Effect of oxygen nonstoichiometry on the photoelectrochemical performance of oxide-nanorod based TiO$_2$/Sb$_2$S$_3$ and ZnO/Sb$_2$S$_3$ heterostructured photoanodes

Vikas Sharma$^1$, Athrey C Dakshinamurthy$^1$, Beauty Pandey$^{2,3}$, Somnath C Roy$^4$ and C Sudakar$^5$

$^1$ Multifunctional Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai-600036, India
$^2$ Environmental Nanotechnology Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai, Tamil Nadu, 600036, India
$^3$ Presently at ICFAI University Tripura, Agartala-799210, India.

E-mail: csudakar@iitm.ac.in

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Abstract

Single crystalline ZnO and TiO$_2$ nanorods are grown on fluorine-doped tin oxide (FTO) substrates by hydrothermal method. The nanorods are annealed under air and reducing conditions to alter the oxygen nonstoichiometry and hence the mid-bandgap defect states. Such an annealing process is shown to impart significant change on the photoelectrochemical (PEC) performance of the photoelectrodes. Large photocurrent densities ($J$) of 0.78 mA cm$^{-2}$ are obtained for air annealed (AA) TiO$_2$ nanorods (TNR) compared to hydrogen annealed (HA) TNR ($J = 0.36$ mA cm$^{-2}$). ZnO nanorods (ZNR), on the contrary, shows photocurrent density of 0.76 mA cm$^{-2}$ and 0.36 mA cm$^{-2}$ for ZNR-HA and ZNR-AA photoanodes, respectively. The contrasting difference in the PEC performance is attributed to the synergetic effect of interfacial impedance with electrolytes and the oxygen nonstoichiometry. Further, to overcome the limitation of light absorption by these materials owing to their wide bandgap, TiO$_2$ and ZnO nanorods are coated with Sb$_2$S$_3$ by chemical bath deposition to form heterostructured TNR-AA/Sb$_2$S$_3$(CBD) and ZNR-HA/Sb$_2$S$_3$(CBD) thin films. Such heterostructures exhibit enhanced photocurrent values of $\sim$1.39 mA cm$^{-2}$ and 3.36 mA cm$^{-2}$ (at 1.6 V versus Ag/AgCl), respectively. The PEC performances of the nanorods are analyzed in terms of the annealing conditions and subsequent introduction of defect states in the bandgap. The present study shows the importance of oxygen defect control at the interface between the oxide and chalcogenide, and its role in the betterment of PEC performance in TiO$_2$/Sb$_2$S$_3$ and ZnO/Sb$_2$S$_3$ heterostructure photoanodes.

1. Introduction

Photoelectrochemical (PEC) water splitting is a clean and promising approach to convert renewable solar energy into a high gravimetric energy density fuel, hydrogen [1, 2]. A typical PEC cell consists of a semiconductor photoelectrode that absorbs light to generate electron-hole pairs. The holes and electrons drive oxidation and reduction reactions with water to simultaneously produce hydrogen and oxygen at opposite electrodes [3]. Ideal characteristics of a semiconductor (SC) photoelectrode include (i) suitable bandgap, $E_g > 1.23$ eV (thermodynamic equilibrium voltage $+0.8$ eV to overcome kinetic barriers) [4], (ii) higher conduction band position than the equilibrium potential of H$^+/H_2$ and lower valence band position compared to the equilibrium potential of O$_2$/H$_2$O for oxygen evolution reaction [4], and (iii) excellent photo-corrosion stability in aqueous solutions [3, 4]. Zinc oxide (ZnO) and titanium dioxide (TiO$_2$) have gained significant attention in the past decade as favorable photoanode materials towards achieving efficient PEC water oxidation because of good electron mobility, excellent optical properties, and low toxicity [5, 6]. Recently, engineering the nanostructures...
of ZnO and TiO₂ have been shown to improve photocurrent yields because of the large surface-to-volume ratio that promote both enhanced light-harvesting and easy separation of photogenerated charges [7]. Despite possessing these excellent properties, ZnO-based photoanodes are not commercialized as an efficient PEC water splitting device because of several limitations such as wide bandgap, photo-corrosion and recombination. Most notably, ZnO suffers from photo-corrosion in the aqueous solution under ultraviolet illumination. Hole trapping on the semiconductor surface is a common problem in many other materials for water splitting [8]. One dimensional (1D) nanostructures such as ZnO and TiO₂ nanorods (NRs) provide continuous and direct electrical transport pathways for photogenerated electrons. However, one of the apparent drawbacks of such oxides is limited absorption of light, mostly in the UV region owing to their large bandgap (3.37 eV) [9], which restrict practical applications. It is commonly accepted that for efficient photoinduced charge separation direct contact between the absorber and the acceptor surfaces is required.

A promising method for enhancing photon absorption by wide bandgap oxide semiconductor in the visible range is to couple such nanostructure with a narrow bandgap inorganic semiconductor material including metal chalcogenides such as CdS, CdSe, In₂S₃, and Sb₂S₃ [10–13]. Among these chalcogenides, antimony sulphide (Sb₂S₃) has received significant attention as a potential candidate in solar energy conversion because of unique structural, electrical and optical properties [14]. Sb₂S₃ crystallizes into the orthorhombic stibinite structure belonging to the Pbmn space group [15]. It has a bandgap ļ 1.7–1.9 eV and hence can absorb a significant fraction of the solar spectrum [16]. Further, when compared to other narrow bandgap semiconductors, Sb₂S₃ has a high absorption coefficient in the visible region (1.8 × 10⁵ cm⁻¹ at 450 nm and 7.5 × 10⁴ cm⁻¹ at 500 nm) [17]. Sun et al have demonstrated, while studying the degradation of azo dyes, that TiO₂/Sb₂S₃ heterostructure yield higher visible light absorption with improved photocatalytic activity [18]. Yang et al have shown in their studies on water splitting by heterojunctions that significant enhancement in the photocurrent density and onset potential is achieved while using TiO₂/Sb₂S₃ heterojunctions [19]. Light absorption and charge carrier transport of photoanode can be tuned by the hydrogenation process in the ZnO-NR (ZNR) and TiO₂-NR (TNR) photoanode by creating mid-gap defect states [20, 21]. It is shown that the oxygen nonstoichiometry in such oxides exhibits a significant impact on the photovoltaic properties of the device [22]. However, the effect of such oxygen nonstoichiometry created due to different annealing conditions on the photoelectrochemical performance of heterojunction structures like TiO₂/Sb₂S₃ and ZnO/Sb₂S₃ remains to be investigated.

In this manuscript, the structural, microstructural and optical studies on vertically oriented single-crystalline ZnO and TiO₂ nanorod/Sb₂S₃ heterostructure photoanodes are reported. Further, the effect of oxygen nonstoichiometry in these oxide nanorods due to varied annealing conditions on photoelectrochemical performance of heterostructure photoanodes are investigated in detail. We explicitly demonstrate that such annealing conditions alter the PEC performance of ZnO/Sb₂S₃ and TiO₂/Sb₂S₃ heterostructures.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (ZnNO₃·6H₂O, 99%; Alfa Aesar), hexamethylenetetramine (HMTA) (C₆H₁₂N₄, 99%; Alfa Aesar), hydrochloric acid (HCl, 99%); Alfa Aesar), ethanol (99%; Alfa Aesar), titanium tetrachloride (TiCl₄, 99%; Alfa Aesar), zinc acetate dihydrate (ZnAc.2H₂O, 99%; Alfa Aesar), antimony chloride (SbCl₅, 99%; Alfa Aesar), sodium thiosulfate (Na₂S₂O₃·5H₂O, 99%; Alfa Aesar), sodium sulfate (Na₂SO₄, 99%; Alfa Aesar), fluorne-doped tin oxide coated transparent (FTO) glass (8Ω/Sq, 2.2 mm thick) are procured and used for synthesis without further purification.

2.2. Synthesis of ZNR by the hydrothermal method

ZnO nanorods are grown on fluorne-doped tin oxide (FTO) substrate with 2 cm² are using the method reported earlier [23]. First, a seed layer of ZnO has been deposited on FTO substrate by spin coating 5 mM ethanol solution of zinc acetate dihydrate at 3000 rpm for 60 s. The spin coating is repeated for 6 times to obtain a dense layer. The ZnO layer on FTO is annealed at 350 °C for 20 min to get a crystalline seed layer. FTO substrate deposited with ZnO seed layer is dipped in 25 mM aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine. This substrate is kept in a Teflon autoclave for the hydrothermal process at 90 °C for 12 h to obtain single-crystalline ZnO nanorods. After natural cooling, substrates are rinsed with water and ethanol several times, followed by drying at 95 °C for 30 min in air. ZnO nanorod (ZNR) deposited substrates are annealed at 450 °C for 3 h in air and hydrogen atmosphere to alter oxygen nonstoichiometry. The air-annealed and hydrogen annealed ZnO nanorods are referred to as ZNR-AA and ZNR-HA, respectively.
2.3. Synthesis of TNR by hydrothermal method

10 ml of deionized (DI) water is mixed with 10 ml of concentrate HCl in a beaker and the mixture is stirred for 5 min. 0.4 ml of TiCl4 is added to the above solution and stirred for another 5 min. FTO substrate is placed at an angle against the wall of the Teflon-lined autoclave with the conducting side facing the wall. Hydrothermal synthesis is performed at 160 °C for 1 h by placing the autoclave in a hot air oven. After the completion of the reaction, the autoclave was kept outside to cool down to room temperature naturally. Finally, TiO2 nanorod (TNR) coated FTO substrate (FTO/TNR) is rinsed thoroughly with DI water and ethanol and kept in an oven for drying. Dried FTO/TNR substrates are further annealed at 450 °C in air and hydrogen atmosphere for 3 h. Air-annealed and hydrogenated FTO/TNR are referred to as TNR-AA and TNR-HA, respectively.

2.4. Synthesis of Sb2S3 by chemical bath deposition (CBD) method

TNR/Sb2S3 and ZNR/Sb2S3 heterostructure photoanodes are fabricated using a chemical bath deposition method (CBD). FTO/TNR and FTO/ZNR are dipped in a reaction mixture containing 2.5 mM of SbCl3 and 0.1 M sodium thiosulphate. The reaction mixture, kept in an ice bath, is constantly stirred under N2 atmosphere for 2 h. Upon Sb2S3 coating, TNR and ZNR photoanodes turned orange indicating the growth of Sb2S3 layer. These sensitized photoanodes are removed from the solution and rinsed several times with DI water followed by annealing at 330 °C under N2 atmosphere for 30 min. This yielded a dark brown crystalline Sb2S3 film coating on FTO/TNR and FTO/ZNR substrates.

2.5. Characterization

The bare and Sb2S3 coated FTO/TNR and FTO/ZNR photoanodes are characterized by x-ray diffraction (XRD), Raman spectroscopy (Horiba jobin-yvon HR 800 UV micro-Raman spectrometer), diffuse reflectance spectroscopy (PVE 300 Bentham), scanning electron microscopy (SEM: FEI Quanta 400 FEG) and high-resolution transmission electron microscopy (HRTEM: FEI Tecnai G2 T20). The photoelectrochemical measurements are performed using a three-electrode electrochemical system: (i) bare TNR and ZNR photoanodes, and TNR/Sb2S3 and ZNR/Sb2S3 heterostructure photoanodes as the working electrodes, (ii) Pt wire as used as the counter electrode, and (iii) Ag/AgCl/saturated KCl electrode as a reference electrode in an aqueous solution containing 0.5 M Na2SO4 (pH = 7). Photoresponse of the photoanodes is measured under 1 Sun condition (100 mW cm−2) with chopped illumination from an Oriel Newport 300 W Xenon lamp equipped with AM 1.5 G filter. Photocurrent and impedance measurements are carried out using CH instrument CHI6054E electrochemical analyzer. The electrochemical impedance spectroscopy (EIS) is carried out under light irradiation with an applied bias voltage of 0.6 V versus Ag/AgCl and a frequency range of 0.1 to 107 Hz. The EIS spectra are fitted using Z-view program (Scribner Associates Incorporated). Photoconversion efficiency is calculated in the J versus V plots.

Figure 1. X-ray diffraction (XRD) patterns of Sb2S3 grown on (a) TNR and (b) ZNR coated FTO substrates. Raman spectra of Sb2S3 grown on (c) TNR and (d) ZNR coated FTO substrates. The films are grown by the CBD method.
3. Results and discussion

3.1. Structural, microstructural and optical studies

The phase purity and structural information of TNR, ZNR, TNR/Sb₂S₃ and ZNR/Sb₂S₃ photoanodes are studied using x-ray diffraction analysis. Figure 1(a) shows the XRD patterns of TNR-AA and TNR-AA/Sb₂S₃ heterostructures. Peaks from (101), (002) and (112) planes at 2θ values of 35.9°, 62.6° and 65.5°, respectively confirm the formation of rutile TiO₂ nanorods on FTO substrate. For the TNR-AA/Sb₂S₃ heterostructure, reflections from (220), (130), (221) confirms the growth of Sb₂S₃ on TNR substrate (figure 1(a)). The intense peak from (002) plane of TiO₂ is still seen suggesting a thin layer of Sb₂S₃ on TNR. Figure 1(b) shows the XRD patterns of ZNR-AA and ZNR-AA/Sb₂S₃ heterostructure. Strong peaks in the XRD spectrum of ZNR-AA at 2θ values of 34.4°, 36.2°, 47.5° and 62.8° are attributed to diffraction from (002), (101), (102) and (103) planes, which corresponds to hexagonal wurtzite structure. XRD spectrum of ZNR-AA/Sb₂S₃ heterostructure shows peaks from (130), (221), (351), (360) and (422) planes confirming the growth of Sb₂S₃. The FTO and ZNR peaks are not seen in the heterostructure suggesting thicker coating of Sb₂S₃ on the ZnO nanorods. XRD studies on TNR-HA, ZNR-HA does not show significant changes from the corresponding air annealed samples as shown in figure S1 (available online at stacks.iop.org/NANOX/1/030038/mmedia).

Figure 2. Field emission scanning electron microscope image of (a) TNR and (b) ZNR coated on FTO substrate. (c) & (d) shows the SEM images of Sb₂S₃ grown on the substrates shown in (a) and (b), respectively. Transmission Electron Microscopy (TEM) image of (e) TNR and (f) ZNR. (g) & (h) shows the TEM image of Sb₂S₃ grown on (a) and (b) substrates, respectively.
Growth of TNR, ZNR photoanodes along with the Sb$_2$S$_3$ grown on these photoanodes is also investigated by Raman Spectroscopy. The rutile TiO$_2$ structure is tetragonal with space group D$^{14}_{4h}$ (P4$_2$/mnm) and has two units of TiO$_2$ per cell [28]. Figure 1(c) shows the Raman spectra of TNR-AA and TNR-AA/Sb$_2$S$_3$ heterostructure. Vibrational modes such as B$_{1g}$ (141 cm$^{-1}$), E$_g$ (447 cm$^{-1}$) and A$_{1g}$ (603 cm$^{-1}$) including the multiphonon mode at 237 cm$^{-1}$ are characteristic of rutile TiO$_2$ [27–29]. Raman spectra of ZNR-AA along with the Sb$_2$S$_3$ grown on FTO/ZNR-AA substrate is shown in figure 1(d). Hexagonal ZnO shows the basic modes at 437 cm$^{-1}$ and 583 cm$^{-1}$, which are attributed to E$_2^\text{(high)}$ and A$_1$/E$_1$/E$_2^\text{(LO)}$, respectively [30, 31]. The small peak observed at 330 cm$^{-1}$ is assigned to the multiphonon E$_2^\text{(high)}$–E$_2^\text{(low)}$ mode [32–36]. Raman spectra of TNR/Sb$_2$S$_3$ and ZNR/Sb$_2$S$_3$ heterostructures are shown in figures 1(c) & (d), respectively. These spectra exhibit the characteristic Sb$_2$S$_3$ pyramid vibrational mode at 147 cm$^{-1}$. It should be noted that these pyramids form the main building unit of Sb$_2$S$_3$ structure [15]. The vibrational mode Sb$_2$S$_3$ is stronger in ZNR-AA/Sb$_2$S$_3$ compared to the TNR-AA/Sb$_2$S$_3$ photoanodes. This could be either due to thinner coating of Sb$_2$S$_3$ on TiO$_2$ or due to the preferential coating of Sb$_2$S$_3$. Other modes at 187 cm$^{-1}$ and 251 cm$^{-1}$ are attributed to the B$_{1g}$ asymmetric bending of S-Sb-S and symmetric bending of S-Sb-S, respectively [37]. Two modes centered at 280 cm$^{-1}$ and 300 cm$^{-1}$ are due to A$_{2g}$/B$_{2g}$ asymmetric stretching vibration of S-Sb-S [37, 38]. A significant increase of background in the Raman spectrum of TiO$_2$-NR-HA and ZnO-NR-HA samples indicate structural changes on the surface in both ZnO and TiO$_2$ oxide due to the reducing ambient (figure S2).

Field emission scanning electron microscope (FESEM) images of TNR-AA and ZNR-AA are shown in figure 2. Growth of TNR is along the c-axis of the tetragonal structure, and ZNR is along the c-axis of hexagonal structure. The rods themselves are oriented randomly on FTO substrate (figures 2(a) & (b)). The average width of TNR and ZNR is found to be ~80 nm and 200 nm, respectively and the average length of nanorods is found to be in the range of 4 to 5 μm. Figures 2(c) and (d) shows the heterostructure growth of Sb$_2$S$_3$ on TNR-AA and ZNR-AA. The tip of the nanorods is conformally coated with Sb$_2$S$_3$ film leaving distinct microstructural features than the uncoated photoanode topography. The tip profile of the nanorods is still visible in spite of the coating suggesting uniform thin coatings. Bright-field TEM images of TNR-AA and ZNR-AA are shown in figures 2(e) and (f), respectively. TEM images of these samples are obtained by loading the nanorods scratched from FTO substrate on to the carbon-coated Cu-grids after dispersing in a solution. The average width of ZNR and TNR
measured from TEM studies are consistent with that measured from FESEM studies. In figures 2(g) and (h) shows the TEM image of Sb$_2$S$_3$ coated on TNR-AA and ZNR-AA substrate, respectively.

Diffuse reflectance spectroscopy is performed to estimate the bandgap of these semiconducting oxides and Sb$_2$S$_3$ heterostructures. Figures 3(a) and (b) shows the reflectance spectra of TNR-AA and ZNR-AA along with the TNR-AA/Sb$_2$S$_3$ and ZNR-AA/Sb$_2$S$_3$ heterostructures, respectively. Corresponding Tauc plots for pristine oxide nanorods and Sb$_2$S$_3$ heterostructure on these photoanodes are shown in figures 3(c) & (d), respectively. A direct bandgap of \( \sim 3.05 \) eV is obtained for TNR. TNR-AA/Sb$_2$S$_3$ shows two band edges, one at 1.62 eV corresponding to Sb$_2$S$_3$ and the other at 3.02 eV due to the TiO$_2$ (figure 3(c)). The direct bandgap of ZNR-AA is obtained to be \( \sim 3.12 \) eV. The ZNR-AA/Sb$_2$S$_3$ coated substrate also shows two band edges, with the Sb$_2$S$_3$ edge appearing at \( \sim 1.64 \) eV and the ZNR absorption edge at \( \sim 3.09 \) eV (figure 3(d)). The diffuse reflection spectra show that the oxide (ZnO and TiO$_2$) and sulphide (Sb$_2$S$_3$) phase remain separate without any noticeable intermixing in the heterostructure. Tauc plots for TNR-HA and ZNR-HA are shown in figures S3(a) & (b), respectively. The estimated indirect bandgap for rutile phase TNR-HA is found to be \( \sim 3.02 \) eV (figure S3(a)).
The hydrogen annealing process seems to have slightly changed the bandgap. The direct bandgap of ZNR-HA is found to be \( \sim 3.2 \) eV, as shown in figure S3(b).

3.2. Photo electrochemical (PEC) water splitting measurement
Photoelectrochemical properties of air and hydrogen annealed oxide nanorods, and their heterostructures are studied by evaluating the corresponding linear sweep voltammetry (LSV) curves. Dark current measurements are performed to check for leakage currents in the samples. It is observed that in the case of TNR-AA, a net photocurrent density (subtracting the dark current) of about 0.24 mA cm$^{-2}$ at 1.0 V (versus Ag/AgCl) is obtained upon illumination, which is an indication of effective photoelectrochemical water splitting in TNR-AA [19]. In a typical photoelectrochemical water splitting reaction, photocurrent is generated by the separation of the electron/hole pairs in the photoanode upon illumination. A photocurrent density of 0.78 mA cm$^{-2}$ (at 1.6 V

![Figure 4. (a) J–V plots of photoelectrochemical cells made using TNR-AA and TNR-AA/Sb$_2$S$_3$(CBD) as photoanodes. (b) Photocurrent measurement of TNR-AA and TNR-AA/Sb$_2$S$_3$(CBD) photoanodes as a function of time to test the stability measured at an applied potential of 1.0 V. (c) Photocurrent density transients for TNR-AA and TNR-AA/Sb$_2$S$_3$(CBD) photoanodes with chopped light illumination (light on/light off) measured with an applied potential of 1.6 V. (d) Nyquist plots for PEC made using TNR-AA, TNR-AA/Sb$_2$S$_3$(CBD) photoanodes (with light ON condition). Inset shows the magnified portion of the plot from the high-frequency region.](image-url)
versus Ag\textsubscript{1}/AgCl\textsubscript{1} is obtained for bare TNR-AA (figure 4(a)), which is further enhanced to 1.39 mA cm\textsuperscript{−2} for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure photoanode (table 1). Two-fold enhancements in the photocurrent density for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure as compared to the bare TNR-AA is attributed to the enhancement in the light absorption in the visible region. It noteworthy that the Sb\textsubscript{2}S\textsubscript{3} coated TNR-AA photoanodes exhibit photocurrent only above 0.75 V, unlike the bare TNR-AA photoanode. This could be due to the increased absorption by the Sb\textsubscript{2}S\textsubscript{3}, not allowing the light to reach the TiO\textsubscript{2}. Measurements are performed under continuous illumination for 10 min by immersing photoanodes in the electrolyte solution to check the stability of photocurrent. Figure 4(b) shows the photocurrent density reducing from ∼0.2 mA cm\textsuperscript{−2} to 0.15 mA cm\textsuperscript{−2} for TNR-AA photoanode, whereas, it is much more stable ∼0.20 mA cm\textsuperscript{−2} for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure photoanode. Figure 4(c) shows the chronoamperometric I-t curves collected at 1 V versus Ag/AgCl under chopped illumination. The rapid photocurrent response upon illumination in both TNR-AA and TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure reveals the ability of photocatalyst to drive the solar photoelectrochemical water splitting reactions [19]. Further, to study the effect of hydrogen annealing on

Table 1. Current density (J-V) analyses on air- and hydrogen- annealed TNR with Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructures are listed.

| Sample (under illumination) | Current density (mA/cm\textsuperscript{2}) at 1.6 V versus Ag/AgCl |
|----------------------------|---------------------------------------------------------------|
| TNR-AA                     | 0.78                                                          |
| TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) | 1.39                                                          |
| TNR-HA                     | 0.36                                                          |
| TNR-HA/Sb\textsubscript{2}S\textsubscript{3} (CBD) | 0.56                                                          |

versus Ag/AgCl\textsubscript{1}) is obtained for bare TNR-AA (figure 4(a)), which is further enhanced to 1.39 mA cm\textsuperscript{−2} for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure photoanode (table 1). Two-fold enhancements in the photocurrent density for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure as compared to the bare TNR-AA is attributed to the enhancement in the light absorption in the visible region. It noteworthy that the Sb\textsubscript{2}S\textsubscript{3} coated TNR-AA photoanodes exhibit photocurrent only above 0.75 V, unlike the bare TNR-AA photoanode. This could be due to the increased absorption by the Sb\textsubscript{2}S\textsubscript{3}, not allowing the light to reach the TiO\textsubscript{2}. Measurements are performed under continuous illumination for 10 min by immersing photoanodes in the electrolyte solution to check the stability of photocurrent. Figure 4(b) shows the photocurrent density reducing from ∼0.2 mA cm\textsuperscript{−2} to 0.15 mA cm\textsuperscript{−2} for TNR-AA photoanode, whereas, it is much more stable ∼0.20 mA cm\textsuperscript{−2} for TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure photoanode. Figure 4(c) shows the chronoamperometric I-t curves collected at 1 V versus Ag/AgCl under chopped illumination. The rapid photocurrent response upon illumination in both TNR-AA and TNR-AA/Sb\textsubscript{2}S\textsubscript{3} (CBD) heterostructure reveals the ability of photocatalyst to drive the solar photoelectrochemical water splitting reactions [19]. Further, to study the effect of hydrogen annealing on

Figure 5. (a) J–V plots of photoelectrochemical cells made using TNR-HA and TNR-HA/Sb\textsubscript{2}S\textsubscript{3} (CBD) as photoanodes. (b) Photocurrent measurement of TNR-HA and TNR-HA/Sb\textsubscript{2}S\textsubscript{3} (CBD) photoanodes as a function of time to test the stability. (c) Photocurrent density transients for TNR-HA and TNR-HA/Sb\textsubscript{2}S\textsubscript{3} (CBD) photoanodes with chopped light illumination (light on/light off). (d) Nyquist plots for PEC is made using TNR-HA, TNR-HA/Sb\textsubscript{2}S\textsubscript{3} (CBD) photoanodes (with light ON condition). Inset shows the magnified portion of the plot from the high-frequency region.
photoelectrochemical performance of oxide nanorods, LSV measurements are performed on TNR-HA and TNR-HA/Sb₂S₃(CBD) photoanodes (figure 5). Similar to air-annealed TNR, the current density is enhanced from 0.36 mA cm⁻² to 0.56 mA cm⁻² (at 1.6 V versus Ag/AgCl) upon coating Sb₂S₃ on TNR-HA photoanodes (figure 5). Further, stability and transient photocurrent response studies performed on hydrogen annealed photoanodes are shown in figures 5(b) & (c). Photocurrent densities appear to be stable at 0.07 mA cm⁻² and 0.08 mA cm⁻² for bare TNR-HA and TNR-HA/Sb₂S₃(CBD) heterostructures, respectively. The rapid photocurrent enhancement upon illumination is observed in hydrogen annealed photoanodes, indicating the suitability for solar water splitting. It is inferred that heterostructure photoanodes made with air annealed TNR-AA/Sb₂S₃(CBD)) shows greater photocurrent density (1.39 mA cm⁻²) in comparison to annealing under hydrogen ambience (0.56 mA cm⁻²). The photoconversion efficiency for TNR-AA and TNR-HA photoanodes along with the respective TNR/Sb₂S₃ heterostructures is calculated using the equation \( \eta(\%) = \frac{J \times (1.23 - E_{app})}{I_0} \times 100 \), where J corresponds to the current density, \( E_{app} \) is the applied potential and \( I_0 \) corresponds to the intensity of the incident light [26, 27]. The efficiency versus \( E_{app} \) plots are shown in the figures S4(a) & (b). Heterostructures of TNR-AA/Sb₂S₃ shows a much larger current density compared to studies that have employed similar photoelectrodes, which is evident from table S1. The decrease in the photocurrent in the case of TNR-HA/Sb₂S₃(CBD) heterostructure photoanodes is mostly due to the creation of oxygen vacancies in TiO₂, which might enable the recapture of conduction band electrons in oxygen-deficient TiO₂ nanostructures [20].

Electrochemical impedance spectroscopy (EIS) is performed on the PEC devices to understand the interface behavior and ionic process (figures 4(d) and 5(d)). The EIS spectra are fitted using Z-view software with an equivalent circuit. The impedance spectra show best fit when a resistance and two parallel RC circuits connected in series are used in the equivalent circuit (figures 4(d) & 5(d)). Parameters estimated after fitting the semicircle are given in table 3. \( R_1 \) is the contact resistance of FTO/Pt; \( R_2 \) is attributed to the charge transfer resistance at the electrolyte/counter electrode; \( R_3 \) is attributed to the complex impedance at the interface of TNR/Sb₂S₃(CBD).
and electrolyte interface. Contact resistance ($R_1$) of bare TNR-AA and TNR-AA/$Sb_2S_3$(CBD) heterostructure is 25.8 $\Omega$ and 12.0 $\Omega$, respectively. Charge transfer resistance ($R_2$) for TNR-AA/$Sb_2S_3$(CBD) heterostructure photoanode shows $\sim 10$ $\Omega$, which is less than the bare TNR-AA ($R_2 \sim 15$ $\Omega$). The decrement in the $R_2$ for TNR-AA/$Sb_2S_3$(CBD) heterostructure indicates an efficient charge transfer at the electrolyte/counter electrode interface. The complex impedance $R_3$ at the interface of photoanode and electrolyte shows $\sim 47.5$ k$\Omega$ for TNR-AA and decreases to $\sim 10.5$ k$\Omega$ for the TNR-AA/$Sb_2S_3$(CBD). Further, electrochemical studies on TNR-HA and TNR-HA/$Sb_2S_3$(CBD) heterostructure photoanodes shows a similar trend. Nyquist plots of bare TNR-HA and TNR-HA/$Sb_2S_3$(CBD) heterostructure are fitted with a semicircle and equivalent circuit model are shown in the figure 5(d). Contact resistance ($R_1$) of bare TNR-HA and TNR-HA/$Sb_2S_3$(CBD) heterostructure shows 6 $\Omega$ and 13 $\Omega$, respectively. While the hydrogen annealing decreases the contact resistance significantly, coating $Sb_2S_3$ slightly increases the same. TNR-HA/$Sb_2S_3$(CBD) and bare TNR-HA photoanode show the impedance $R_2 \sim 17.5$ k$\Omega$ and $\sim 20.2$ $\Omega$, respectively (table 3). The resistance $R_3$, which is attributed to the complex impedance at the interface of photoanode and electrolyte redox couples, also shows significant decrease upon $Sb_2S_3$ coating.

Table 2. Current density (J-V) analyses on air- and hydrogen- annealed ZNR with $Sb_2S_3$(CBD) heterostructures are listed.

| Sample (under illumination) | Current density (mA/cm$^2$) at 1.6 V versus Ag/AgCl |
|-----------------------------|---------------------------------------------------|
| ZNR-AA                      | 0.36                                              |
| ZNR-AA/$Sb_2S_3$(CBD)       | 1.33                                              |
| ZNR-HA                      | 0.76                                              |
| ZNR-HA/$Sb_2S_3$(CBD)       | 3.36                                              |

Figure 7. (a) J-V plots of photoelectrochemical cells made using ZNR-HA and ZNR-HA/$Sb_2S_3$(CBD) as photoanodes. (b) Photocurrent measurement of ZNR-HA and ZNR-HA/$Sb_2S_3$(CBD) photoanodes as a function of time to test the stability. (c) Photocurrent density transients for ZNR-HA and ZNR-HA/$Sb_2S_3$(CBD) photoanodes with chopped light illumination (light on/light off). (d) Nyquist plots for PEC made using ZNR-HA, ZNR-HA/$Sb_2S_3$(CBD) photoanodes (with light ON condition). Inset shows the magnified portion of the plot from the high-frequency region.
TNR-HA photoanode has $R_0 \sim 145.9 \text{ k} \Omega$, which decreases to $\sim 13 \text{ k} \Omega$ for the TNR-HA/Sb$_2$S$_3$(CBD) (table 3). It is observed from EIS studies that TNR-AA and TNR-AA/Sb$_2$S$_3$(CBD) shows lower impedance ($R_0$) compared to the corresponding hydrogen annealed photoanodes. This can be attributed to the predominant oxygen vacancy defects in the case of TNR-HA. A systematic study from our earlier work using electron energy loss spectroscopy investigations on the chemical and defect structure details made on various TiO$_2$ morphologies prepared by a wide range of synthesis techniques showed detectable fraction of Ti existing in $+3$ oxidation state in the hydrogen annealed samples [30]. Also, oxygen vacancies present in the TiO$_2$ were evidenced through this analysis and its effect on the bandgap was thoroughly studied. Since Sb$_2$S$_3$ is made on all the photoanodes using the same processing parameters, we expect the differences in the heterostructures mainly arise due to the defect-related changes in oxide part of the photoanode heterostructure. The difference in the extent of oxygen vacancies present in the TNR-AA and TNR-HA samples are inferred from EPR signal centered at $g \sim 1.99$ as shown in our earlier studies [22]. The signal is stronger for TNR-HA compared to the TNR-AA samples, implying higher oxygen vacancy concentration in the former. EPR signals result from the unpaired electrons trapped at oxygen vacancy defects at regular sites. Such defects are proposed to be higher on the surface of TiO$_2$ oxide particles [30]. Similar studies on ZNR-AA and ZNR-HA samples also revealed that hydrogen annealed ZNR shows an EPR signal at $g \sim 1.95$, whereas ZNR-AA shows very minimal EPR signal. The signal at $g \sim 1.95$ corresponds to the intrinsic oxygen vacancy defect states, which is generally assigned to shallow donors, singly ionized oxygen defects, Zn vacancies, oxygen and Zn interstitials [22].

PEC measurements are also carried out on air annealed and hydrogen annealed zinc oxide nanorods (ZNR) and their heterostructures (ZNR/Sb$_2$S$_3$) to study photocatalytic behavior. A low photocurrent density of 0.36 mA cm$^{-2}$ (at 1.6 V versus Ag/AgCl) is obtained for bare ZNR-AA (figure 6(a)). On the contrary, current density is enhanced from 0.75 mA cm$^{-2}$ (for dark) to 1.33 mA cm$^{-2}$ (under illumination) for ZNR-AA/Sb$_2$S$_3$(CBD) heterostructure photoanode (table 2). Four-fold enhancement in the photocurrent density for ZNR-AA/Sb$_2$S$_3$(CBD) heterostructure as compared to the bare ZNR-AA is clearly seen, which is prominently due to enhanced absorption in the visible region upon coating with Sb$_2$S$_3$. Photocurrent stability test shows that the stable photocurrent density after 10 min of continuous illumination are 0.01 mA cm$^{-2}$ and 0.02 mA cm$^{-2}$ (at 1 V versus Ag/AgCl), respectively for bare ZNR-AA and ZNR-AA/Sb$_2$S$_3$(CBD) heterostructures (figure 6(b)). These values are lower than what has been noted in LSV. In fact, a sharp decrease in the current density with time can be seen from the plots given in figure 6(b). Especially, such a decrease is either attributed to the degradation of Sb$_2$S$_3$ in the presence of electrolyte or to the poor adherence of Sb$_2$S$_3$ on the oxide surface. Chronoamperometric I-t curves are collected at 1 V versus Ag/AgCl under chopped illumination (figure 6(c)). These plots also show rapid photocurrent response upon illumination in both ZNR-AA and ZNR-AA/Sb$_2$S$_3$(CBD) heterostructure which is indicative of the ability for solar water splitting reactions.
ZnO is shown to be a better option over the ZNR-AA photoanode. Interestingly, in the case of ZNR-HA, the PEC trend shows incremental nature upon hydrogen annealing of oxide nanorods (figure 7(a)). This is opposite to the trend observed with TNR photoanode. An enhancement in the current density from 0.40 mA cm⁻² (dark) to 0.76 (light) mA cm⁻² (at 1.6 V versus Ag/AgCl) is observed for bare ZNR-HA photoanode. Further enhancement in the current density from 0.76 mA cm⁻² to 3.36 mA cm⁻² (at 1.6 V versus Ag/AgCl) (table 2) is achieved upon coating Sb₂S₃ on ZNR-HA photoanodes (figure 7(a)). Stability and transient photocurrent response studies are performed on hydrogenated photoanodes (figures 7(b) & (c)). These studies further assert the advantage of coating Sb₂S₃ over ZNR-HA. Photocurrent densities appear to be stable at hydrogen annealed photoanodes as well. It is inferred that the heterostructure photoanodes made with hydrogen annealed ZNR shows greater photocurrent density (3.36 mA cm⁻²) in comparison to air annealing conditions (1.33 mA cm⁻²). It is evident from table S1 that the ZnO photoanodes in the present study show improved current densities compared to studies that have employed similar photoelectrodes. Improvement in the photocurrent density upon hydrogen treatment in ZNR could be due to the decreased hole trapping. This also increases the conductivity reducing the defect-related recombination [21]. Further, with suppressed oxygen vacancies in ZnO at the Sb₂S₃/oxide interface, oxidation of Sb₂S₃ to Sb₂O₃ could be prevented significantly favoring such improvement.

Nyquist plots of bare ZNR-AA and ZNR-AA/Sb₂S₃(CBD) heterostructure are fitted with semicircles with the equivalent circuit model given in the figure 6(d). The values of the contact resistance (R_c) of bare ZNR-AA and ZNR-AA/Sb₂S₃(CBD) heterostructure are ~18 Ω and 12.5 Ω (table 4). ZNR-AA/Sb₂S₃(CBD) heterostructure photoanode shows the impedance (R_c) ~10 kΩ, which is tenfold less than that of the bare ZNR-AA (R_c ~ 120 kΩ). Reduction in R_c for ZNR-AA/Sb₂S₃(CBD) heterostructure shows the efficient charge transfer at the electrolyte/counter electrode interface. The resistance of photoanode and electrolyte redox couple also shows R_c ~ 218.9 kΩ for ZNR-AA photoanode. This is found to decrease to R_c ~ 115 kΩ for the ZNR-AA/Sb₂S₃(CBD) photoanode (table 4). EIS studies are performed on ZNR-HA and ZNR-HA/Sb₂S₃(CBD) heterostructure photoanodes to understand the effect of hydrogen annealing on the interfacial charge transfer process. Nyquist plots of bare ZNR-HA and ZNR-HA/Sb₂S₃(CBD) heterostructure with fitted semicircle are shown in the figure 7(d). Contact resistance (R_c) for bare ZNR-HA and ZNR-HA/Sb₂S₃(CBD) heterostructure photoanode shows 7.1 and 14.2 Ω. ZNR-HA/Sb₂S₃(CBD) heterostructure photoanode shows the impedance (R_c) ~ 1 kΩ, which is less than the bare ZNR-HA (R_c ~ 7.5 kΩ). The complex impedance for photoanode-electrolyte interface (R_c) is found to be ~84.45 kΩ and ~8.6 kΩ for ZNR-HA and ZNR-HA/Sb₂S₃(CBD), respectively (table 4). Bare ZNR-HA/Sb₂S₃(CBD) shows less complex impedance (R_c) compared to the ZNR-AA and ZNR-AA/Sb₂S₃(CBD) photoelectrodes. This implies that the surface structural modification due to hydrogen annealing of ZnO-NR helps in easy electron transfer at this interface [21, 22].

We also obtained the PL spectra on the ZnO and TiO₂ nanorod for both the air-annealed and hydrogen-annealed samples. These plots are given in figures 8(a), (b). Four peaks were observed in the PL spectrum of

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**Table 3.** The electrochemical impedance spectroscopy analyses on air and hydrogen annealed TNR with Sb₂S₃ heterostructures are listed.

| Sample          | R_0(Ω) | R_1(Ω) | R_2(Ω) | CPE1(10⁻⁵ F) | CPE2(10⁻⁵ F) |
|-----------------|--------|--------|--------|--------------|--------------|
| TNR-AA          | 25.8   | 15     | 47.5   | 97.5         | 95.2         |
| TNR-AA/Sb₂S₃(CBD) | 12     | 10     | 10.5   | 97.9         | 87.96        |
| TNR-HA          | 6      | 20.2   | 145.9  | 1.5          | 99.2         |
| TNR-HA/Sb₂S₃(CBD) | 13     | 17.5   | 13     | 9.79         | 102          |

**Table 4.** The electrochemical impedance spectroscopy analyses on air and hydrogen annealed ZNR with Sb₂S₃ heterostructures are listed.

| Sample          | R_0(Ω) | R_1(Ω) | R_2(Ω) | CPE1(10⁻⁵ F) | CPE2(10⁻⁵ F) |
|-----------------|--------|--------|--------|--------------|--------------|
| ZNR-AA          | 18     | 120    | 218.9  | 0.55         | 0.59         |
| ZNR-AA/Sb₂S₃(CBD) | 12.5   | 10     | 115    | 17.9         | 9.9          |
| ZNR-HA          | 7      | 7.5    | 84.45  | 0.85         | 19           |
| ZNR-HA/Sb₂S₃(CBD) | 14     | 1      | 8.6    | 57.5         | 5.5          |
In this study, we have successfully grown the single-crystalline nanorods of TiO$_2$ and ZnO through the hydrothermal approach. Annealing conditions are shown to significantly affect the photoelectrochemical performance of photoanodes fabricated with these oxide nanorods. High photocurrent densities of 0.78 mA cm$^{-2}$ and 0.76 mA cm$^{-2}$ (at 1.6 V versus Ag/AgCl) are obtained for photoanodes made with TNR-AA and ZNR-HA, respectively. The performance of these photoanodes is further enhanced by forming heterostructure with Sb$_2$S$_3$ through CBD method. These heterostructured photoanodes show enhanced photocurrent density of 1.76 mA cm$^{-2}$ and 3.36 mA cm$^{-2}$ (at 1.6 V versus Ag/AgCl) for TNR-AA/Sb$_2$S$_3$(CBD) and ZNR-HA/Sb$_2$S$_3$(CBD) photoanodes, respectively. This enhancement is predominantly attributed to an increase in light absorption by the heterostructure in the visible region. The decrease in the photocurrent density of oxygen-deficient TiO$_2$ nanostructures obtained by hydrogen annealing of TNR is attributed to the creation of oxygen vacancies which promote the recapture of conduction band electrons. However, in the case of ZnO, hydrogen annealed ZNR shows enhanced photoelectrochemical performance. This is possible due to the decreased hole trapping, thereby increasing the conductivity, and also due to reduced defect-related recombination. Further, oxidation of Sb$_2$S$_3$ to Sb$_2$O$_3$ at the oxide/Sb$_2$S$_3$ interface could be very different in ZnO and TiO$_2$ surfaces. ZnO seems to minimize such oxidation under hydrogenated condition, whereas the oxidation of Sb$_2$S$_3$ seems to get suppressed upon coating it on air-annealed TiO$_2$.

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ORCID iDs

Vikas Sharma https://orcid.org/0000-0002-5756-2165
Somnath C Roy https://orcid.org/0000-0003-4685-8742
C Sudakar https://orcid.org/0000-0003-2863-338X

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