Architecting a Double Charge-Transfer Dynamics In$_2$S$_3$/BiVO$_4$ n–n Isotype Heterojunction for Superior Photocatalytic Oxytetracycline Hydrochloride Degradation and Water Oxidation Reaction: Unveiling the Association of Physicochemical, Electrochemical, and Photocatalytic Properties

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ABSTRACT: To surmount incompatibility provoked efficiency suppression of an anisotype heterojunction and to pursue an improved intrinsic photocatalytic activity by manipulating oriented transfer of photoinduced charge carriers, an In$_2$S$_3$/BiVO$_4$ (1:1) n–n isotype heterojunction was fabricated successfully through a simple two-step calcination method, followed by a wet-chemical deposition method. The formation of an n–n isotype heterojunction was confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and UV–visible diffuse reflectance spectroscopy. The photocatalytic efficiency of the In$_2$S$_3$/BiVO$_4$ catalyst was examined over degradation of oxytetracycline hydrochloride (O–TCH) and oxygen ($O_2$) evolution reaction. Consequently, an n–n In$_2$S$_3$/BiVO$_4$ isotype heterojunction exhibits a superior O–TCH degradation efficiency (94.6%, 120 min) and $O_2$ evolution (695.76 μmol, 120 min) of multiple folds as compared to the pure BiVO$_4$ and In$_2$S$_3$ solely. This is attributed to the proper band alignment and intimate interfacial interaction promoted charge carrier separation over the n–n isotype heterojunction. The intimate interfacial contact was confirmed by transmission electron microscopy (TEM), high-resolution TEM, and field emission scanning electron microscopy analysis. The proper band alignment was confirmed by Mott–Schottky analysis. The photoelectrochemical linear sweep voltammetric study shows a superior photocurrent density (269 μA/cm$^2$) for In$_2$S$_3$/BiVO$_4$ as compared to those for pristine BiVO$_4$ and In$_2$S$_3$, which is in good agreement with the photocatalytic results. Furthermore, the superior charge antirecombination efficiency of the n–n isotype heterojunction was established by photoluminescence, electrochemical impedance spectroscopy, Bode analysis, transient photocurrent, and carrier density analysis. The improved photostability of the heterojunction was confirmed by chronoamperometry analysis. An orderly corelationship among physicochemical, electrochemical, and photocatalytic properties was established, and a possible mechanistic pathway was presented to better understand the outcome of the n–n isotype heterojunction. This study presents an effective way to develop new n–n isotype heterojunction-based efficient photocatalysts and could enrich wide applications in other areas.

1. INTRODUCTION

Semiconductor-oriented visible photon-driven heterogeneous photocatalysis has gathered huge interest in the current era as a green sustainable futuristic resolution to the major global tribulations such as energy scarcity and environmental catastrophe.$^1$–$^3$ The generalized principle involves light harvesting, resulting in photoinduced charge carrier formation over the semiconductor surface. $^3$–$^8$ The generalised principle involves light harvesting, resulting in photoinduced charge carrier formation which ultimately promotes redox reaction over the semiconductor surface. $^3$–$^8$ An assorted number of strategies are carried out to manipulate intrinsic physicochemical and optoelectronic characteristics of semiconductors in order to fabricate a robust photocatalyst with superior conversion efficiency, that is, solar to chemical energy. However, the efficiency of traditional anisotype heterojunctions developed so far between semiconductors of different charge carrier densities is restricted by a high recombination rate of photoinduced electron–hole pairs because of interfacial incompatibility and low redox potential of the respective conduction band (CB) and valence band (VB) edge.$^9$–$^{10}$ To remove the constraint, various isotype n–n functional heterojunctions of CN/CNS-
toward water oxidation and antibiotic degradation.20 Extending analysis. The intimate interfacial contact and superior compatibility between the two materials, which further induces the separation of photoinduced electrons and holes more effectively via providing a strong driving force by creating a space charge accumulation/depletion region at the junction interfaces.20 Nevertheless, the benchmark has not yet been achieved, and the construction of an effective n−n isotype heterojunction material is still a big challenge for the research community.

In this context, visible-light-responsive n-type monoclinic bismuth vanadate (BiVO₄) has attracted tremendous attention because of its suitable band gap, that is, 2.3−2.7 eV, nontoxicity, high stability, wide light absorbance range, and especially its weak hole localization property, which is due to the destructive effect of the [VO₄] tetrahedron, suitable for O₂ evolution.20,23−25 However, the catalytic efficiency of pristine BiVO₄ could not reach up to the mark because of the lower photogenerated charge carrier mobility and higher photo-generated electron−hole pair recombination rates. Hence, to nullify this associated drawback of BiVO₄, researchers started adopting the isotype heterojunction technique, that is, combining n-type BiVO₄ with another suitable n-type semiconductor, and interestingly, the author’s group has reported an n−n-type M-BiVO₄/T-BiVO₄ heterojunction toward water oxidation and antibiotic degradation.26−29 Extending the search for a better match for BiVO₄ n-type β-indium sulfide (β-In₂S₃), a group III−VI metal sulfide with an ideal band gap of 2.0−2.3 eV, has evolved as a potential semiconductor photocatalyst because of its low toxicity, narrow band gap, good photostability, good photosensitivity, and photoc conductivity.18,26,27 Taking these advantageous features into account, an In₂S₃/BiVO₄ n−n isotype heterojunction was designed, which could be beneficial in enhancing the antirecombination rate of photogenerated carriers on behalf of the high conductivity of In₂S₃ leading to charge channelization and maintaining the water decomposition property with respect to the monoclinic crystal structure of BiVO₄. However, the In₂S₃/BiVO₄ n−n isotype heterojunction-based photocatalyst for oxyztracycline hydrochloride (O-TCH) degradation and oxygen evolution remains unavailable so far, and the demanding association among physicochemical, photoelectrochemical, and photocatalytic properties of the BiVO₄-based n−n isotype hybrid catalysts has not yet been investigated in detail.

Considering the aforementioned background, we herein fabricated an n−n isotype heterojunction of M-BiVO₄ and In₂S₃ with an equimolar ratio through a simple two-step calcination process followed by a wet-chemical deposition method and examined the photocatalytic activity of the so-formed photocatalyst toward O-TCH degradation and oxygen evolution separately. The enhanced photoinduced charge carrier antirecombination process over the n−n isotype heterojunction interface results in higher activity and is validated by photoluminescence (PL), electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), transient photocurrent, Bode analysis, and carrier density analysis. The intimate interfacial contact and superior compatibility between BiVO₄ and In₂S₃ were confirmed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and field emission scanning electron microscopy (FESEM) analysis. The proper band alignment of BiVO₄ and In₂S₃ in the n−n isotype heterojunction is established by the Mott−Schottky (MS) study. A possible mechanistic pathway was proposed and discussed for the n−n isotype heterojunction based on the experimental and analytical investigations. Furthermore, the physicochemical, electrochemical, and photocatalytic properties are correlated and discussed in depth. This n−n isotype heterojunction-based photocatalytic system will provide a new direction in designing double charge-transfer-oriented catalytic composites for energy generation and organic/inorganic pollutant degradation.

2. EXPERIMENTAL SECTION

2.1. Fabrication of the In₂S₃/BiVO₄ n−n Isotype Heterojunction. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 99%, MERCK), ammonium metavanadate (NH₄VO₃, 99%, LOBA CHEMIE), nitric acid (HNO₃, 69%, MERCK), ammonium hydroxide (NH₄OH, 28−30%, MERCK), indium chloride (InCl₃), thioacetamide (C₃H₇NS), and ethanol (C₂H₅OH, 99.9%) of analytical grade are used for the synthesis procedure without any further purification. Deionized (DI-H₂O) water was used throughout the experiments. An In₂S₃/BiVO₄ n−n isotype heterojunction catalyst with an equimolar ratio of Bi and In was fabricated using a simple two-step calcination process, followed by a wet-chemical deposition method. In a distinctive procedure, pristine monoclinic BiVO₄ was synthesized by a coprecipitation method with an optimized calcination temperature, a technique we previously reported, followed by wet-chemical deposition of In₂S₃.20,28 The schematic representation of the synthesis procedure of the In₂S₃/BiVO₄ n−n isotype heterojunction is given in Scheme 1.

Scheme 1. Schematic Illustration of the Facile Fabrication Technique of the In₂S₃/BiVO₄ n−n Isotype Heterojunction

About 0.020 mole of bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) was initially dissolved in 165 mL of 2 M HNO₃. A stoichiometric quantity of ammonium metavanadate (NH₄VO₃) was added maintaining the overall molar ratio of metal ions present in the resulting solution to Bi/V = 1:1. A homogeneous yellow color solution was then obtained by continuously stirring the resulting mixture for 2 h. The final pH of the resulting solution was adjusted to 9 by the slow addition of ammonium hydroxide under continuous stirring, leading to the formation of a yellowish orange precipitate. The stirring was continued for next 1 h for better product formation. The resulting precipitate was then centrifuged, washed several times with distilled water and ethanol to remove the unwanted product, and dried in a hot air oven for 24 h at 70 °C. Monoclinic BiVO₄ was obtained by finely grinding the dried sample, followed by a heat treatment of 600 °C for 5 h with a 10 °C/min heating rate in a muffle furnace. The product was then collected and Grinded finely for further photocatalytic studies. About 0.003 mole of the synthesized monoclinic BiVO₄ catalyst was added to a 80 mL aqueous solution containing a certain amount of InCl₃ and C₃H₇NS. 

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with a molar ratio of In/S = 2:3 and Bi/In = 1:1. The mixture was vigorously stirred at 85 °C for 3 h, leading to a brown precipitate. The precipitate was then centrifuged, washed several times with DI water, and well dried in a hot air oven at 70 °C for 24 h. The sample was collected and grinded well for further characterization. The sample was indexed as In2S3/BiVO4. For comparison, pristine In2S3 was obtained by the above-specified methodology without addition of BiVO4.

2.2. Analytical Characterizations. Powder X-ray diffraction (PXRD) patterns were investigated using a Rigaku Ultima IV diffractometer with a monochromatic Cu Kα X-ray radiation source (λ = 1.5 Å) in a scan range of 2θ = 10°–80° and with a 5° min⁻¹ scan rate. The applied voltage and current were well maintained at 40 kV and 40 mA, respectively. The structures and surface morphologies were neatly studied by conducting TEM analysis on a Philips Tecnai G2 instrument (200 kV) and FESEM analysis on Zeiss Supra SS, respectively. The surface chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) in an ESCA+ spectrometer (monochromatized Al Kα, 1486.7 eV) adopting the Cl peak at 284.9 eV for binding energy (BE) correction. UV–visible diffuse reflectance spectroscopy (UV–vis DRS) was performed by a JASCO 750 UV/visible spectrophotometer with a BaSO4 pallet as the reference. A JASCO spectrophotometer FP8300 was used to record the powder PL spectrum at an excitation wavelength of 325 nm. A JASCO FT/IR-4600 spectrometer was used to record the Fourier transform infrared (FTIR) spectrum using the potassium bromide (KBr) matrix. All measurements were performed at room temperature unless particularly specified.

2.3. Electrochemical Measurements. Photoelectrochemical measurement was performed on an IVIUM-n-STAT electrochemical workstation using a conventional three-electrode pyrex electrochemical cell consisting of a prepared electrode as the working electrode, a platinum (Pt) wire as the counter electrode, and an Ag/AgCl as the reference electrode in an electrolytic solution of 0.1 M Na2SO4 (pH = 6.1). The electrophoretic deposition method was introduced to fabricate the working electrodes. About 20 mg of the prepared photocatalyst powder with 20 mg of iodine was well dispersed in 20 mL of acetone. Two fluorine-doped tin oxide (FTO) electrodes arranged in a parallel manner and separated by 10–15 mm were placed in the catalyst-suspended solution. A 60 V bias was applied under potentiostatic control between the two FTOs for 5 min, maintaining the coating surface area to 1 cm × 1 cm. LSV study and EIS measurements were executed under visible light irradiation. EIS studies were analyzed over a frequency range of 0.1–10,000 Hz with 1 V amplitude at zero bias. Transient photocurrent intensity was carried out for a time interval of 300 s at 0.6 V applied potential under the illumination of chopped visible light. Chronoamperometry (CA) study was carried out for a time interval of 600 s at 0.6 V applied potential under continuous illumination of visible light. MS analysis was carried out in the dark at an applied frequency of 500 Hz with a 25 mV applied potential. All the visible light irradiated measurements were conducted using a 300 W xenon lamp with a cutoff filter of λ ≥ 400. It was noted that no photo response was observed with a cleaned FTO without catalyst coating.

2.4. Photocatalytic O-TCH Degradation. Photocatalytic degradation of oxytetracycline aqueous solution was cautiously accomplished in a quartz photocatalytic reactor under visible light illumination (300 W Xe lamp, λ ≥ 420 nm, 100 mW/cm²). Initially, 20 mg of the prepared catalyst was homogeneously dispersed in a 20 mL solution (aq) of O-TCH of concentration 20 mg L⁻¹. The resulting suspension was stirred for 30 min magnetically in the dark to accomplish the adsorption—desorption equilibrium. The resulting suspension was then illuminated with visible light for 120 min under magnetic stirring. Eventually, the resulting suspension was centrifuged and analyzed using a UV–vis spectrometer at 275 nm. The process was repeated with different irradiation...
times to elucidate the rate of the degradation reaction instead of periodically collecting the solution with a syringe to avoid error.

2.5. Photocatalytic Water Oxidation Reaction. Initially, 20 mg of the as-synthesized photocatalyst was suspended in a 20 mL aqueous solution of 0.05 M AgNO₃ under continuous magnetic stirring until the mixture attains homogeneity, followed by N₂ purging for 30 min to remove the dissolved oxygen. Photocatalytic water oxidation reaction was achieved under visible light illumination (300 W Xe lamp, λ ≥ 420 nm) in a sealed quartz batch reactor of 100 mL capacity. The Xe light source was maintained at a distance of 10 cm apart from the top of the suspension. The temperature of the aqueous bulk suspension was maintained at room temperature by cold water circulation. The evolved O₂ was collected via the downward water displacement technique and characterized via a molecular sieve column gas chromatography instrument (5 Å) with a thermal conductivity detector.

3. RESULTS AND DISCUSSION

The scrupulous fabrication technique of the In₂S₃/BiVO₄ n−n isotype heterojunction with superior interfacial contact is represented in Scheme 1.

Details of the crystallographic structures of as-synthesized photocatalysts were initially inspected by the XRD technique, and the obtained results are shown in Figure 1. In brief, all the featuring diffraction peaks of pristine BiVO₄ and In₂S₃ were well indexed with a monoclinic phase (JCPDS CARD no. 01-083-1698) and a β phase (JCPDS CARD no. 00-032-0456), respectively. Further, the XRD patterns of the heterojunction with an equimolar ratio of BiVO₄ and In₂S₃ show maximum characteristic diffraction peaks of the combination of both the entities, suggesting a good integration of BiVO₄ and In₂S₃ in the In₂S₃/BiVO₄ n−n isotype heterojunction. Additionally, the crystallite sizes of the as-synthesized samples were estimated by taking the full width at half-maximum value of the most intense peak, that is, (112) for BiVO₄ and (440) for In₂S₃, respectively, and then by adopting Scherrer’s eq 131

$$ D = \frac{(k \lambda)}{(\beta \cos \theta)} $$

Here, D denotes the crystallite size of the sample, λ denotes the irradiation wavelength, k denotes a constant (0.94), β denotes the half-maxima peak width, and θ denotes the diffraction angle of the peak under examination. The crystallite sizes of pristine monoclinic BiVO₄ and In₂S₃ were estimated to be 38.87 and 18.18 nm, respectively. Nevertheless, the crystallite size of both BiVO₄ and In₂S₃ decreased after the formation of a heterojunction to 37.8 and 14.73 nm, respectively, elucidating a synergistic interaction between the two materials in the formed heterojunction. Moving to the neat material, diffraction
peaks of the pristine BiVO₄ sample (Figure 1a) are distinguishably intense and sharp, indicating its highly crystalline character, while the diffractogram of the In₂S₃ sample is broad and weak, which is due to the small crystal size or the semicrystalline nature of the catalyst. Moreover, well-distinguishable sharp diffraction peaks of BiVO₄ nanocrystals were observed in the In₂S₃/BiVO₄ composite, establishing the highly crystalline character of BiVO₄ nanocrystals in the heterojunction. The intensities of the major diffraction peaks of BiVO₄ (112) and In₂S₃ (440) were reduced and revealed to be shifted toward a higher diffraction angle after the formation of the In₂S₃/BiVO₄ n–n isotype heterojunction composite with a shifting value of 0.1° relative to their pristine phases, suggesting an intimate contact between BiVO₄ and In₂S₃. The details are presented in Figure 1a,b.

The bond vibrational chemistry of the In₂S₃/BiVO₄ heterojunction and both parent materials, that is, In₂S₃ and BiVO₄, was established by FTIR analysis. The typical FTIR spectra of BiVO₄ (Figure 1d) show broad absorptions (within 1000–500 cm⁻¹) associated with ν3 asymmetric stretching vibration of the VO₄ unit. In brief, the peak representing ν3 (VO₄⁻) is centered around 740 cm⁻¹, whereas ν1 depicting symmetric stretching vibration of the VO₄ unit ν1 (VO₄⁻) is positioned at 840 cm⁻¹, which corresponds to the monoclinic phase of BiVO₄. The FTIR absorption bands of the unadulterated In₂S₃ catalyst indicate the typical molecular structure of In₂S₃. The strong absorption bands at 3450 and 1621 cm⁻¹ in the coprecipitated In₂S₃ sample were attributed to the bonding frequency of the adsorbed hydroxyl (–OH) groups. Furthermore, the occurrence of a weak IR signal at 1120 cm⁻¹ was ascribed to the ν(S–O) vibrational frequency in SO₄²⁻. Further, the vibrational band centered at 1033 cm⁻¹ was attributed to the ν(S–O) stretching frequency. Again, for the In₂S₃/BiVO₄ heterojunction, appearance of absorption peaks of ν3 (VO₄⁻), ν1 (VO₄⁻), ν(S–O), and −OH bonding vibrations with relative decreased intensity indicates the coexistence of BiVO₄ and In₂S₃ in the composites. This was further established by XPS analysis.

The surface chemical composition, oxidation states, and confirmation of double charge-transfer dynamics in the fabricated In₂S₃/BiVO₄ nanocomposite were investigated by XPS analysis. The corresponding survey spectrum shown in Figure 2a indicates the existence of Bi, V, O, In, and S elements in the prepared sample devoid of any contaminants. The appearance of the prominent carbon peak at 284.9 eV was attributed to the adventitious hydrocarbon of the XPS instrument. The deconvoluted narrow scan XPS spectra of Bi displayed in Figure 2b represent three distinct peaks centered at 258.8, 161.9, and 163.8 eV. The foremost and hindmost peak with a peak difference of 5 eV attributed to the spin–orbit separation of Bi 4f₁/₂ and Bi 4f₃/₂ doublets indicate the +3 state of the Bi atom. The ternary peak appearing along with the peaks of Bi centered at 161.9 eV corresponds to the 2p state of sulfur. This further corroborates proper incorporation of In₂S₃ with BiVO₄ in the heterojunction. The corresponding characteristic peaks centered at 516.5 and 523.8 eV are attributed to V 2p₁/₂ and V 2p₃/₂ states of V (Figure 2c). A peak separation of 7.3 eV indicates the existence of V in the +5 valence state. O 1s symmetric spectra displayed two distinct deconvoluted peaks centered at 529.5 and 532 eV (Figure 2d). The former one corresponds to the lattice oxygen of the Bi–O and V–O bond, whereas the latter one is ascribed to the hydroxyl (–OH) group present in the sample. As shown in Figure 2e, two high-resolution In 3d peaks were found at a lower BE value of 444.9 eV (In 3d₃/₂) and a higher BE value of 452.5 eV (In 3d₅/₂). The peak difference of 7.6 eV indicates the +3 state of indium. As displayed in Figure 2, the respective BE values of Bi, V, and O in the n–n isotype heterojunction suffered a negative shift as compared to the corresponding values of unadulterated BiVO₄, indicating the flow of electrons from In₂S₃ to BiVO₄. Furthermore, shifting in BE confirms the occurrence of strapping interaction between BiVO₄ and In₂S₃, exhibiting a higher photocatalytic activity. Consequently, the intensity ratio of Bi/In < 1 indicates distribution of In₂S₃ nanoparticles over BiVO₄ microcrystals. This is further confirmed by UV, TEM, and FESEM analysis.

Moreover, the UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was taken into account to study the optical response of all the as-synthesized nanocatalysts that have a vital function in the photocatalytic performance. It was observed that all the fabricated samples show light absorbance in the visible regions, that is, pristine monoclinic BiVO₄ and In₂S₃ exhibit absorption edges at nearly 552 and 620 nm, respectively (Figure 3a), whereas the nanocomposite depicts a wide absorbance extending up to the IR region.

Further, two prominent absorption bands were observed for the In₂S₃/BiVO₄ hybrid (Figure 3a), viz., (i) the lower intense one is assigned to the absorption of BiVO₄ microcrystals and (ii) the higher intense one is attributed to the characteristic absorption of In₂S₃ nanocrystals, which indicates that most of the surface of BiVO₄ microcrystals is covered by In₂S₃ nanocrystals. Accompanied by the introduction of In₂S₃, the obtained In₂S₃/BiVO₄ n–n isotype heterojunction composite exhibits a red shift in the absorption edge (726.28 nm) showing a superior visible light response. The well-detectable red shift of the optical absorption edge is also reflected in the color change of BiVO₄ (1) to yellow and that
of In$_2$S$_3$/BiVO$_4$ (3) to reddish brown (Figure 3a, inset) and the smaller band gap energy as compared to pristine BiVO$_4$ (Figure 3b). Moreover, the optical band gap energy of the fabricated samples was approximated adopting eq 1:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

(2)

where $\alpha$ symbolizes the absorption coefficient, $h$ symbolizes Planck’s constant, $A$ represents a constant, $\nu$ symbolizes the light frequency, $E_g$ represents the band gap energy, and $n = 1$ and 4 represent direct and indirect band gaps, respectively.

As represented in Figure 3b, the approximated band gap energies of pure BiVO$_4$ (direct), In$_2$S$_3$ (direct), and BiVO$_4$/In$_2$S$_3$ are 2.36, 2.22, and 1.91 eV, respectively. Interestingly, the band gap of isotype heterojunctions is located below parent combining materials (BiVO$_4$ and In$_2$S$_3$), which further indicates the proper coupling of electronic structures of BiVO$_4$ and In$_2$S$_3$ in the n–n isotype heterojunction. This further indicates that the In$_2$SO/BiVO$_4$ n–n isotype heterojunction can show an enhanced photocatalytic performance via producing more photogenerated charge pairs under visible light illumination.

The surface morphology of BiVO$_4$, In$_2$S$_3$, and In$_2$S$_3$/BiVO$_4$ heterojunctions was studied by FESEM analysis to better understand the reaction kinetics (Figure 8b,c). Following the pseudo-first-order kinetic model was used to obtain the tentative results to better understand the reaction kinetics (Figure 8b,c). Following the

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Figure 4. (a,b) Corresponding low- and high-magnification FESEM images of BiVO$_4$ and (c,d) corresponding low- and high-magnification FESEM images of In$_2$S$_3$.

5) show an Annona reticulate-shaped morphology with smaller polyhedron-shaped particles contributing to a larger irregular microsphere. The irregular microcrystals have a size in the range of 3.5–9.5 μm, as observed in Figure 4a,b. The appeared tiny pores on the crystal surface are ascribed to the removal of gas during the calcination process.

Additionally, the low-resolution FESEM images of In$_2$S$_3$ (Figure 4c) show agglomerated rice-shaped nanoparticles with a particle size ranging in between 120 and 300 nm. Again, the magnified FESEM image of In$_2$S$_3$ gives a closer view where hierarchically assembled copious two-dimensional nanorice geometry of irregular length is clearly seen in Figure 4d. Further, the low-resolution FESEM analysis of the In$_2$S$_3$/BiVO$_4$ n–n heterojunction shows irregular distribution of In$_2$S$_3$ rice-structured particles over larger microspheres of BiVO$_4$ (Figure 5a). This further indicates the UV–vis analysis results.

Moreover, the high-resolution FESEM image (Figure 5b) depicts the zoomed view where deposition of two-dimensional irregular rice-shaped In$_2$S$_3$ over BiVO$_4$ surface is more crystal clear and corroborates the intimate interfacial contact of BiVO$_4$ and In$_2$S$_3$, which is complementary for faster interfacial charge transfer and better activity. The energy-dispersive X-ray spectroscopy (EDX) patterns in Figure 5c highlight the existence of Bi, V, O, In, and S in the heterojunction with a stoichiometric proportion of Bi/V = 1.01:1 and In/S = 0.64:1. The result further confirmed by XPS analysis is described in the respective section.

The microstructure, interior morphology, and heterojunction interface of BiVO$_4$, In$_2$S$_3$, and In$_2$S$_3$/BiVO$_4$ n–n isotype heterojunctions were further studied by TEM and HRTEM investigations (Figures 6 and 7). The low-magnified TEM images of BiVO$_4$ illustrate a microspherical morphology with a particle size range of 3.5–9.5 μm (Figure 6a). The findings are well concordant with the FESEM analysis. An interlayer d-spacing value of 0.308 nm was observed from the HRTEM image of monoclinic BiVO$_4$ and is attributed to the (112) crystal plane (Figure 6b). The characteristic low-resolution TEM images of In$_2$S$_3$ (Figure 6a) illustrate an aggregation of irregular rice-shaped nanoparticles with a particle size range of 200–300 nm. Further, the HRTEM results depict an interlayer lattice spacing of 0.324 nm that is attributed to the (311) plane of In$_2$S$_3$ (Figure 6b).

The typical TEM images of the In$_2$S$_3$/BiVO$_4$ n–n heterojunction sample show distribution of irregular nanoparticles of In$_2$S$_3$ over the circumference of spherical nanoparticles of BiVO$_4$ (Figure 7a). The result is in good agreement with FESEM analysis. Moreover, the HRTEM images of In$_2$S$_3$/BiVO$_4$ depict two diverse d-spacing values of 0.308 and 0.324 nm, which are ascribed to the (112) and (311) planes of BiVO$_4$ and In$_2$S$_3$, respectively (Figure 7b). A precise contact between the lattice fringes of In$_2$S$_3$ and BiVO$_4$ in the heterojunction as represented in Figure 7c confirms an intimate interfacial contact and superior compatibility between the two combining semiconductors. The intense circular rings of the selected area electron diffraction (SAED) pattern are in good consistency with the (112) and (331) planes of BiVO$_4$ and In$_2$S$_3$, respectively, and further establish a configuration of an intimate contact. Moreover, the intense circular rings illustrate the polycrystalline nature of the combining materials. Consequently, deposition of the smaller In$_2$S$_3$ particle will facilitate the charge transfer to the surface attributable to the faster mean free paths of the photogenerated carriers compared to the smaller sizes of the particles.

We performed degradation of O-TCH aqueous solution, a representative of organic noxious waste, to assess the photocatalytic efficiency of In$_2$S$_3$/BiVO$_4$ samples in comparison to that of pristine BiVO$_4$ and In$_2$S$_3$ under visible light irradiation. Commercial Degussa P25 was used for a comparative efficiency study of In$_2$S$_3$/BiVO$_4$ Degradation of O-TCH was found to be negligible and minimal without any catalyst and in the presence of P25 (Figure 8a). The In$_2$S$_3$/BiVO$_4$ n–n isotype heterojunction was found to accomplish about 94.6% of O-TCH degradation in 120 min, achieving 1.79- and 1.36-fold efficiencies than that of pristine BiVO$_4$ (52.7%) and In$_2$S$_3$ (69.5%), respectively. A pseudo-first-order kinetic model was used to obtain the tentative results to better understand the reaction kinetics (Figure 8b,c). Following the
degradation efficiencies, the rate constant of the In$_2$S$_3$/BiVO$_4$ (0.0243 min$^{-1}$) n–n isotype heterojunction was found to be 5 and 7 times higher than that of pristine BiVO$_4$ (0.0062 min$^{-1}$) and In$_2$S$_3$ (0.0098 min$^{-1}$), respectively (Figure 8d). An elevated photocatalytic efficiency of In$_2$S$_3$/BiVO$_4$ can be ascribed to the superior interfacial compatibility between BiVO$_4$ and In$_2$S$_3$ in the formed n–n isotype heterojunction,
resulting in effective exciton separation and better availability of electron–hole pairs to carry out the degradation process.

Furthermore, the photocatalytic reusability study suggests the higher stability of the In$_2$S$_3$/BiVO$_4$ catalyst (Figure 9a). A negligible decay (1.82%) in degradation efficiency after the fourth cycle is attributed to the inescapable loss of the In$_2$S$_3$/BiVO$_4$ catalyst throughout the periodic recuperation process performed after each cycle and also because of wear and tear of the catalyst surface. PXRD analysis of the sample after the fifth cycle shows a well-preserved crystal structure with a negligible decrease in intensity (Figure 9b), which further establishes the superior stability of the isotype hybrid.

Extending the research further, involvements of possible active radicals in the photocatalytic degradation reaction were investigated by introducing various trapping agents. In detail, p-benzoquinone (p-BQ), methanol (MEOH), isopropanol (IPA), and dimethyl sulfoxide (DMSO) were, respectively, used as $\cdot$O$_2^-$, h$^+$, $\cdot$OH, and e$^-$ scavengers. A superoxide radical was found to be an active suppressing agent for the degradation process with a decrease in degradation efficiency from 94.6% without the trapping agent to 24% with p-BQ.
A drastic decrease in UV−vis absorption intensity shows an obvious superior transformation of nitroblue tetrazolium chloride (NBT) by the excess $^{\cdot}\text{O}_2^-$ produced (Figure 9d). Furthermore, introduction of MEOH, IPA, and DMSO leads to a decrease in degradation efficiency, that is, 57, 76, and 37%, respectively, confirming the involvement of $^{\cdot}\text{O}_2^-$, $^{\cdot}\text{e}^-$, and $^{\cdot}\text{h}^+$ as active species instead of $^{\cdot}\text{OH}$ in the visible-light-promoted O-TCH degradation over the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction. This is in agreement with the electronic band structures of BiVO$_4$ and In$_2$S$_3$ as confirmed by the MS plots.

Moreover, the photocatalytic water oxidation efficiency of the n−n isotype heterojunction was premediated by oxygen evolution reaction in the presence of the sacrificial reagent AgNO$_3$. Perceptibly, the In$_2$S$_3$/BiVO$_4$ heterojunction shows a higher rate of oxygen evolution (695.7 μmol) as compared to pristine BiVO$_4$ (436.4 μmol) and In$_2$S$_3$ (312.2 μmol) in 120 min of visible light irradiation (Figure 10a). The recyclability investigation was also carried out to ascertain better stability of the heterojunction toward oxygen evolution reaction. As shown in Figure 10b, the heterojunction exhibits significant steadiness up to four consecutive cycles (such as C1, C2, C3, and C4) with minor alterations in the $\text{O}_2$ generation rate. The insignificant interlude after the third cycle was ascribed to the formation of a metallic silver cluster because of Ag$^+$ photoreduction on the surface of the catalyst that interrupts the visible light penetration.

To reveal the mechanistic pathway of initiation, separation, transfer, and recombination of the photogenerated charge carriers, the PL study of the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction was carried out carefully in comparison to those of pristine BiVO$_4$ and In$_2$S$_3$ ($\lambda_{\text{ex}} = 325$, rt). An elevated PL intensity suggests an elevated recombination rate of the photogenerated charge carriers, resulting in lower photocatalytic efficiency and vice versa. As shown in Figure 11a, the pure BiVO$_4$ shows a broad absorption peak centered at 538 nm corresponding to the band gap emission. In contrast, a negligible emission intensity of the fractional value compared to that of pristine BiVO$_4$ and In$_2$S$_3$ ($\lambda_{\text{ex}} = 325$, rt) was shown by In$_2$S$_3$/BiVO$_4$ at an identical spectrometric circumstance signifying an obvious decline in the recombination rate of the photogenerated charge pairs in the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction. The PL quenching was perceptibly ascribed to prior injection of the photoexcited electrons from In$_2$S$_3$ to BiVO$_4$, resulting in an enhancement in the spatial charge separation and the lifetime of the photogenerated charge.
 carriers. The finding was further established by the photoelectrochemical measurements.

In order to explore more about the migration and separation of the photogenerated charge carriers, the fabricated samples were investigated by implementing the EIS study under the zero applied potential. As presented in Figure 11b, the Nyquist impedance (EIS) spectra of all the fabricated samples represent characteristic plots of the single semicircular nature. This further corroborates the occurrence of charge-transfer processes in the prepared samples and more importantly indicates that the transfer process is effective in the designed n−n isotype composite.20

The semicircular arc with higher frequency is attributable to the interfacial charge-transfer process, while a smaller arc radius of the material in EIS spectra represents the lower interfacial charge-transfer resistance ($R_{\text{CT}}$) value, thus indicating a faster charge-transfer mechanism and vice versa.46,49 As shown in the impedance plot, the semicircular Nyquist plot of the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction shows a noticeably diminished arc diameter as compared to those of the pure BiVO$_4$ and In$_2$S$_3$ samples under visible light illumination. This authenticates the charge-transfer process via the internal electric field, thus significantly enhancing the antirecombination rate of the photogenerated charge carriers and substantially increasing the conductivity and photocurrent density.50 An analogous Randle circuit model was created by fitting the obtained EIS plot to quantify the impedance results (Figure 11b, inset). Here, (i) $R_S$ represents the solution resistance, (ii) $R_{\text{CT1}}$ and $R_{\text{CT2}}$ represent electrode−electrolyte and the In$_2$S$_3$/BiVO$_4$ heterojunction interface charge-transfer resistance, respectively, and (iii) $Q_{\text{CE1}}$ and $Q_{\text{CE2}}$ represent constant phase elements of the electrode−electrolyte interface and the In$_2$S$_3$/BiVO$_4$ heterojunction interface, respectively.20

In detail, the measured $R_{\text{CT1}}$ values of the fitted Nyquist curves of BiVO$_4$, In$_2$S$_3$, and In$_2$S$_3$/BiVO$_4$ were found to be 11,540, 2085, and 2071 $\Omega$ cm$^{-2}$, respectively. A drastic decrease in $R_{\text{CT1}}$ value confirms the significant improvement in the charge-transfer process in the electrode−electrolyte interface after formation of an In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction. Further, the measured $R_{\text{CT2}}$ values of BiVO$_4$, In$_2$S$_3$, and In$_2$S$_3$/BiVO$_4$ were found to be 1116, 2603, and 872 $\Omega$ cm$^{-2}$, respectively. The drastic decrease in the charge-transfer resistance value of the In$_2$S$_3$/BiVO$_4$ heterojunction interface justifies a drastic improvement in the interfacial charge-transfer process. This favors faster reaction kinetics and enhanced photocatalytic activity, which defines that architecting a vertical In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction leads to an increase in the interface to volume ratio as compared to individual BiVO$_4$ and In$_2$S$_3$, significantly improving the charge transfer from bulk to the catalyst surface and improving the charge antirecombination process, leading to a longer electron lifetime.51

This further was established by electrochemical Bode phase analysis of the catalysts (Figure 11c). The characteristic Bode frequency peak of In$_2$S$_3$/BiVO$_4$ underwent a negative shift toward the lower frequency value as compared to the pristine BiVO$_4$ and In$_2$S$_3$ catalyst. This concludes that the relatively fast charge-transfer process leads to an enhanced injected electron lifetime in the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction as the Bode frequency ($f$) is inversely proportional to the electron lifetime.20 Further, the injected electron lifetime was quantitatively elucidated by eq 3

$$\tau_e = 1/(2\pi f_{\text{max}}^2)$$

where $\tau_e$ represents the injected electron lifetime and $f_{\text{max}}$ is the frequency of the Bode peak in agreement with the lowermost frequency value. The Bode phase of In$_2$S$_3$/BiVO$_4$ was found to give an electron lifetime of 0.44 ms, which is about 1.76 and 1.46 times higher than that of pristine BiVO$_4$ (0.25 ms) and In$_2$S$_3$ (0.3 ms), respectively. The result shows that the architected In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction boosts the fast charge-transfer process because of the synergistic effect of the n−n junction, thus enhancing the photocatalytic efficiency.

Generation and separation dynamics of the charge carrier in the interface of the In$_2$S$_3$/BiVO$_4$ n−n junction was revealed by evaluating the transient current intensity under the illumination of chopped light. The resultant photocurrent−time (I−t) curves (Figure 11d) show a relatively higher transient intensity of the In$_2$S$_3$/BiVO$_4$ n−n heterojunction compared to those of the bare pristine BiVO$_4$ and In$_2$S$_3$ for each light on−off cycle. This signifies that the construction of an In$_2$S$_3$/BiVO$_4$ n−n heterojunction drastically enhances the surface charge antirecombination process, which is in accordance with the EIS and PL study.52,53

Furthermore, to better validate the aforementioned merits about enhanced charge migration upon the introduction of In$_2$S$_3$ to form an n−n isotype heterojunction, MS plots were elaborated to estimate charge carrier densities of the catalysts, as the carrier density of a catalyst electrode has an inverse relationship with the slope of the linear part of the MS plots.54 Evidently, the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction showing a relatively smaller slope exhibits a higher carrier density as compared to pristine BiVO$_4$ and In$_2$S$_3$ solely (Figure

![Figure 12. Carrier density comparison study of In$_2$S$_3$/BiVO$_4$ with (a) BiVO$_4$ and (b) In$_2$S$_3$.](https://dx.doi.org/10.1021/acsomega.9b04323)
12a,b). Quantitative evaluation of the charge carrier densities ($N_d$) of the electrode materials can be made by

$$N_d = \left(\frac{2}{ee_0}\right)\left(\frac{d(1/C^2)}{dV}\right)^{-1}$$

where "e" symbolizes the electronic charge unit ($1.602 \times 10^{-19}$ C), "$e_0$" symbolizes the dielectric constant of the electrode material, "$\varepsilon_0$" symbolizes the permittivity of vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$), "C" symbolizes the capacitance, and "V" symbolizes the applied electrode potential. Moreover, the increased charge carrier density will result in an increase in electrical conductivity ($\sigma$) of the In$_2$S$_3$/BiVO$_4$ n–n isotype heterojunction proving

$$\sigma = e\mu$$

where "e" symbolizes the electronic charge unit ($1.602 \times 10^{-19}$ C), "$\mu$" symbolizes charge carrier’s concentration, and "$\mu$" symbolizes the charge carrier mobility. The increased conductivity greatly favors in improving the charge transport and separation processes, thus increasing the photocurrent density. This is in accordance with the LSV study.

The photoelectrochemical outcomes show the higher photocurrent density of the In$_2$S$_3$/BiVO$_4$ n–n heterojunction reflected on the characteristic linear sweep voltammograms (Figure 13a,b). The variation of photocurrent ($I$) with change in applied potential ($V$) was observed both in the dark and under visible light irradiation. No noticeable current was observed in the dark; conversely, under light illumination, the gradually increasing photocurrent was visualized for all the three nanocatalysts ascribed to the generation and separation of charge carriers over the semiconductor when the electrode materials absorb light energy beyond the band gap energy value. An initiation of photocurrents at $-0.49$, $-0.59$, and $-0.42$ V for BiVO$_4$, In$_2$S$_3$, and In$_2$S$_3$/BiVO$_4$, respectively, and the persistent increasing nature with increased applied potential attest the fact that charge separation occurs in all the three catalysts under visible light irradiation; however, the saturation level is significantly lower in the n–n heterojunction compared to that in the pristine phases. Promoted by interfacial fast charge transfer, the In$_2$S$_3$/BiVO$_4$ n–n isotype heterojunction showed a higher photocurrent density of 269 $\mu$A/cm$^2$ at a potential of +1 V under visible light illumination, which is about 2.27 and 1.65 times higher than those of the pure BiVO$_4$ (119 $\mu$A/cm$^2$) and In$_2$S$_3$ (164 $\mu$A/cm$^2$), respectively. This further shows the higher efficiency of the n–n isotype heterojunction toward O-TCH degradation and water oxidation reaction under the illumination of visible light.

Additionally, the photocurrent durability of the In$_2$S$_3$/BiVO$_4$ n–n isotype heterojunction catalyst was observed by the CA.
study (Figure 13c). The characteristic $I-t$ plot obtained for In$_2$S$_3$/BiVO$_4$ shows better stability in photocurrent generation. Quantitatively, the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction shows a photocurrent of 13.16 μA, initially followed by a decay of 23%, that is, 10.7 μA for few seconds and remained constant for 600 s. Conversely, the pristine BiVO$_4$ underwent a decay of 36% from 9.7 to 7.15 μA, and in In$_2$S$_3$, the current value reduces to 32% from 11.62 to 8.81 μA for few seconds and then remained constant for 600 s. The result shows that the higher photoelectrochemical activity of the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction is attributable to the lower charge-transfer resistance value and higher electron lifetime. This is ascribed to the intimate interfacial contact between the n−n isotype junctions, leading to efficient charge transfer. This indicates a superior stability of n−n isotype heterojunctions toward the photocatalytic process contributable to the actual alteration of the texture, optical, electronic, and photoelectrochemical properties of unadulterated materials in the heterojunction.

In addition, band-edge potentials of pristine BiVO$_4$ and In$_2$S$_3$ were calculated by MS analysis to evaluate the probable band configuration in the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction. Positive slopes in the MS plot (Figure 14a,b) confirm the n-type characteristics of both BiVO$_4$ and In$_2$S$_3$. By extrapolating the space charge capacitance (C$^{-2}$) value to 0, the flat band potential ($E_b$) values are calculated to be −0.69 and −1.33 V versus Ag/AgCl for BiVO$_4$ and In$_2$S$_3$, respectively. As the flat band potential of the n-type material gives the approximate values of the CB position, the CB values are calculated to be −0.12 and −0.77 eV at the normal hydrogen electrode (NHE) for BiVO$_4$ and In$_2$S$_3$, respectively. Considering this, the VB positions of BiVO$_4$ and In$_2$S$_3$ are calculated by eq 6

$$E_{CB} = E_{VB} - E_g$$

where $E_{CB}$, $E_{VB}$, and $E_g$ represent the CB position, VB position, and band gap value (obtained from UV−vis DRS analysis), respectively. Consequently, the VB positions of BiVO$_4$ and In$_2$S$_3$ are found to be 2.24 and 1.45 eV at NHE, respectively. It is a fact that the authentic band gap configuration of BiVO$_4$ and In$_2$S$_3$ in the In$_2$S$_3$/BiVO$_4$ n−n hybrid will diverge from the above-mentioned assumption. Despite that, the intimate interfacial contact and different flat band potentials of BiVO$_4$ and In$_2$S$_3$ in In$_2$S$_3$/BiVO$_4$ can lead to the formation of a built-in electric field in the heterojunction interface, favoring a rapid migration and superior separation of the photoinduced charge carriers.

In general, the Fermi level of the n-type semiconductor is closer to the CB minimum and nearly 0.2 eV lower than the bottom potential. Considering the above-mentioned data, a schematic diagram of the band configuration is presented in Scheme 2, and a probable mechanistic pathway was projected to better explain the (i) transportation and separation of charge carriers, (ii) photocatalytic degradation of O-TCH, and (iii) photocatalytic water oxidation reaction over the In$_2$S$_3$/BiVO$_4$ n−n isotype heterojunction interface under visible light illumination. In the dark, with a Fermi level at more negative potential, electrons will be injected from the CB of In$_2$S$_3$ to the CB of BiVO$_4$ until equilibrium is reached (equalized Fermi level $E_{F1} = E_{F2} = E_{F0}$). This transfer process would lead to a built-in electric field across the heterojunction interface, facilitating a faster migration and separation of the photoinduced charge carriers.
causes the formation of a depletion layer (positive region) and accumulation layer (negative region) on In$_2$S$_3$ and BiVO$_4$, respectively. Such a phenomenon promotes the development of a built-in electric field around the junction area with the field directed from In$_2$S$_3$ to BiVO$_4$ (Scheme 2b). Under visible light irradiation, the built-in field promotes the electron flow from BiVO$_4$ toward In$_2$S$_3$; however, because of the higher negative potential of the CB of In$_2$S$_3$, the migration of electrons is restricted and under the same conditions photoelectrons start moving to the CB of BiVO$_4$ from In$_2$S$_3$, causing the accumulation of more photoexcited electrons over the n–n isotype heterojunction interface. Further, the photoexcited electrons over the CB interface of In$_2$S$_3$/BiVO$_4$ being at a more negative reduction potential than O$_2$/$\text{O}_2^-$ ($-0.046$ eV) reduce the dissolved O$_2$ in the aqueous solution to highly active $\cdot \text{O}_2^-$ species. Furthermore, the uninterrupted photoinduced holes in the VB of BiVO$_4$ (+2.24 eV) rapidly migrates to the VB of In$_2$S$_3$. Considering the trapping experimentation and preceding reports, the active species responsible for O-$\cdot$ formation of an n–n isotype heterojunction of the In$_2$S$_3$/BiVO$_4$ hybrid with superior photocatalytic activity was fabricated through a simple two-step calcination process, followed by a wet-chemical deposition technique. This process causes In$_2$S$_3$ to form an intimate interface contact with BiVO$_4$. The resultant heterojunction produced an enhanced photocatalytic activity and photostability toward O-TCH degradation and water oxidation reaction, compared to pristine components under visible light illumination. The high photocatalytic activity of the n–n isotype heterojunction was attributable to the simultaneous effect of a superior intimate interface contact between the two components and a superior visible light absorption ability of the sample, leading to an increased effectual separation and migration of photoexcitons. Thus, the formation of an n–n isotype heterojunction through the coupling of In$_2$S$_3$ with BiVO$_4$ interprets a superlative opportunity to develop a proficient photocatalyst for energy and environmental remediation.

4. CONCLUSIONS

An n–n isotype heterojunction of the In$_2$S$_3$/BiVO$_4$ hybrid with superior photocatalytic efficiency was fabricated through a simple two-step calcination process, followed by a wet-chemical deposition technique. This process causes In$_2$S$_3$ to form an intimate interface contact with BiVO$_4$. The resultant heterojunction produced an enhanced photocatalytic activity and photostability toward O-TCH degradation and water oxidation reaction, compared to pristine components under visible light illumination. The high photocatalytic activity of the n–n isotype heterojunction was attributable to the simultaneous effect of a superior intimate interface contact between the two components and a superior visible light absorption ability of the sample, leading to an increased effectual separation and migration of photoexcitons. Thus, the formation of an n–n isotype heterojunction through the coupling of In$_2$S$_3$ with BiVO$_4$ interprets a superlative opportunity to develop a proficient photocatalyst for energy and environmental remediation.

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