eV/1.19 eV for the different BiVO$_4$ hydrothermal deposition contents (5 h, 10 h, and 20 h, respectively).

We recorded the PL decay profiles of the as-prepared specimens in Figure 15 by exciting the specimens with 375 nm laser pulses. We collected the PL decay trace at 678 nm (ca. 1.8 eV) for the plain BiVO$_4$ film sample, and we conducted the other PL-decay traces at 447 nm (ca. 2.8 eV), which originated from the $e^-_{CB}$ trapped in the V$_0$ defect indirect radiative recombination transition to the h$_{VB}^+$ in BiVO$_4$ and TiO$_2$, respectively. When irradiated by UVC light, the staggered band offset consequently induces a built-in electric field in the m&t-BiVO$_4$ and m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunction specimens, which drive the photogenerated electron injection into the CBs of BiVO$_4$ and TiO$_2$. These photogenerated $e^-_{CB}$ preferentially transfer to the V$_0$ defect levels, which results in a substantial variation in the PL decay kinetics. By comparing the emission decay profiles for the pristine TiO$_2$-NTAs, plain m&t-BiVO$_4$ films, and TiO$_2$-NTAs decorated with different...
BiVO$_4$ NP amounts, we can obtain the penetrating information for interpreting the fate of the charge carriers between the relevant specimens.

Figure 15. Time-resolved PL spectra of pure TiO$_2$-NTAs, plain BiVO$_4$ films, and m&t-BiVO$_4$/TiO$_2$-NTAs with various BiVO$_4$ NPs hydrothermal-deposited times, respectively.

The lifetime of a carrier can be probed from the TRPL spectrum, and it complies with the biexponential rate law: $I(\tau) = A_1\exp(-\tau/\tau_1) + A_2\exp(-\tau/\tau_2)$ [114], where $\tau_1$ and $\tau_2$ are the fast and slow components, respectively, which originate from defect-induced nonradiative recombination and radiative recombination, respectively. Both $A_1$ and $A_2$ correspond to the decay amplitude [115]. We used the formula $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ to calculate the average lifetime of a carrier ($\tau_{avg}$). As detailed in Table 7, the $\tau_{avg}$ values were 4.99 ns, 4.53 ns, 4.29 ns, 3.86 ns, and 4.06 ns for the pristine TiO$_2$-NTAs, plain m&t-BiVO$_4$ films, and m&t-BiVO$_4$/TiO$_2$-NTAs with BiVO$_4$ NP hydrothermal preparation times of 5 h, 10 h, and 20 h, respectively. The magnitude order of the $\tau_{avg}$ for the as-obtained specimens accords well with that previously reported [116,117], and it has consistently corroborated the validity of the simplified kinetics model considered for the synergistic effect between the hydrothermal deposition content and V$_{o}$ defect concentration in mediating the CT of m&t-BiVO$_4$/TiO$_2$-NTAs heterojunction nanohybrids. Evidently, all the specimens with the characteristic heterostructure indicated shortened $\tau_{avg}$ values relative to the pristine TiO$_2$-NTAs and single BiVO$_4$ films, and m&t-BiVO$_4$/TiO$_2$-NTAs sample with BiVO$_4$ NP hydrothermal preparation times of 5 h, 10 h, and 20 h, respectively. The magnitude order of the $\tau_{avg}$ for the as-obtained specimens accords well with that previously reported [116,117], and it has consistently corroborated the validity of the simplified kinetics model considered for the synergistic effect between the hydrothermal deposition content and V$_{o}$ defect concentration in mediating the CT of m&t-BiVO$_4$/TiO$_2$-NTAs heterojunction nanohybrids. Evidently, all the specimens with the characteristic heterostructure indicated shortened $\tau_{avg}$ values relative to the pristine TiO$_2$-NTAs and single BiVO$_4$ films, and especially for the m&t-BiVO$_4$/TiO$_2$-NTAs sample with a deposition time of 10 h, which possessed the shortest $\tau_{avg}$ value (3.86 ns), intimately stemming from the highest band-offset values ($\Delta E_c$ and $\Delta E_v$), which suggests that the shorter lifetime reflects the higher carrier injection efficiency [114]. Interestingly, the two dominant benefits that are expected from BiVO$_4$ NP incorporation (i.e., separation and fast charge transport) have compatible effects on the CT rate. We also analyzed the interfacial CT kinetics for the BiVO$_4$/TiO$_2$-NTAs type-II nano-heterojunctions, presuming that the heterojunction interfaces between BiVO$_4$ and TiO$_2$ were accountable for the observed reduced carrier lifetime. We can evaluate the CT rate constant ($k_{ct}$) by the following equation: $k_{ct} (\text{BiVO}_4 \rightarrow \text{TiO}_2) = 1/\tau_{avg} (\text{BiVO}_4)$, where $\tau_{avg}$ represents the BiVO$_4$, which is the alternative semiconductor forming a heterostructure. The calculated $k_{ct}$ values were $3.27 \times 10^7$ s$^{-1}$, $5.86 \times 10^7$ s$^{-1}$, and $4.59 \times 10^7$ s$^{-1}$ for m&t-BiVO$_4$/TiO$_2$-NTAs with diverse BiVO$_4$ deposition times of 5 h, 10 h, and 20 h, respectively. The variation tendencies of the $k_{ct}$ values were proportional to the changing trends of the VB offset values, which presented the driving force to promote the photogenerated h$^+$$v_B$ transfer from the VB of TiO$_2$ to the VB of the adjacent BiVO$_4$ because the carrier radiative lifetime of TRPL is directly dependent on the recombination lifetime of the minority carriers in nano-heterojunctions. Simultaneously, the $k_{ct}$ value of the m&t-BiVO$_4$/TiO$_2$-NTAs-10 specimen was higher than that of the others, which indicates that the enlarged band offset ($\Delta E_c$ and $\Delta E_v$) associated
with the $V_o$ defect concentration induces a stronger built-in field force, which achieved the most effective charge spatial separation and active charge-transport injection of the photoinduced $e^-_{\text{CB}} - h^+_{\text{VB}}$ pairs on the different sides of the m&t-BIVO$_4$/TiO$_2$-NTAs heterojunction, and promoted a great number of the $e^-_{\text{CB}}$ of TiO$_2$ and $h^+_{\text{VB}}$ of BiVO$_4$ to participate in the redox reaction.

Table 7. Average lifetime of PL ($\tau_{\text{avg}}$) for pristine TiO$_2$-NTAs and BiVO$_4$/TiO$_2$-NTAs nanoheterojunctions with different BiVO$_4$ hydrothermal-depositing times 5 h, 10 h, and 20 h, respectively.

| Sample Codes          | $\lambda_{\text{ex}}$ (nm) | $\lambda_{\text{em}}$ (eV) | $\tau_1$ (ns) | $A_2/(A_1 + A_2)$ (%) | $\tau_2$ (ns) | $A_2/(A_1 + A_2)$ (%) | $\tau_{\text{avg}}$ (ns) |
|-----------------------|-----------------------------|-----------------------------|----------------|-----------------------|----------------|-----------------------|--------------------------|
| pristine TiO$_2$-NTAs | 375                         | 2.8                         | 2.33           | 54.0                  | 6.16           | 46.0                  | 4.99                     |
| plain BiVO$_4$ films  | 375                         | 1.8                         | 2.38           | 52.8                  | 5.56           | 47.2                  | 4.53                     |
| m&t-BIVO$_4$/TiO$_2$-NTAs-5 | 375                 | 2.8                         | 2.35           | 60.1                  | 5.53           | 39.9                  | 4.29                     |
| m&t-BIVO$_4$/TiO$_2$-NTAs-10 | 375              | 2.8                         | 2.21           | 42.8                  | 4.47           | 57.2                  | 3.86                     |
| m&t-BIVO$_4$/TiO$_2$-NTAs-20 | 375               | 2.8                         | 2.31           | 56.5                  | 5.09           | 43.5                  | 4.06                     |

We conducted photodegradation tests of the as-prepared nano-heterostructures to testify to the feasibility of the as-proposed transient CT mechanisms associated with the synergistic effect. We proposed the following chemical reactions:

$$\text{TiO}_2\text{-NTAs} + \nu \rightarrow h^+_{\text{VB}} (\text{TiO}_2) + e^-_{\text{CB}} (\text{TiO}_2) \quad (5)$$

$$\text{m&t-BIVO}_4 + \nu \rightarrow h^+_{\text{VB}} (\text{BiVO}_4) + e^-_{\text{CB}} (\text{BiVO}_4) \quad (6)$$

$$\text{m&t-BIVO}_4/\text{TiO}_2\text{-NTAs} + \nu \rightarrow e^-_{\text{CB}} (\text{BiVO}_4/\text{TiO}_2) + h^+_{\text{VB}} (\text{BiVO}_4/\text{TiO}_2) \quad (7)$$

$$e^-_{\text{CB}} + O_2 \rightarrow O_2^- \quad (8)$$

$$O_2^- + H^+ \rightarrow HO_2 \quad (9)$$

$$e^-_{\text{CB}} + H^+ + HO_2 \rightarrow H_2O_2 \quad (10)$$

$$H_2O_2 + e^-_{\text{CB}} \rightarrow OH + OH^- \quad (11)$$

$$O_2^-, OH, h^+_{\text{VB}} + \text{MO} \rightarrow \text{degradation products} \quad (12)$$

We conducted the UV–visible photodegradation performance inspections for the TiO$_2$-NTAs-based heterostructure nanohybrids irradiated by a standard solar simulated light source. We positioned the as-prepared samples at the center of self-constructed reaction container using double-sided tape, aligning the MO dye adsorbed face upwards and towards the lamp. Initially, we performed the self-degradation test of the MO, aiming to eliminate the influence of the photobleaching effect. Thus, we present the adsorption process and photodegradation efficiency ($\eta$) results for the intrinsic self-decomposition of the MO, pristine TiO$_2$ NTAs, plain BiVO$_4$ films, and BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions with different BiVO$_4$ NP hydrothermal deposition amounts, and with and without UV-visible lamp irradiation (photon-flux of 77.5 W/m$^2$) for 180 min, respectively, in Figure 16. We detected the degraded MO solutions at 20 min intervals to calculate the dye concentration as per the equation [118]: $\eta = (C_i - C_f)/C_i \times 100\%$, where $C_i$ and $C_f$ are the initial and final concentrations of the MO solution after irradiation, respectively. The self-photodegradation of MO is not significant (less than 5%). In addition, the samples of pristine TiO$_2$-NTAs and pure BiVO$_4$ films exhibited less photodegradation activity (27% and 56%, respectively), compared with that of the BiVO$_4$/TiO$_2$-NTAs nanohybrids under UV–visible lamp irradiation, which was mainly ascribed to the inferior capability of the light absorption in the UV-visible region and the higher reduction potential position for the CB. Apparently, the m&t-BIVO$_4$/TiO$_2$-NTAs nano-heterojunctions manifested more elevated photodegradation performances for the MO dye than the single TiO$_2$ and BiVO$_4$ semiconductors due to the cooperative effect of the prolonged light-absorption scope and staggered energy-band structure of the type-II heterostructure, which can acquire more energetic carriers to participate in the oxidation-reduction reaction. Notably, the photodegradation characteristics
for the m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs specimens were enhanced from ca. 85% to ca. 97% with the BiVO\textsubscript{4} hydrothermal synthesized time increase from 5 h to 10 h, while the deposition time of the BiVO\textsubscript{4} further increased to 20 h, the \( \eta \) of which decreased to approximately 93%, which provides convincing evidence that the upgraded CT rate may be slightly more dominant than the carrier lifetime.

We used the pseudo-first-order kinetic model to quantitatively study the reaction dynamics. This model assumes that \( \ln(C_0/C_t) = kt \) \[119\], where \( k \) is the reaction rate constant, \( C_0 \) is the initial concentration of the reactant, and \( C_t \) is the concentration of the reactant at time (t). In Figure 17, we explicitly show that m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs-10 has the maximum \( k \) value, which indicates the optimum photodegradation activity among the as-formed nano-heterojunctions.

Figure 16. Adsorption process and photodegradation rate (\( \eta \)) of blank test, pristine TiO\textsubscript{2}-NTAs, pure BiVO\textsubscript{4} films, and m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs with various BiVO\textsubscript{4} amounts (5 h, 10 h, and 20 h) under conditions of dark and UV-Visible light irradiation, respectively.

Besides the degradation efficiency, the stability and usability of a photocatalyst are also critical factors that affect its feasibility. We successively conducted cyclic photodegradation
tests of the TiO$_2$-NTAs-based nano-heterostructures under the same circumstances six times, as depicted in Figure 18.

![Figure 18](image)

Figure 18. Cyclic photodegradation tests of the blank test, pristine TiO$_2$-NTAs, pure BiVO$_4$ films, and BiVO$_4$/TiO$_2$-NTAs with different BiVO$_4$ deposited amounts (5 h, 10 h, and 20 h) under UV-Visible light irradiation, (a) 1st, (b) 2nd, (c) 3rd, (d) 4th, (e) 5th, (f) 6th, respectively.

According to the results of the six cyclic tests, the degradation activities of the as-formed nanohybrids had a slight decrease, as expected, which was mainly ascribed to the inescapable weight loss, which only approached 15% for the maximal deterioration of the photodegradation performance. This highlights the fact that the as-obtained m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions had comparatively excellent photodegradation stabilities.

The purpose of the free-radical-trapping experiments was to determine which substances were reactive, such as h$^+$, OH, and O$_2^-$, as well as which of them undertakes the primary role for the photodegradation towards MO dye, as exhibited in Figure 19.

![Figure 19](image)

Figure 19. Photodegradation rate $\eta$ of MO dye for the sample of m&t-BiVO$_4$/TiO$_2$-NTAs-10 without and with the presence of various scavengers irradiated by UV-Visible light, respectively.

The $\eta$ value of m&t-BiVO$_4$/TiO$_2$-NTAs-10 was ca. 97% without radical scavengers, and the $\eta$ values were ca. 73% and ca. 53% with methanol and IPA, respectively. Furthermore, we continuously injected the high-purity N$_2$ throughout the degradation reaction, with the aim of eliminating the dissolved O$_2$ and inhibiting the generation of O$_2^-$ . The removal rate
for the MO was only ca. 24%, compared with the 97% under normal atmospheric conditions. Thus, both the OH and O$_2^-$ radical groups are the collective reactive species involved in the degradation process, and O$_2^-$ especially plays a dominant role in the reaction, which is strongly dependent on the number of V$_0$ defects.

The oxidase-mimicking ability of BiVO$_4$/TiO$_2$-NTAs nanohybrids makes them an optimal choice of biosensing platforms for accurately determining the GSH levels. We present the GSH detection mechanism of the m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions in Figure 20. Under the excitation of simulated solar light, BiVO$_4$ and TiO$_2$ simultaneously absorb photons to generate e$^-_{CB}$–h$^+_{VB}$ pairs. Owing to the existence of the stepped-energy-band heterostructure, photoinduced e$^-_{CB}$ can quickly transfer from the CB of BiVO$_4$ to the CB of TiO$_2$, and then transfer to the external circuit. At the same time, the photoexcited h$^+_{VB}$ migrate from the VB of TiO$_2$ to the VB of BiVO$_4$, driven by the force of the built-in electric field between BiVO$_4$ and TiO$_2$. The direction of the built-in electric field is the same as that of the applied positive bias (0.5 V vs. Ag/AgCl), pointing from the TiO$_2$ to the BiVO$_4$. During the CT process, GSH can be oxidized to glutathione disulfide (GSSG), trapped by the holes in the VB of BiVO$_4$ and restraining the rapid recombination of e$^-_{CB}$–h$^+_{VB}$ pairs, which result in the substantial promotion of the photocurrent response compared with the transient I–t tests in Figure 8a. Therefore, the relationship between the GSH concentration and amplified photocurrent effect forms the basis of the biosensing function.

We quantitatively tested the constructed m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterojunctions for PEC biosensing in GSH solutions of various concentrations (0 µM–500 µM), and we recorded the concentration-current curves in 0.1 M PBS solution (pH 7.0) at the potential of 0.5 V (vs. Ag/AgCl) under simulated sunlight irradiation, as exhibited in Figure 21a. The photocurrent responses of the as-synthesized specimens gradually increased with the increase in the GSH concentration, and the photocurrent density of m&t-BiVO$_4$/TiO$_2$-NTAs-10 was substantially higher than that of the m&t-BiVO$_4$/TiO$_2$-NTAs-5 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 with the increase in the GSH concentration, confirming that the former has a superior photoinduced carrier CT efficiency and separation ability to the others, which is mainly due to the greater values of the $\Delta E_c$ and $\Delta E_v$ for m&t-BiVO$_4$/TiO$_2$-NTAs-10 mediated by the synergistic effect. In addition, the photocurrent response of m&t-BiVO$_4$/TiO$_2$-NTAs-10 had an excellent linear relationship with the GSH concentration ($R^2 = 0.9889$), with a linear range from 0 to 500 µM, as shown in Figure 22b. This upper detection limit is more pertinent to detecting GSH in biological specimens because the cellular GSH concentration is at mM levels [120]. Simultaneously, the PEC biosensing performance for m&t-BiVO$_4$/TiO$_2$-NTAs-10 showed a limit of detection (LOD) of 2.6 µM (a signal-to-noise ratio of 3), with a sensitivity of 960 mA cm$^{-2}$ M$^{-1}$, which was 1.92-fold and 1.38-fold greater than those for the m&t-BiVO$_4$/TiO$_2$-NTAs-5 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 specimens, respectively.

We review the analysis performance of the GSH using m&t-BiVO$_4$/TiO$_2$-NTAs heterostructure nanohybrids in this work and other modified materials found in the literature in Table 8. The linear response range was wider than those of the colorimetric biosens-
ing, fluorescence biosensor, and other PEC methods. The m&t-BiVO$_4$/TiO$_2$ NTAs also displayed a lower detection limit for GSH compared with the fluorimetry and other PEC methods. Most important of all, the proposed BiVO$_4$/TiO$_2$-NTAs nano-heterostructure PEC biosensing approach is characterized by excellent stability and selectivity.

Figure 21. (a) Photocurrent performance of the m&t-BiVO$_4$/TiO$_2$-NTAs type-II heterostructure nanocomposites with various BiVO$_4$ NPs hydrothermal-deposited times in the presence of 0, 50, 100, 150, 200, 300, 400, and 500 µM GSH (from left to right) in 0.1 M PBS solution (pH 7.0) at the potential of 0.5 V irradiated by simulated sunlight, respectively; (b) the plots of m&t-BiVO$_4$/TiO$_2$-NTAs heterojunction nanoelectrodes with various BiVO$_4$ NPs deposition times 5 h, 10 h, and 20 h with linear relationship toward photocurrent density and concentration of GSH, respectively.

Figure 22. (a) Time-based photocurrent performance for the sample of m&t-BiVO$_4$/TiO$_2$-NTAs-10 irradiated by several cycles in 0.1 M PBS solution containing 100 µM GSH at the potential of 0.5 V (vs. Ag/AgCl) under simulated sunlight irradiation; (b) photocurrent ratio $I/I_0$ of the m&t-BiVO$_4$/TiO$_2$-NTAs-10 electrode in 0.1 M PBS solution containing 200 µM GSH with the successive addition of different interfering substances (the concentration of all other interfering species is 200 µM).

Table 8. Linear range and limit of detection (LOD) comparison of various methods for detecting GSH.

| Sensor Type           | Sensing Method  | Linear Range (µM) | LOD (µM) | Ref. |
|-----------------------|-----------------|-------------------|----------|------|
| BSA-AuNP@ZnCo$_2$O$_4$| Colorimetric biosensing | 0.5–15            | 0.0885   | [121]|
| CuPd@H-C$_3$N$_4$     | Colorimetric biosensing | 2–40              | 0.58     | [122]|
| In$_2$O$_3$/In$_2$S$_3$| PEC biosensing   | 1–100             | 0.82     | [123]|
| N$_2$S-Cdots-MnO$_2$  | fluorimetry      | 0–250             | 28.5     | [124]|
| Bi$_2$S$_3$/TiO$_2$-NTAs| PEC biosensing | 15–200            | 7        | [125]|
| m&t-BiVO$_4$/TiO$_2$-NTAs| PEC biosensing | 0–500             | 2.6      | This work |
To be effective, PEC biosensors should possess good stability and selectivity. We chose the m&t-BiVO$_4$/TiO$_2$-NTAs-10 specimen as the candidate for the stability and selectivity testing, as it has the optimal PEC activity among all the as-fabricated nanohybrids. We evaluated the photoexcited biosensing stability of the selected sample by measuring the time-based photocurrent response under several on/off irradiation cycles in a 0.1 M PBS solution containing 100 μM GSH at a potential of 0.5 V (vs. Ag/AgCl), irradiated by simulated sunlight irradiation. Within 260 s, the detection process of the nano-heterojunction had cycled 20 times, and as exhibited in Figure 22a, there was almost no decay on the photocurrent and 96.5% of its initial value was retained, which demonstrates that the BiVO$_4$/TiO$_2$-NTAs electrode had the desirable stability in the GSH detection. For probing the selectivity of the constructed nano-heterostructure photoelectrode, we adopted the ratio of the photocurrent intensity ($I/I_g$) to characterize the effects of a series of interfering substances on the photocurrent. $I$ and $I_g$ represent the photocurrents before and after the addition of other interferents, respectively. For the characterization, we used metal ions (K$^+$, Cu$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$), glucose, and ascorbic acid (AA). As displayed in Figure 22b, we did not observe any salient photocurrent variation with the successive addition of 200 μM AA, glucose, and other metal ions into the electrolyte containing 200 μM GSH. Among them, AA is a good electron donor and can be photocatalytically oxidized by the as-prepared nano-heterojunctions, and AA also caused the photocurrent to slightly increase, but it had little effect on the experimental results. Eventually, we verified the biosensing stability of the m&t-BiVO$_4$/TiO$_2$-NTAs photoelectrode via intermittent photocurrent response tests.

We present the graphical sensitivity vs. time relations of the as-prepared specimens at room temperature in Figure 23. The parameter sensitivity (S) for gas-sensing can be defined as follows [126]: 

$$S = I_a/I_g$$

where $I_a$ is the experimentally recorded stable current values during the targeted gas flow, and $I_g$ is the recorded stable current during the air gas flow. The response time ($τ_{res}$) is defined as the time to reach 90% of the final equilibrium value. When the NH$_3$ permeation reached $t = 200$ s, the S values were exponentially increased, as expected, while they were exponentially decreased when the air injection reached $t = 850$ s. Simultaneously, there were smaller S values (ca. 0.5 and 0.8) for the gas-sensing of the pristine TiO$_2$ NTA and pure BiVO$_4$ film sensors owing to their larger electronic transfer impedances and narrower light-absorption scopes, which led to lower photoexcited current responses. The S value increased from ca. 1.8 to ca. 2.4 with the increase in the BiVO$_4$ hydrothermal deposition times from 5 h to 10 h; however, the S value decreased to ca. 2.2 with the increase in the of BiVO$_4$ preparation time to 20 h, which are consistent with the abovementioned observed trends in the photodegradation and PEC biosensing. In addition, the $τ_{res}$ values for the pristine TiO$_2$ NTAs and plain BiVO$_4$ films were 307 s and 302 s, respectively. As a comparison, the $τ_{res}$ of the m&t-BiVO$_4$/TiO$_2$-NTAs-5 sample was about 290 s towards the sensing of NH$_3$ gas, while those for the m&t-BiVO$_4$/TiO$_2$-NTAs-10 and m&t-BiVO$_4$/TiO$_2$-NTAs-20 samples were around 250 s and 271 s, respectively. The gas-sensing performances of the selectivity and response speed for the m&t-BiVO$_4$/TiO$_2$-NTAs nano-heterostructure are superior to those of the individual BiVO$_4$ and TiO$_2$ semiconductors. The specimen of m&t-BiVO$_4$/TiO$_2$-NTAs-10, especially, is the ideal platform for gas-sensing, possessing a higher sensitivity and faster response speed in comparison with those of the m&t-BiVO$_4$/TiO$_2$-NTAs-5 and m&t-BiVO$_4$/TiO$_2$-NTAs-20.

Combined with the obtained results, we propose a reasonable theory to explain the gas-sensing mechanism toward NH$_3$. The conductivity of nano-heterostructures is proportional to the concentration of conducting electrons. In the beginning, the atmospheric O$_2$ can be converted to O$_2^-$, attaching to the active sites of the V$_6$ defects in nano-heterojunctions, which leads to a reduced concentration of carriers. With the injection of NH$_3$ gas, reductive NH$_3$ molecules can react with O$_2^-$ (i.e., 4NH$_3$ (gas) + 3 O$_2^-$ (adsorption) → 6H$_2$O (gas) + 2N$_2$ (gas) + 6e$^-$), liberating the electrons as free charges and increasing the conductivity of the nano-heterostructures, and the electrically neutral N$_2$ gas will be released back to the ambiences. The increased concentration of e$^-_{CB}$ due to the exposure of the
hetero-nanosystem to NH\textsubscript{3} gas is a result of the electron-donating properties of analyte gas. Specifically, the m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs heterostructure nanocomposites can inject redundant electrons into the CB of TiO\textsubscript{2} from the CB of BiVO\textsubscript{4} irradiated by UV–vis light, which facilitates the formation of O\textsuperscript{2−}. The m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs-10 sample manifested the best performances for photodegradation and gas-sensing, which are tightly associated with the O\textsuperscript{2−} concentration, which is mainly attributed to the number of V\textsubscript{O} defect active sites and the superior capacity of CT associated with the greater \( \Delta E_{c} \) and \( \Delta E_{v} \) values.

![Figure 23](image)

**Figure 23.** Sensitivity of pristine TiO\textsubscript{2}-NTAs, pure BiVO\textsubscript{4} films and m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs nanohybrids with different BiVO\textsubscript{4} NPs depositing amounts as a function of time, respectively.

4. Conclusions

In conclusion, we constructed the m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs type-II nano-heterojunctions via m&t-BiVO\textsubscript{4} NPs integrated with the ordered arrangement of TiO\textsubscript{2} NTAs using the low-cost hydrothermal-deposition approach. The as-synthesized m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs nanohybrids exhibited dramatically improved photodegradation, PEC biosensing, and NH\textsubscript{3} gas-sensing performances compared with the single semiconductor under UV–visible irradiation, as expected, which is consistent with the variation trend of the PEC activity tests, which is mainly ascribed to the positive synergistic effect between the content ratio of the m&t-BiVO\textsubscript{4} related to the hydrothermal preparation time and the number of V\textsubscript{O} defects mediated by the pH value, which induce the uplifted band offset and promote the exposed reaction active sites related to V\textsubscript{O} defects. We verified the deduction by the probing results of the NTRT-PL and TRPL spectra, correspondingly proposing semi-qualitative and semi-quantitative analyses for the interfacial CT dynamics process, which demonstrates the promotion of the separation of the photoinduced e\textsuperscript{−}–h\textsuperscript{+} pairs and elevated charge injection efficiency for the as-obtained nano-heterojunctions. Thus, it is expectable that the m&t-BiVO\textsubscript{4}/TiO\textsubscript{2}-NTAs nano-heterojunctions not only provide in-depth comprehension for the interfacial CT process between different photocatalysts, but also contributes new insight into the design of devices for PEC biosensing and NH\textsubscript{3} gas-sensing with superior performances.

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