

Article

Fabrication and Photoelectrochemical Activity of In_2S_3 Infused TiO_2 Nanorod Heterostructure Photoelectrodes for Solar Water Splitting

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Abstract

Titanium dioxide (TiO_2) and indium sulfide (In_2S_3) combined nanoarray films, fabricated via the hydrothermal and chemical bath deposition (CBD) methods, were employed as photoelectrocatalysts for water splitting applications through the photoelectrochemical (PEC) process. The resulting heterostructure nanoarray catalyst morphology, composition, and optical absorption have been analyzed. The photon illumination and its effect on the electrochemical impedance and photocurrent generation measurements exposed that the infusion of In_2S_3 on the TiO_2 films comprehensively reduced the charge carrier transport resistance ($700 \text{ Ohm}\cdot\text{cm}^2$) and enhanced the photocurrent ($0.28 \text{ mA}/\text{cm}^2$) with an increment of photo potential response (-1.02 V vs. Ag/AgCl). Further, the heterostructure films effectively degrade the organic molecules in the electrolyte under UV light illumination. The enhanced catalytic reaction is ascribed to the role of In_2S_3 deposition on the TiO_2 , which effectively improves the charge carrier collection at the surface by In_2S_3 and promotes the dissociation of organic molecules at the interface.

Keywords: photo anodes; photoelectrochemical; water splitting; semiconductor; heterostructure

1. Introduction

Electrochemical hydrogen evolution as a renewable source is the appropriate method to obtain green energy gas due to high gravimetric energy density ($120 \text{ MJ}/\text{kg}$) [1]. Compared with other methods, the photo(electro)catalytic method provides water splitting into hydrogen in an unpretentious technique to meet urgent energy and environmental requirements [1–3]. However, deficient surface reaction sites and photogenerated electron–hole pairs from the semiconductor generate a lower volume of hydrogen [4,5]. The surface and electronic states of semiconductor photoelectrocatalyst development need to play pivotal roles in addressing these challenges.

Recently, heterostructure photo electrocatalysts have provided great advantages in photon-irradiated electron–hole pair separation and conduction due to the in-built electric field development under illumination with favorable band edges [6–8]. Under photoirradiation, the photoexcited electron and hole carriers transport confirm light-induced carriers in the semiconductors that enable photocatalytic redox reaction for hydrogen evolution [9–11]. In a single material semiconductor interface, the surface recombination occurrence is higher during the redox reaction [12–15]. For this, a staggered heterostructure photocatalyst is



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used to increase the successful transfer of the carriers [16,17]. The carrier's dynamics of the photo absorptive materials at the top of the layer with a suitable band edge favor the hydrogen evolution reaction [18]. Hence, integrating a heterostructure photo electrocatalyst with a wideband gap base layer as the electron collector could effectively induce the carrier's recombination [19]. Likewise, the photoexcited holes from the oxidative layer rapidly transfer to the electrochemical cell for the water splitting reaction [20]. The separation of photo-irradiated electrons and holes strongly develops the internal built-in field in the photoanode [21].

Metal sulfides are considered promising photocatalysts for water splitting applications owing to designable heterostructures, suitable energy band gaps, and superior photoelectric characteristics [22–24]. Among the diverse metal sulfide materials, indium sulfide (In_2S_3) stands out as a highly promising, chemically stable, and low-toxicity rare-earth molecular compound for water splitting applications [25,26]. Its band gap energy, typically ranging from 1.9 to 2.4 eV, is particularly suitable as it enhances visible light absorption [27–30]. The micromorphological In_2S_3 and its heterostructures with TiO_2 , ZnO , WO_3 , In_2O_3 , Fe_2O_3 , CuO , and NiO metal oxides effectively increase light-induced photocurrent densities from $0.1 \mu\text{A}/\text{cm}^2$ to $1 \text{ mA}/\text{cm}^2$ [31]. The dimensionally modulated nanostructure of In_2S_3 effectively increases the catalytic reaction in the water oxidation reaction [32]. To enhance catalytic efficiency by improving the surface area, various nanostructures, including nanorods, nanospheres, and nanosheet morphologies have been achieved using diverse wet-chemical and energy-assisted synthetic techniques, such as microwave irradiation, sonochemical, and hydrothermal/solvothermal methods [33–35]. Also, the combination of metal oxide with In_2S_3 has been widely studied as a photoelectrocatalyst for renewable [29] and optoelectronic applications [30], including photoanode devices [36]. The metal oxide layers with 1D nano-surface morphology, grown by hydrothermal and CVD techniques, are used to improve the surface area of In_2S_3 [37–39]. The metal oxide layer holds good stability and forms heterojunctions with In_2S_3 [40].

To reduce recombination, the TiO_2 nanoarrays passivated with various nanoparticles with metal sulfide heterostructures are a recent, facile technique inherited by modern researchers [41,42]. The In_2S_3 nanoparticles on TiO_2 nanorods enhance the photoinduced charge carrier separation to 0.2 mAcm^{-2} [43]. In addition, the metal sulfides' heterostructure has been made to absorb more photons in the visible range than TiO_2 , which absorbs mostly UV photons. The narrow band gap metal sulfides (CdS , CdSe , CuS , ZnS) strongly make a heterostructure with TiO_2 and improve the inbuilt potential based on the band edge, which decides the reaction type in the heterostructure materials. However, the heterostructure of TiO_2 with CdS , ZnSe , CdSe , PbS , ZnS reported a reasonably good performance and exhibited good electrochemical properties [44–48]. The photo corrosion effect is inevitable in the metal sulfide photo catalysts; however, In_2S_3 strongly holds the stability against photo-corrosion due to the ternary sulfide phase and charge carrier flow by a type II heterostructure [34,35].

In the present work, we examined the TiO_2 and In_2S_3 heterostructure photoelectrode for PEC water splitting applications. The nanoarray morphology and passivation of In_2S_3 particles around TiO_2 nanorods have been established by a two-step synthesis method. The photoelectrocatalytic water-splitting capabilities of $\text{TiO}_2/\text{In}_2\text{S}_3$ have been examined. The photocurrent densities, charge carrier transport mechanisms, environment remediation, solar energy to hydrogen conversion, and applied bias-based photon-to-electron conversion have been analyzed. The resulting $\text{TiO}_2/\text{In}_2\text{S}_3$ nanoarrays exhibit a convenient, simple fabrication process and are highly efficient for water splitting abilities and hydrogen evolution applications.

2. Experimental Methods

2.1. Materials

The chemicals are analytical reagent grades, which have been used without further processing. The titanium isopropoxide (TIP, 98%, Daejung, Daejeon, Republic of Korea), concentrated HCl (35.46%, Daejung, Daejeon, South Korea extra pure), InCl_3 (98%, Sigma-Aldrich, St. Louis, MO, USA), citric acid, and thioacetamide (Daejung, extra pure, Daejeon, Republic of Korea). The chemical solutions were prepared using deionized water. The F: SnO_2 deposited glass slides were used as a substrate. Initially, the substrates were ultrasonically cleaned according to the standard cleaning procedure. The F: SnO_2 deposited glass slides ($\sim 7 \Omega/\text{cm}$, $1 \text{ cm} \times 1.5 \text{ cm} \times 2 \text{ mm}$) were used as substrates for all photoelectrochemical measurements and dye degradation experiments.

2.2. Preparation of TiO_2 Photoanodes

In the growth experiment (Figure 1), the precursor solution was formulated by combining titanium alkoxides in aqueous media with warm water, utilizing concentrated HCl as a hydrolysis catalyst for hydrothermal growth. The hydrochloric acid was dropped into the solution as a catalyst, and the pH of the solution was adjusted to a strong acidic nature. Hydrochloric acid plays a role in the hydrolysis (Equations (1) and (2)) of the precursor and lowers the surface kinetic energy of the TiO_2 growth plane and side wall, promoting the one-dimensional growth on the FTO. The hydrothermal reaction is as follows at 180°C for 6 h.

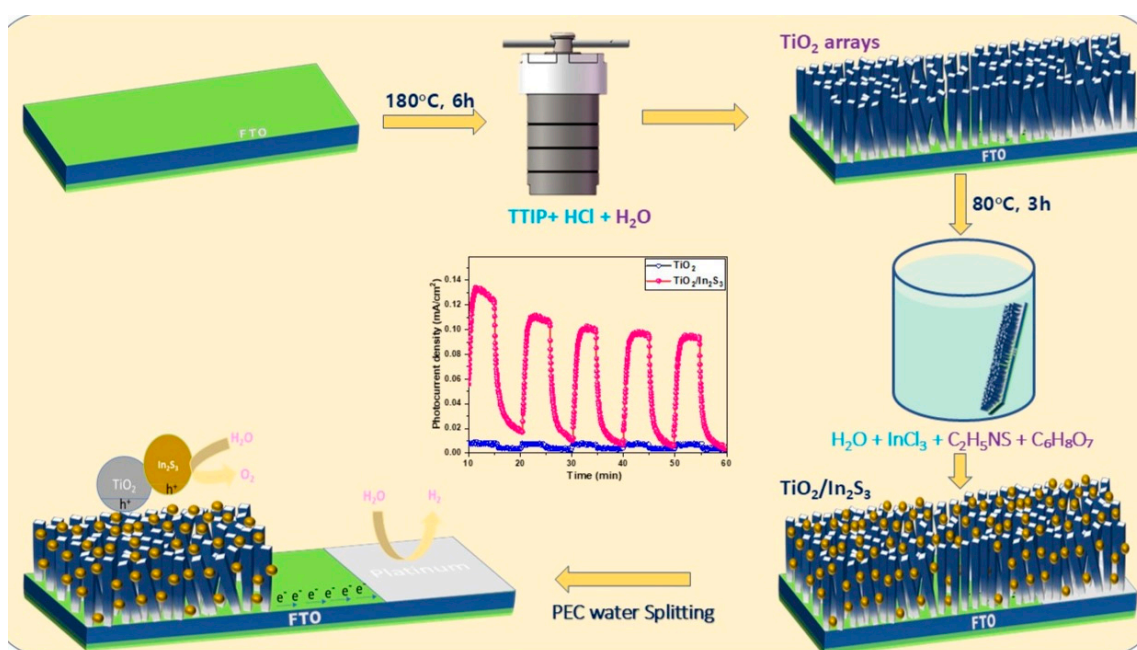
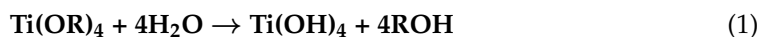


Figure 1. Schematic diagram of growth and PEC water splitting of $\text{TiO}_2/\text{In}_2\text{S}_3$ photoanode.

2.3. Preparation of In_2S_3 Infused TiO_2 Photoanodes

In_2S_3 nanoparticles were deposited on the TiO_2 nanorods using a simple chemical bath deposition (CBD) process. In a typical growth process, 0.01 M of indium chloride, 240 mg of thioacetamide, and 480 mg of citric acid monohydrate were dissolved in 20 mL of water. The dissolved solutions have been added and stirred vigorously for 15 min at room temperature. The resultant clear solution was then transferred to a constant temperature

bath at 80 °C. The synthesized TiO₂ nanorods have been immersed in the solution to deposit the In₂S₃ on the nanorods. The reaction has been carried out for 3 h and cooled naturally to room temperature. The deposited orange-yellow colored In₂S₃ photoanode was washed several times with ethanol and dipped in deionized water to eliminate the unreacted constituents from the nanorod surface of the photoanode and annealed at 150 °C for 3 h.

2.4. Preparation and Characterization of Photoanodes

The surface view of TiO₂ and In₂S₃-infused TiO₂ was examined by field emission scanning electron microscopy (FESEM, Carl Zeiss and Oxford instruments, Gyeongsan. The crystalline structures of the prepared photoanode were identified using an X-ray diffractometer (XRD, Pan Analytical Pro, Gyeongsan, Republic of Korea) with Cu K α radiation ($\lambda = 0.15406$ nm), and the acceleration voltage and the applied current were 40 kV and 40 mA, respectively. X-ray photoelectron spectroscopy (XPS, Gyeongsan) was performed on a K-alpha, Thermo Scientific, USA, using Al K α as the X-ray source (1486.6 eV). Photoluminescence (PL) spectra were obtained by a Horiba spectrometer-Japan, (Gyeongsan) with an excitation source of a He-Cd laser (325 nm).

2.5. Photoelectrochemical Measurements

Photoelectrochemical analyses were performed using a 0.1 M Na₂SO₃ electrolyte solution in the Corr test electrochemical workstation. The three-electrode system of TiO₂ and In₂S₃/TiO₂ photoanode as the working electrode, Pt plate as the counter electrode, and an Ag/AgCl as the reference electrode was used. A xenon lamp (Oriel LCS, Republic of Korea) is used for a solar light source with a UV cut-off filter. Electrochemical impedance spectra (EIS) were recorded at a 0.1 V potential in the 10 Hz to 10 K Hz band frequencies. The photocurrent output was recorded for the bias potential of −0.95 to 0.2 V with a sweeping voltage of 20 mV.

2.6. PEC Degradation Experiments

The dye degradation experiments were tested using a photoanode. In an unbiased condition, the working electrode and electrolyte solution with organic dye molecules have been maintained in a neutral condition (pH = 7). The PEC reactions of the photoactive working electrode were assessed by the dissociation of rhodamine B concentration. In a characteristic process, the photoelectrode was kept in an apparatus comprising the dye solution, ensuring dye adsorption/desorption by the photoelectrode. At intervals of time, the degraded dye samplings have been visibly ensured.

3. Results and Discussion

3.1. UV–Visible Light Absorption

Figure 2 shows the results of analyzing the TiO₂ and TiO₂/In₂S₃ photoanodes' UV–vis absorption spectra, which reveal their visible light absorption characteristics. The TiO₂ photoanode displays stronger UV light absorption, and In₂S₃-infused TiO₂ increases the light absorption capabilities more than TiO₂. After In₂S₃ is infused in TiO₂, the heterostructure photoanode exhibits better optical properties with an extended reduction in the reflectivity, and the absorption edge increases to 500 nm. The vertical TiO₂ nanorods allow the incident light to reflect several times between the nanorods clearly explained the advantages of nanorods structure. More photons are absorbed by the semiconductor and produce more photo excitons in the photoanode.

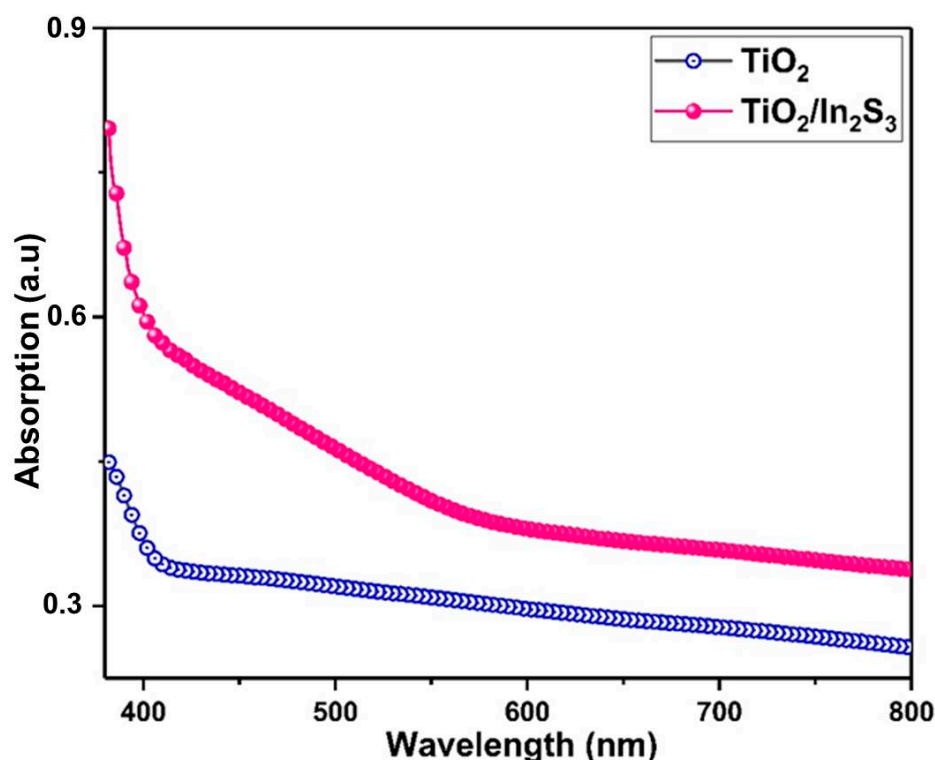


Figure 2. UV-visible light absorption spectrum of the TiO_2 and $\text{TiO}_2/\text{In}_2\text{S}_3$.

3.2. Morphology Characterization

To analyze the surface texture, field emission scanning electron microscope (FESEM) analyses were performed for the TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ (Figure 3). From Figure 3a, it is assessed that the TiO_2 surface morphology has a nanorod shape structure, which is consistent with the previous reports [49,50]. The typical nanorod image (Figure 3a) states that the diameter of the rods is approximately 150 nm and the length of the nanorod is approximately 1 μm , which is evidence that the growth of TiO_2 has a large surface area. The nanorod morphology of the TiO_2 substantially interacts with the dye molecules as physisorption and admits to dissociation through photo-electro catalytic reactions [51]. In contrast, with the addition of In_2S_3 , more void structures have been introduced at the surface (Figure 3b). TiO_2 nanorods expose top and sidewall facets clearly. A surface-view SEM image (Figure 3b) reveals the actual surface morphology of pure TiO_2 nanorod array films. From Figure 3b, the In_2S_3 particles are spread on the TiO_2 nanorods uniformly and cover the entire TiO_2 surface.

The high magnification HRTEM images of $\text{TiO}_2/\text{In}_2\text{S}_3$ nanoarray reveal that the interface of the semiconductors is a heterostructure formation (Figure 3c–h). The higher magnification, shown in Figure 3f, reveals well-defined and clear lattice fringes for the {101} planes of TiO_2 nanorods with a d-spacing of 0.35 nm, which is in excellent agreement with the tetragonal anatase phase of TiO_2 [45,46]. Similarly, from the HRTEM image (Figure 3h), the In_2S_3 particle on the TiO_2 nanorods exhibits the fringe pattern for the {311} and {220} planes with the d-spacing of 0.32 and 0.38 nm, respectively. The SAED pattern (Figure 3g) for the $\text{In}_2\text{S}_3/\text{TiO}_2$ heterostructure clearly indicates the crystalline phase of the TiO_2 for the (101) plane and the low crystalline phase for the In_2S_3 nanocrystals. The distinct observation of characteristic lattice fringes for both TiO_2 and In_2S_3 within the morphological region provides direct crystallographic evidence for the formation of a heterostructure, facilitating the efficient charge transfer and enhanced photoelectrochemical performance. The elemental composition and ratio of the $\text{TiO}_2/\text{In}_2\text{S}_3$ nanoarray are confirmed by Energy-Dispersive X-ray Spectroscopy (EDS) spectrum (Figure S1), clearly

showing the presence of all elements, and the calculated atomic weight percentages from EDS were Ti (55.30%), O (37.25%), In (6.20%), and S (1.25%). The quantifiable detection of indium and sulfur confirms the synthesis and integration of the In_2S_3 layer in the TiO_2 nanoarrays.

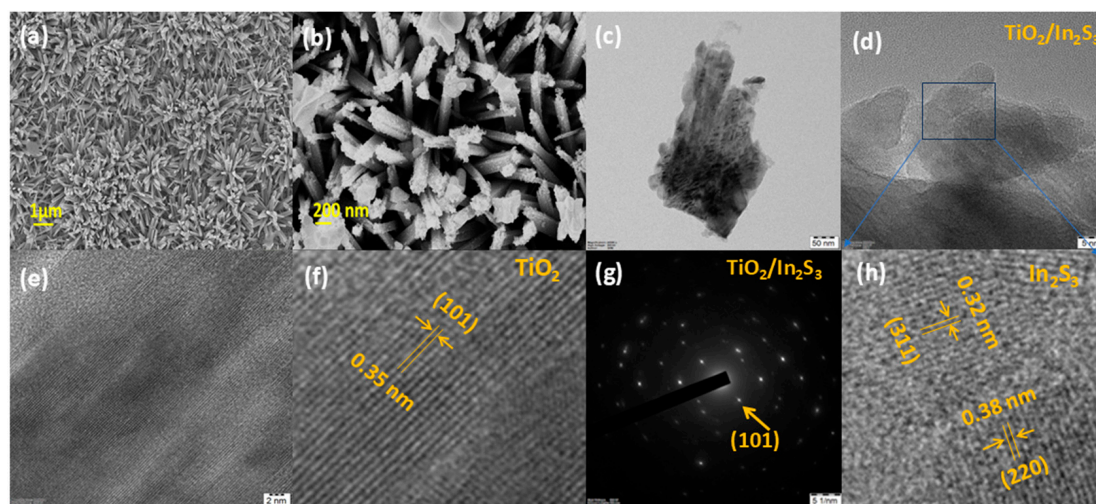


Figure 3. FESEM images of (a) TiO_2 and (b) $\text{TiO}_2/\text{In}_2\text{S}_3$ nano-arrays. (c) TEM images of the $\text{TiO}_2/\text{In}_2\text{S}_3$. (d) HRTEM images of the $\text{TiO}_2/\text{In}_2\text{S}_3$. (e) The fringe pattern of TiO_2 . (e) The low magnification of TiO_2 nano rods. (f) The fringe pattern of (101) plane of TiO_2 nanorods. (g) The selective area electron diffraction pattern of the $\text{TiO}_2/\text{In}_2\text{S}_3$. (h) The magnified view of the fringe pattern of In_2S_3 in $\text{TiO}_2/\text{In}_2\text{S}_3$ heterostructure.

3.3. XRD Analysis

Figure 4 illustrates the XRD pattern corresponding to the as-synthesized TiO_2 nanorods, In_2S_3 , and $\text{TiO}_2/\text{In}_2\text{S}_3$. The heterostructure thin films were confirmed by their respective crystallographic planes. The diffraction peak of TiO_2 nanorod array film comprises the mixed anatase and rutile phases of TiO_2 . The presence of diffraction peaks at 25.31° , 37.83° , 48.02° , 53.95° , and 55.12° is assigned to the (101), (004), (200), (105), and (211) crystal planes of the anatase phase of TiO_2 (JCPDS No. 21-1272). The typical diffraction peaks at 27.42° and 36.12° reveal the (110) and (101) planes in the rutile phase of TiO_2 [52]. The strong peaks at 26.53 , 33.64 , 51.51 , 61.72 , and 65.52 are ascribed to the FTO-coated glass substrates [53], and no diffraction peaks related to the In_2S_3 were observed superficially due to the low concentration of In_2S_3 (0.1 mg), which has been confirmed further by the SAED for the heterostructure films. However, the XRD pattern of the In_2S_3 thin film reveals the diffraction peaks at 23.40° , 27.34° , 32.68° , 33.24° , and 47.72° , which can be indexed to miller indices at (220), (311), (222), (400), (331), and (440) of the JCPDS (00-032-0456), and confirm strong In_2S_3 formation over the chemical bath deposition synthesis [54]. Also, from the diffraction pattern of the $\text{In}_2\text{S}_3/\text{TiO}_2$ film having the asymmetric peak for the (110) plane, which shows strong metal–oxygen influence, the presence of the O-In-S system could be inferred [55,56].

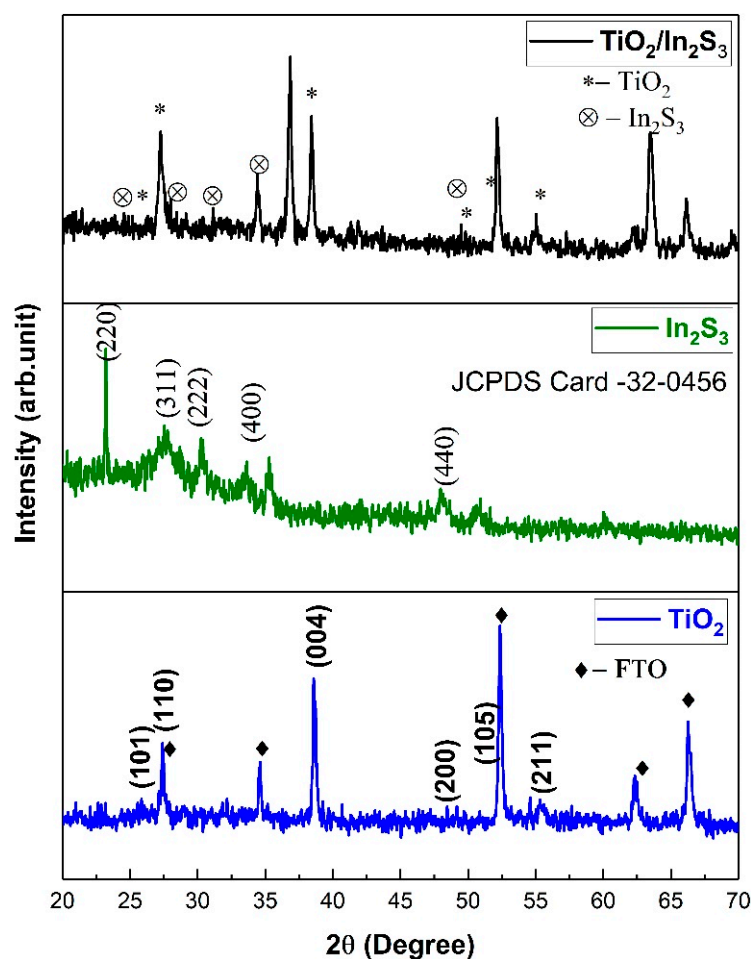


Figure 4. The XRD pattern of TiO_2 , In_2S_3 and $\text{TiO}_2/\text{In}_2\text{S}_3$.

3.4. XPS Analysis

The surface elemental composition of the TiO_2 nanorods and In_2S_3 heterostructure film is studied by the high-resolution XPS spectra that were collected, which are depicted in Figure 5. In Figure 5a, the survey spectra for $\text{TiO}_2/\text{In}_2\text{S}_3$ nanoarray thin films are shown. The TiO_2 layer is confirmed by the binding energies of titanium (Ti 2p) and oxygen (O 1s), while the In_2S_3 heterostructure is formed by sulphur (S 2p) and indium (In 3d). The presence of Sn and F peaks, expected from the fluorine-doped tin oxide (F:SnO_2) substrate, is also confirmed. The XPS peak of C 1s at 285.08 eV is assigned to the carbon residual. From the high-resolution Ti 2p spectrum (Figure 5b), peaks located at 459.58 eV and 465.8 eV are observed to be $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ orbitals of Ti^{4+} [35]. The higher binding energy values of the Ti 2p intimate the tight binding of the heterostructure of $\text{TiO}_2/\text{In}_2\text{S}_3$. Figure 5c shows the XPS spectrum of In 3d with two symmetrical peaks at the binding energies of 444.4 eV for $\text{In } 3d_{5/2}$ and 452.28 eV for $\text{In } 3d_{3/2}$ [35,57]. The S 2p peaks (Figure 5d) at 162.82 and 161.13 eV were defined to $\text{S } 2p_{1/2}$ and $\text{S } 2p_{3/2}$, respectively, which clearly indicates the absence of S-O bonding in the In_2S_3 phase [58,59]. From Figure S2, the O1s peak is assigned at 530.21 to 531.9 eV, which agrees with (Ti–O) lattice oxygen and hydroxyl groups (–OH) [59,60]. From the analysis of XRD, SEM, and XPS, the existence of $\text{In}_2\text{S}_3/\text{TiO}_2$ heterostructures was confirmed.

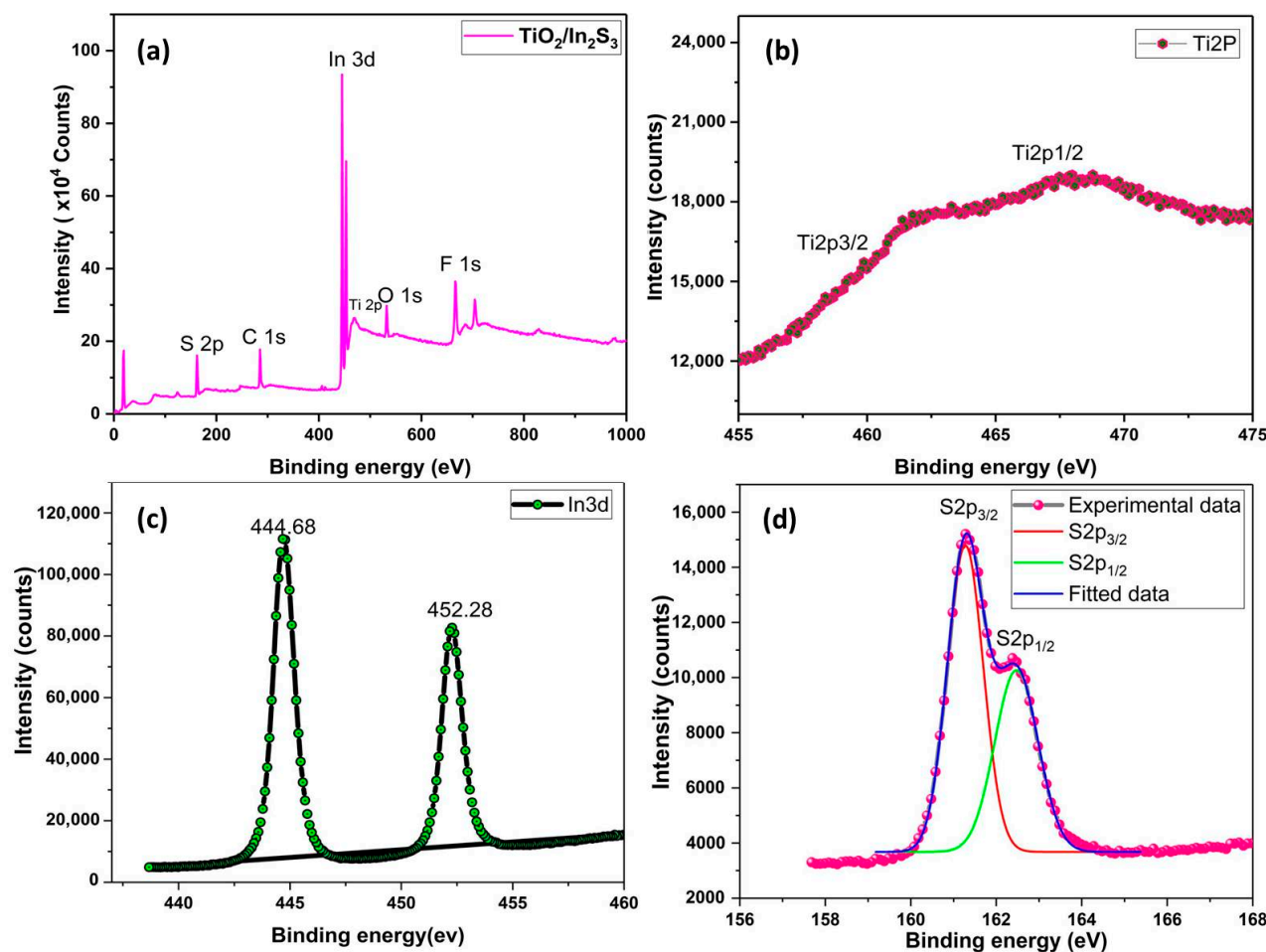


Figure 5. (a) XPS survey scan, (b) Ti 2p, (c) In 3d, and (d) S 2p of $\text{TiO}_2/\text{In}_2\text{S}_3$ heterostructure photoanode.

3.5. PL Spectra Analysis

The photo-induced carriers in excitation and recombination have been measured using photoluminescence spectra (Figure 6a). The electron–hole pairs are produced when the TiO_2 nano-array is excited by near-UV light. The photoexcited electrons from the conduction band of TiO_2 will experience a shift to the valence band, ensuring a low emission intensity [61]. Figure 6a shows the PL spectra of the $\text{TiO}_2/\text{In}_2\text{S}_3$ heterostructure film. Visibly, In_2S_3 displays a substantial effect on the PL intensity, which shows that a greater number of photoexcitations occurred in In_2S_3 . In the case of the $\text{In}_2\text{S}_3/\text{TiO}_2$ heterostructure, photoexcited carriers of In_2S_3 were injected into TiO_2 and inhibited the recombination in the In_2S_3 surface layers. The PL band edge results show a feasible path under photoexcitation. The parting of electron–hole pairs to the redox reaction is enabled by a high number of photoexcited holes compared to the TiO_2 , which enhances the hydrogen evolution for the heterostructure photoanodes ($\text{TiO}_2/\text{In}_2\text{S}_3$).

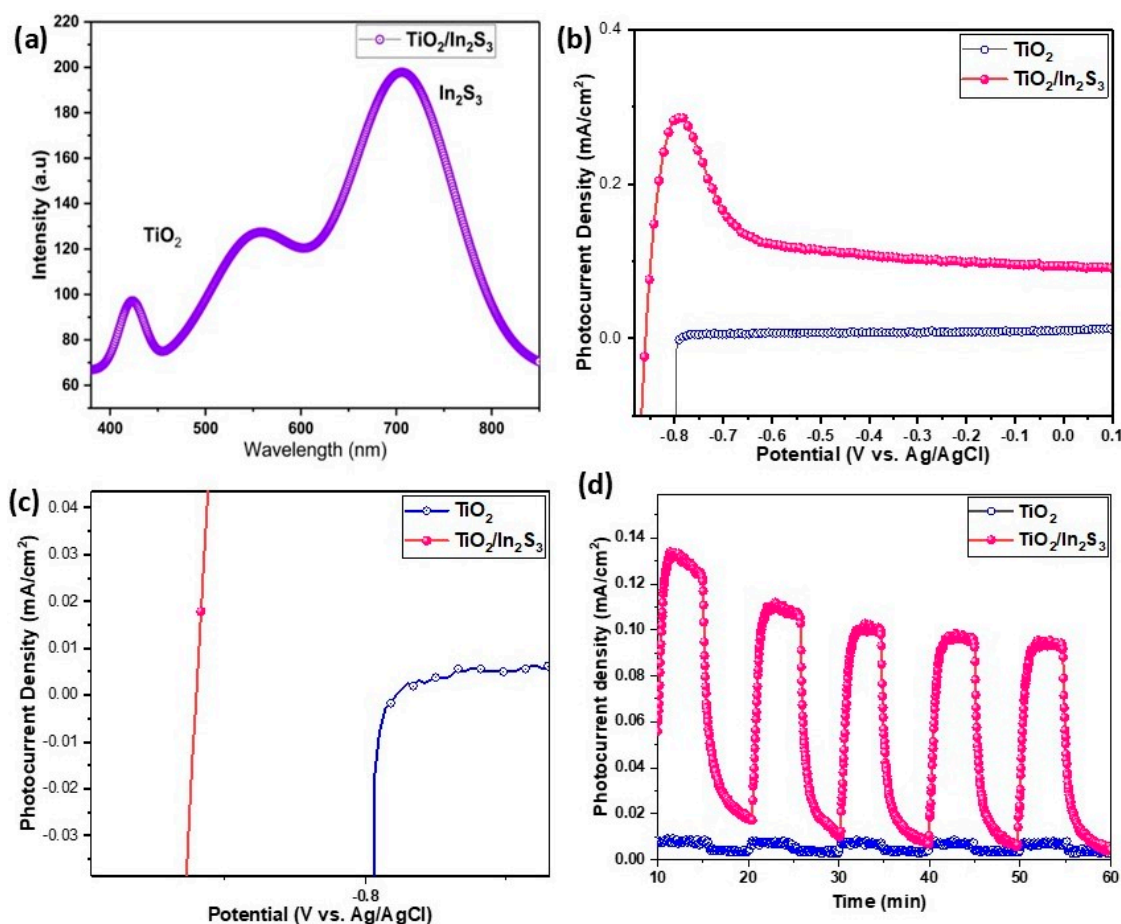


Figure 6. (a) The photoluminescence spectrum of the TiO₂/In₂S₃ photoanode, (b) LSV graph of TiO₂ and TiO₂/In₂S₃ photoelectrodes, (c) onset potential negative shift for TiO₂/In₂S₃, and (d) chronoamperometric photocurrent stability of photoelectrodes.

3.6. Photoelectrochemical Performances of Photoelectrodes

3.6.1. Photocurrent Measurements

The photocurrent evolution to the respective applied bias potential and time has been examined as linear sweep voltammetry and chronoamperometry analysis (Figure 6b,d). Noticeably, under solar light illumination, the photocurrent of the TiO₂ photoelectrodes increased progressively and remained stable up to 0.1 V vs. Ag/AgCl with the increase in bias potential. At the wide potential range (−0.9 to 0.1 V vs. Ag/AgCl), the TiO₂ photoanode shows stable photocurrent density, which ensures the stability and redox reaction of the photoelectrodes. However, the TiO₂ photoanode exhibited a comparatively low photocurrent compared to TiO₂/In₂S₃, which indicates that more photoexcited carriers developed in the TiO₂/In₂S₃ electrodes. Precisely for the TiO₂ electrode, it generates 0.5 $\mu\text{A}\cdot\text{cm}^{-2}$ photocurrent at −0.6 V vs. Ag/AgCl. After infusing In₂S₃ into TiO₂ nanoarrays, the photocurrent of TiO₂/In₂S₃ rises distinctly to 0.28 $\text{mA}\cdot\text{cm}^{-2}$ at −0.8 V vs. Ag/AgCl. The onset potential has been found as −0.8 V vs. Ag/AgCl for the TiO₂, and it has been improved with the infusion of In₂S₃ as −0.9 V vs. Ag/AgCl. The instant response to the illumination has been identified by the transient linear sweep measurement. The very low dark current shows that there is no ionic conduction process between the electrodes. The photocurrent density as a function of time measurement (Figure 6d) shows a 95% photocurrent retention over the 1 h period for In₂S₃/TiO₂ photoelectrodes. The outcome is very consistent with the photoluminescence spectra and impedance results, which ensures the enhancement of the photoactivity of the electrodes.

3.6.2. EIS Measurements

Figure 7a shows the EIS response of the TiO_2 and $\text{TiO}_2/\text{In}_2\text{S}_3$ under visible light illumination. The radius of the Nyquist plot shows the carrier transfer resistance during the reaction. The circuit resistance of the TiO_2 ($27 \text{ Ohm}\cdot\text{cm}^2$) photoanode is increased to $35 \text{ Ohm}\cdot\text{cm}^{-2}$ ($\text{TiO}_2/\text{In}_2\text{S}_3$). In the absence of visible light illumination, the TiO_2 photoanode exhibits a resistance of $8000 \text{ Ohm}\cdot\text{cm}^2$ at $0.4 \text{ V vs. Ag/AgCl}$. Under light illumination, an inbuilt potential is developed in the photoanode, facilitating the movement of charge carriers to the reaction site. The In_2S_3 passivated TiO_2 exhibits $750 \text{ Ohm}\cdot\text{cm}^2$. The photoanode generally exhibits a CPE value on the order of $3.16 \times 10^{-5} \text{ F}$, which is used as a fitting parameter to conclude the charge transport resistance. The in situ grown In_2S_3 on TiO_2 nanorods with a nanostructured surface and vertical nanorod structure accelerates the photoexcited carriers towards the FTO film. The crystalline TiO_2 has a continual and well-ordered interior structure, which makes a high electric conductivity under photoexcitation and an inbuilt potential established by the heterostructure [62,63]. Furthermore, the bare facets of TiO_2 and In_2S_3 have participated in the redox reaction by transferring carriers to the electrolyte for hydrogen evolution. The low resistance for the $\text{In}_2\text{S}_3/\text{TiO}_2$ reveals a tolerance of more photoinduced holes at the interface and involves the redox reaction. As reported previously, the reaction rate increasing at the surface can be validated as higher conductivity and low resistance behavior of the photoanodes [64–66]. The lowest real part of the impedance at higher frequencies substantiates the faster redox reaction by the photoelectrode. The results reveal the $\text{In}_2\text{S}_3/\text{TiO}_2$ photoanodes ability to hold the highest PEC efficiency.

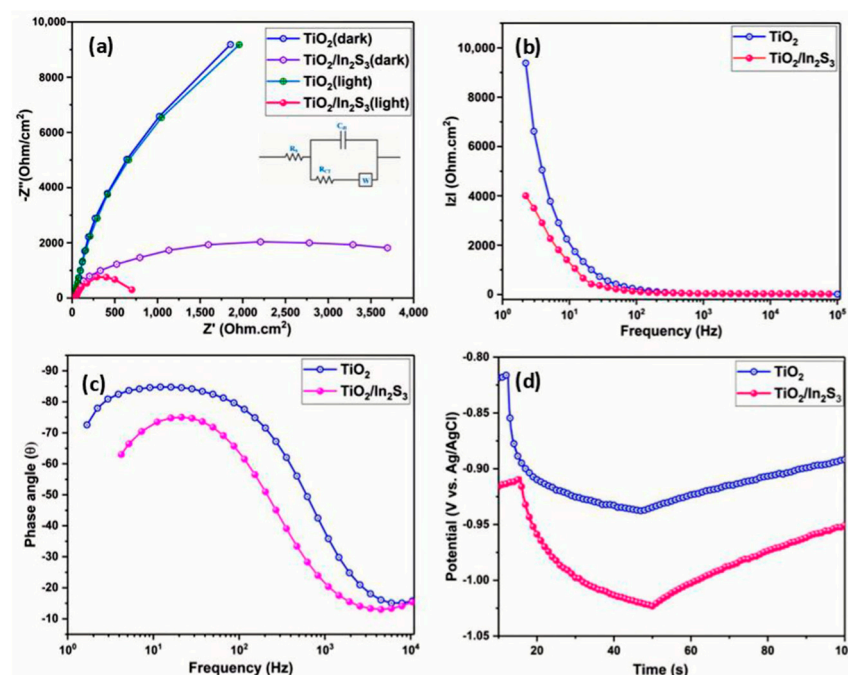


Figure 7. (a): Electrochemical impedance spectrum of TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ photoelectrodes, (inset: equivalent circuit diagram of EIS), (b) Bode magnitude plot for the TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ photoelectrodes, (c) Bode phase plot for the TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ photoelectrodes, and (d) open circuit potential of TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ photoelectrodes.

3.6.3. OCP and Charge Transport Properties

For a complete understanding of the photoexcited charge carrier process at the interface of electrode and electrolyte, the PEC impedance spectra have been measured and shown in Figure 7b. TiO_2 exhibits high resistance to moving the charge carriers for the redox reaction. However, the In_2S_3 deposition on the TiO_2 visualizes low resistance, which

indicates that a greater number of photoexcited carrier transfers have happened in a certain time. The enhanced photoexcited hole transfer leads to an enhanced photocurrent. However, the Bode phase plots in Figure 7c,d provide perceptions of the carrier kinetics in the photoelectrode. The photoelectrodes' characteristic relaxation frequency peaks at 12 and 28.1 Hz for TiO_2 , and $\text{TiO}_2/\text{In}_2\text{S}_3$ implies a decrease in electrochemical process time for the heterostructure electrode. In addition, the peak shift means that the photoelectrode progressively accelerates the redox reaction at the interface and significantly reduces the phase value. The low surface recombination indirectly means that a high number of carriers are present in the photoelectrode for the redox reactions, which is further evidenced by an open-circuit potential (OCP) measurement, as shown in Figure 7d. The built-in potential development by the photoelectrode demonstrates the OCP value from -0.93 V vs. Ag/AgCl to -1.02 V vs. Ag/AgCl, under light illumination. The negative deployment of the OCP validates the n-type semi-conductance of the photoelectrode. The heterostructure displays a larger photovoltage ($V_{\text{ph}} = \text{OCP}_{\text{dark}} - \text{OCP}_{\text{light}}$), indicative of 0.122 V vs. Ag/AgCl for TiO_2 and 0.126 V vs. Ag/AgCl for $\text{In}_2\text{S}_3/\text{TiO}_2$, which shows that the $\text{In}_2\text{S}_3/\text{TiO}_2$ photoanode has suppressed surface carrier recombination. The slow decay of the OCP indicates longer lifetime spans of carriers at the interface of the $\text{TiO}_2/\text{In}_2\text{S}_3$, which has been confirmed with the growth and decay time of the photoanodes (Figures S3 and S4). The Bode magnitude plot reveals that the conductance of the carriers is higher at $\text{TiO}_2/\text{In}_2\text{S}_3$. The Mott–Schottky analysis (Figure 8a,b) indicates that the shift of flat band potential towards more negative (0.99 V vs. Ag/AgCl) values for the $\text{TiO}_2/\text{In}_2\text{S}_3$. The TiO_2 photoanode has a flat band potential of 0.64 V vs. Ag/AgCl. The carrier concentration and space charge layer have been calculated using the Mott–Schottky relations [67]. The calculated amount of increased n-type carriers ($6.13 \times 10^{17} \text{ cm}^{-3}$) with the decrease in space charge layer width (W_{SCL}) of 10 nm is the reason for localizing the higher collection efficiency of charges in the $\text{TiO}_2/\text{In}_2\text{S}_3$ photoanode. Moreover, the flat band potential difference of 0.35 V vs. Ag/AgCl between the TiO_2 and $\text{TiO}_2/\text{In}_2\text{S}_3$ confirms the type II conduction band edges between the semiconductors.

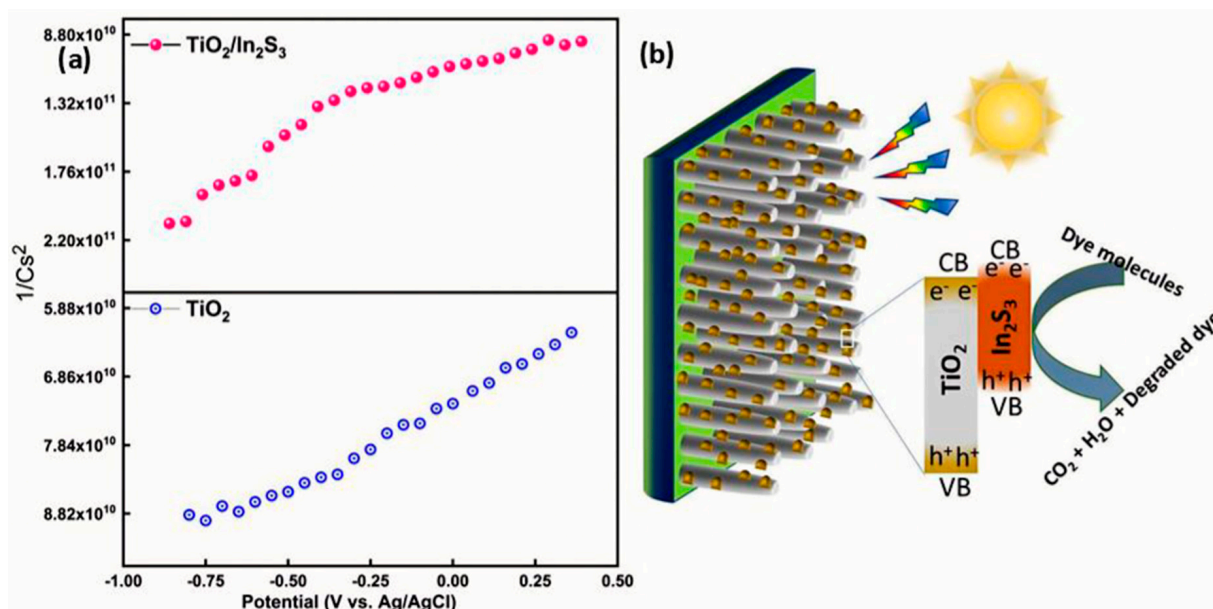


Figure 8. (a): Mott–Schottky plot for the TiO_2 , $\text{TiO}_2/\text{In}_2\text{S}_3$ photoelectrodes, and (b) schematic photo (electro) catalytic redox reactions on the photoelectrodes. The more photoexcited In_2S_3 molecule under visible light degrades the dye molecule into the small fragments of organic moieties.

4. Photocatalytic Reaction Mechanism

A thorough investigation of H_2 production features has been conducted by the fabrication of the photoanode and counter electrode integration. Figure 8b shows the wireless cell configuration for the light-induced hydrogen generation from the photoanodes of TiO_2/In_2S_3 and Pt electrode components. The In_2S_3 acts as a visible light absorber, and the photoexcited charges have been transported to the FTO through the higher band gap of TiO_2 nanorods. The interface between the TiO_2 and In_2S_3 stores the electron for a certain time and allows the redox reaction to acquire the hydrogen from the counter electrode. The photoelectrochemical studies ensure that the long lifetime of the charge carrier is converted into hydrogen through the water splitting reaction. The In_2S_3/TiO_2 photoanodes work under visible light, as well as UV light irradiation. To confirm the redox reaction, an organic molecule has been tested for a one-hour duration (Figure 8b). Utilizing the redox reaction, the TiO_2/In_2S_3 photoanode has been used for hydrogen generation activity in environmental remediation applications.

4.1. Applied Bias Photon-to-Current Efficiency (ABPE)

Applied bias photon-to-current efficiency (ABPE) has been measured as an important index to evaluate the hydrogen generation in photoelectrochemical water splitting, which is directly reflected in the half-cell solar-to-hydrogen (HSTH) conversion efficiency. The ABPE values have been calculated from the LSV measurement. The ABPE value of the TiO_2 nanorods array was only 0.007% at 0.1 V (vs. RHE), while the ABPE values of the TiO_2/In_2S_3 photoanode amplified to 0.33% at 0.04 V (vs. RHE) maximum ABPE value (Figure 9a).

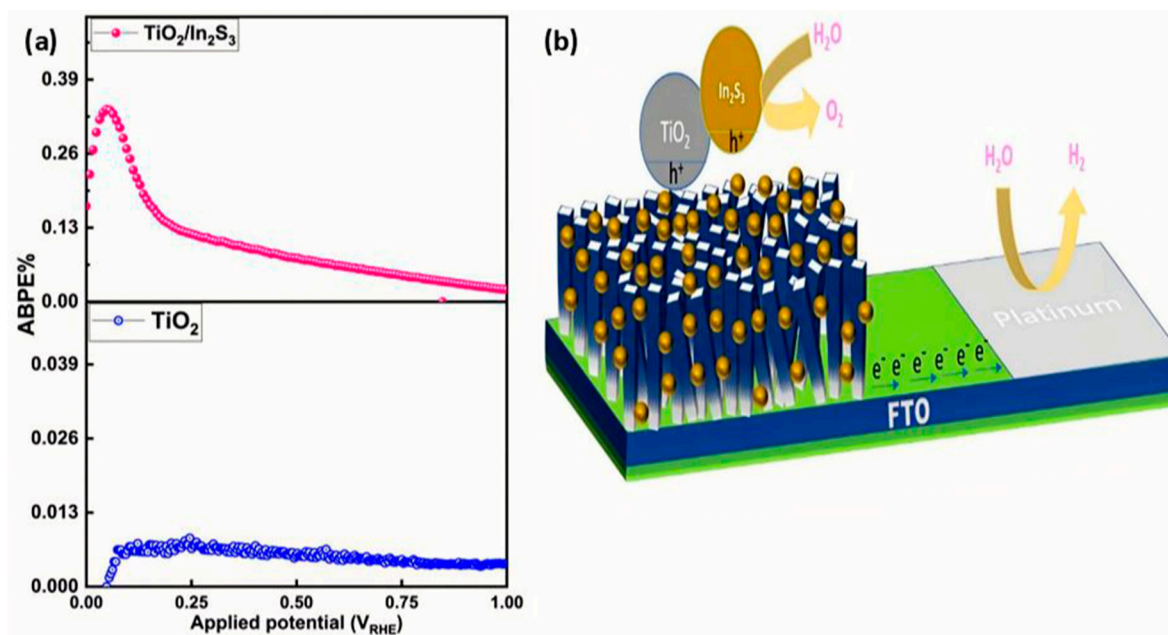


Figure 9. (a) ABPE conversion of TiO_2 , TiO_2/In_2S_3 photoelectrodes, and (b) the schematic view of the redox reaction mechanism in the TiO_2/In_2S_3 photoanode.

4.2. Solar to Hydrogen Generation

Here, a plausible technique for photocatalytic, as well as photo-electrocatalytic water oxidation of TiO_2/In_2S_3 , has been evidenced. As shown in Figure 9b, under UV-vis light illumination, In_2S_3 triggered as heterostructures excited and yielded more electron-hole pairs and persuaded the water-splitting reaction at a 0 V bias. The continuous electron-hole pair parting rate with the bias potential increases the redox reaction. The photoelectrode displays a practical photon-to-electron conversion of 0.26% at 0 V vs. RHE. The visible

photoexcited electrons in the conduction band (CB) of In_2S_3 are transported to the CB of TiO_2 , and for an instant, the photoexcited holes from TiO_2 are transferred to the In_2S_3 owing to their photo-potential to complete the reaction cycle.

As a result, water oxidation and hydrogen generation have been initiated. The solar-to-hydrogen generation from the counter electrode has been calculated as 0.33% for the $\text{TiO}_2/\text{In}_2\text{S}_3$ photoanode.

5. Conclusions

In this study, we successfully developed and assembled a high-performance TiO_2 and In_2S_3 layered heterostructure photoanode by combining the hydrothermal and CBD methods. The heterostructure nanoarrays explicitly demonstrate the superior photoelectrochemical (PEC) performance of the coupled TiO_2 and In_2S_3 system, compared to the pristine TiO_2 photoanode due to the highly efficient In_2S_3 heterojunction at the electrode interface. The PEC performance of the photoanodes (photocurrent evolution, electrochemical impedance, charge transport time) has been greatly enhanced by the In_2S_3 semiconductor particle assembly. The increase in carrier concentration ($6.13 \times 10^{17} \text{ cm}^{-3}$) and the decrease in the space charge layer (10 nm) improve the charge separation efficiency of the heterostructure photoanode. The $\text{TiO}_2/\text{In}_2\text{S}_3$ photoanode produces a maximum photocurrent of 0.28 mA cm^{-2} at -0.8 V vs. Ag/AgCl , which is a highly low onset potential for the hydrogen evolution. This enhancement results confirmed ABPE (0.33%) and STH (0.26%). The facile fabrication and the robust physicochemical evidence presented here strongly validate the TiO_2 and In_2S_3 layered heterostructure nanoarray as a highly promising material for sustainable solar energy conversion. This successful strategy provides a clear and scalable pathway for designing next-generation photoanodes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano16010044/s1>. Figure S1: EDS spectrum of $\text{TiO}_2/\text{In}_2\text{S}_3$ heterostructure. Figure S2: O1s spectrum of $\text{TiO}_2/\text{In}_2\text{S}_3$. Figure S3: Photocurrent growth and decay time for TiO_2 photoanode. Figure S4: Photocurrent growth and decay time for $\text{TiO}_2/\text{In}_2\text{S}_3$ photoanode.

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