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## Improving light harvesting and charge carrier separation enabling enhanced photoelectrochemical hydrogen production by Sb<sub>2</sub>S<sub>3</sub>-decorated TiO<sub>2</sub> nanotube arrays on porous Ti-photoanodes



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### ABSTRACT

The Ag <sup>+</sup> ions doped TiO<sub>2</sub> nanotube arrays fabricated on Ti mesh through an electrochemical anodization process, and n/n heterostructure formed by coating the TiO<sub>2</sub> nanotube array photoanode with an n-type stibuite (Sb<sub>2</sub>S<sub>3</sub>) layer improve photoelectrochemical water splitting reaction by enhancing light harvesting and charge carrier separation. Sb<sub>2</sub>S<sub>3</sub> is chosen because of its suitable band gap position and strong visible light response. The Ag <sup>+</sup> ion incorporated TiO<sub>2</sub> nanotube array coated with Sb<sub>2</sub>S<sub>3</sub> exhibits a photocurrent density of 6.5 mA cm<sup>-2</sup> vs. RHE, whereas bare TiO<sub>2</sub> nanotube array coated with Sb<sub>2</sub>S<sub>3</sub> and pristine TiO<sub>2</sub> nanotube array exhibit photocurrent densities of 3.6 and 0.27 mA cm<sup>-2</sup>, respectively, under the same conditions, which is nearly 1.8 and 24 times greater than the TiO<sub>2</sub> nanotube array coated with Sb<sub>2</sub>S<sub>3</sub> and pristine TiO<sub>2</sub> nanotube array photoanodes. The applied bias photon-to-current efficiency of Ag <sup>+</sup> ion incorporated TiO<sub>2</sub> nanotube array coated with Sb<sub>2</sub>S<sub>3</sub> is attributable to higher conductivity of TiO<sub>2</sub> nanotube array caused by increased oxygen vacancies and broad optical activity of Sb<sub>2</sub>S<sub>3</sub>. The 1-dimensional TiO<sub>2</sub> nanotube array device structure in the Ti mesh improves charge separation and light harvesting while reducing photogenerated charge carrier recombination and the potential of this novel device structure for advanced energy conversion applications is highlighted in this study.

#### 1. Introduction

Artificial photosynthesis presents a promising avenue for converting solar energy into chemical energy, specifically in the form of fuel with minimal environmental impact. Hydrogen, in particular stands out as an attractive and sustainable energy source due to its lack of greenhouse gas emissions [1]. Water splitting has received a lot of attention in recent decades, particularly electrocatalytic and photoelectrochemical water splitting technologies [2,3]. Among the various approaches, metal oxide-based semiconducting materials have emerged as highly promising candidates for efficient photoelectrochemical (PEC) cells. These materials exhibit desirable properties such as suitable band gaps, flat band potentials, low electrical resistance, and corrosion resistance in aqueous solutions, thereby enabling efficient solar-to-hydrogen (STH) conversion efficiency [4]. Despite extensive research on metal oxides, TiO<sub>2</sub> is the forefront material for photoanodes due to its oxidative stability, availability, high corrosion resistance, environmental friendliness, well-matched energy band edges to the redox level of water, and the ability to tune electronic properties by modifying lattice defects [3]. However, the poor electronic conductivity of TiO<sub>2</sub> ( $\sim$ 1x10<sup>-12</sup> S cm<sup>-1</sup> to 1x10<sup>-7</sup> S cm<sup>-1</sup>), high band gap energy (3.2 eV) restricts its excitation to UV light while high recombination rate of photogenerated charge carriers results in a poor hydrogen conversion efficiency. By structural modification of the TiO<sub>2</sub>, i.e. nanotubes, nanorods, and nanowires [5], metal (e.g., Mo(MoS<sub>2</sub>) [6], and Au [7]) or non-metal doping (e.g., C [8], H [9]), and sensitizing with low bandgap semiconducting materials [10], light harvesting and charge recombination properties were able to be partially optimized.

An improved electron-hole separation and the extended light absorption of  $TiO_2$  are the prerequisites to enhancing the solar energy conversion efficiency. The development of composites with  $TiO_2$  heterojunction interfaces between  $TiO_2$  and component materials with

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#### Table 1

Photocurrent densities and APBE for the TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> heterostructure.

Photoelectrode	Photocurrent density/mA cm <sup>-2</sup>	ABPE/%	Reference electrode	Electrolyte	Ref.
FTO/TiO <sub>2</sub> NRA/Sb <sub>2</sub> S <sub>3</sub>	1.39	0.9	@ 1.6 vs. Ag/AgCl	0.5M Na <sub>2</sub> SO <sub>4</sub>	[52]
FTO/TiO <sub>2</sub> nanorod/ Sb <sub>2</sub> S <sub>3</sub>	0.79	Not reported	@ 1.23 V vs. RHE	0.5 M Na <sub>2</sub> SO <sub>4</sub>	[19]
FTO/TiO <sub>2</sub> nanorod/ Sb <sub>2</sub> S <sub>3</sub>	0.97	0.32	@ 0 vs. Ag/AgCl	0.5 M Na <sub>2</sub> SO <sub>4</sub>	[53]
FTO/TiO <sub>2</sub> NRA/Sb <sub>2</sub> S <sub>3</sub>	0.5	2	@ -0.1 vs. SCE	0.05 M Na₂SO₄	[54]
FTO/TiO <sub>2</sub> NRA/Sb <sub>2</sub> S <sub>3</sub>	1.79	Not reported	@1.16vs. Ag/AgCl	0.5 M Na₂SO₄	[55]
FTO/TiO <sub>2</sub> /Bi NP/Sb <sub>2</sub> S <sub>3</sub>	4.21	2	@1.23 V vs. RHE	0.1 M Na2SO4	[23]
FTO/Bi NP/ Sb <sub>2</sub> S <sub>3</sub>	2.8	Not reported	@1.23 V vs. RHE	0.1 M Na₂SO₄	[56]
FTO/TiO <sub>2</sub> / BiSbS <sub>3</sub>	5.0	2	@ 0.3 V vs. RHE	$Na_2S + Na_2O_3$	[57]
Ti mesh/TiO <sub>2</sub> NTA/Sb <sub>2</sub> S <sub>3</sub>	6.5	3.6	@ 0.8 vs. RHE	0.5 M Na <sub>2</sub> SO <sub>4</sub>	In this work

matching band potentials, as well as apparent visible light absorption, can result in a type II electronic architecture that can localize electron and hole wave functions, extending the exciton lifetime [11,12]. In this regard, in a type II electronic architecture,  $TiO_2$  nanotube arrays (NTAs) fabricated through electrochemical anodization on a Ti metal substrate with a Ti/TiO<sub>2</sub> Schottky junction have received considerable interest in recent decades due to their high specific surface area and ability to decouple light absorption and carrier transport directions, 1-D  $TiO_2$  nanotubes [13]. Furthermore, Ti/TiO<sub>2</sub> heterostructures with a Ti metal layer beneath the  $TiO_2$  NTAs limit charge recombination by efficiently collecting excited charge transfer from the nanotubes to the cathode via the external wire [14]. The incorporation of low band gap semiconducting materials i.e.CdS, and  $Sb_2S_3$  in a type II electronic architecture, can efficiently harvest and utilize sunlight for significant

improvements in photoresponse [11,15]. In this regard, among low-band gap semiconductors, earth abundant and comparatively non-toxic n-type  $Sb_2S_3$  is a promising light-harvesting material for water splitting [16]. Though  $Sb_2S_3$  has a theoretical maximum solar conversion efficiency of 28% for PEC water splitting with a band gap of 1.7 eV and a high absorption coefficient, the STH efficiency of heterojunctions formed with  $Sb_2S_3$ -metal oxides has been reported to be much lower than the theoretically predicted efficiency [17]. The reduced efficiency has been attributed mostly to charge carrier transport properties of TiO<sub>2</sub> [18]. On the other hand,  $Sb_2S_3$  has not yet been extensively investigated for PEC applications [19]. In Table 1, the highest photoresponses reported for native TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> heterostructures and modified TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> heterostructures are given and for the comparison, the efficiency of this investigation is also included.

The goal of this study is to address the low electrical conductivity of  $TiO_2$  and enhance charge separation by fabricating 1-D  $TiO_2$  nanotube in the porous Ti-mesh and to develop an efficient and cost-effective photoanode material for solar water splitting. Furthermore, the anode properties were further enhanced by the doping of silver ion in to the  $TiO_2$  NT and modified with earth abundant light harvesting  $Sb_2S_3$  nanoparticles.

#### 2. Experimental details

## 2.1. Synthesis of $Sb_2S_3$ nanoparticles and the fabrication of thin film $Sb_2S_3$ photocathodes

#### 2.1.1. Fabrication of TNTA

A schematic illustration of the synthesis and fabrication of TNTA-Ag/ Sb<sub>2</sub>S<sub>3</sub> photoanode is given in Fig. 1. The anodization of the Ti mesh was done according to our previous method [20]. The Ti foil (1 cm  $\times$  2 cm, thickness 0.8 mm, porosity 30%, particle size 0.25–0.38 mm, Baoji Qinneng Metal Materials Co., Ltd, China) was cleaned in 10% HF solution for 1 min and sonicated in distilled water for 15 min and allowed for air drying. For anodization of Ti mesh, a solution containing 50 ml of ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, BDH, 99.9 %), 1 ml H<sub>2</sub>O, 0.3 wt% ammonium fluoride (NH<sub>4</sub>F, Fluka, 98%) electrolyte was used. Before anodizing, one side of the Ti foil was covered with a tape to avoid being oxidized and, the electrolyte solution was magnetically stirred for 30 min. Then the



Fig. 1. A schematic diagram of the synthesis of the  $TNTA-Ag/Sb_2S_3$  photoanode and its application in photoelectrochemical water splitting.



Fig. 2. FESEM images of pristine TNTA (a) Surface view, (b) Cross section view, (c) The surface view of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> and (d) the elemental mapping of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub>.

anodization was carried out at a current density of 0.03 A/cm<sup>2</sup> in a two-electrode configuration in a water bath maintained at 30 °C for 3, 6 and 9hrs. After anodizing, the Ti foil was immersed in Ethanol ( $C_2H_6O$ , BDH, 100%) and sonicated for 30 s and finally, it was annealed at 450 °C for 2 h with a ramping of 2.5 °C/min and allowed for natural cooling [21]. During the silver doping and optimizing the Ag<sup>+</sup> ion content, 3, 6 and 10 mg of silver nitrate (AgNO<sub>3</sub>, Sigma Aldrich, 99.8+%), were added to the anodizing electrolyte solution. Doping 6 mg of AgNO<sub>3</sub> loading is the optimized Ag<sup>+</sup> ion loading in PEC context.

### 2.1.2. Preparation of Sb<sub>2</sub>S<sub>3</sub> layer

The Sb<sub>2</sub>S<sub>3</sub> precursor solutions with 0.125 M, 0.25 M and 0.5 M were prepared as reported in our previous work [22]. The optimized Sb<sub>2</sub>S<sub>3</sub> precursor solution was prepared as follows. In a typical method, 114 mg of thiourea (TU, ACROS Organics, 99%) was dissolved in 1 ml of 2-methoxyethanol (2-ME,ACROS Organics, 99%) and magnetic stirred for 15min. Then, the 228 mg of antimony chloride (SbCl<sub>3</sub>, MACKLIN, 99%) was added to it and magnetic stirred for another 60 min. Then 70  $\mu$ l of the precursor solution was spin coated on the anodized Ti foil at 3000 rpm for 30 S and, was heated on the hot plate at 150 °C for 10 min with 5 min ramping. This step was repeated for twice and thrice to prepare Sb<sub>2</sub>S<sub>3</sub> layers with different thicknesses for the precursor solution. Finally, the cells were annealed in the tube furnace under N<sub>2</sub> environment at 280 °C for 10 min with a ramping of 6 °C/min and allowed for natural cooling.

# 2.1.3. Characterization and PEC performance measurement of TNTA-Ag/ $Sb_2S_3$ photoanode

To study the crystal structure of the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub>, XRD analysis was carried out with a PANanalyticalX'pert Highscore diffractometer (X'Pert PRO MPD, PW3040/60) with Cu K $\alpha$  (=0.154060 nm) radiation and a scanning step of 10° per minute. A Hitachi S-4800 field emission scanning electron microscope (FE-SEM) was used for surface morphology analysis, and JEOL JEM-2100F operating at 2 kV were used for transmission electron microscopy (TEM) and high-resolution TEM images. The elemental compositions and corresponding distribution of the samples are determined using energy-dispersive X-ray spectroscopy

(EDS). The surface composition of as-synthesized samples was analyzed using the X-ray photoelectron spectroscopy with a Thermos ESCALAB 250Xi multifunctional image electron spectrometer. RENISHAW in Via Raman Spectroscopy System with a 514 nm laser was used for Raman spectroscopy measurements. A Shimadzu UV-2450 UV-VIS spectrophotometer was used to examine the optical properties of the samples with  $BaSO_4$  as the reference.

The PEC performance of the Ti–TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> thin-film photoanode was investigated using the ZAHNER ZENNIUM electrochemical work-station under chopped illumination in a three-electrode system, where Ag/AgCl served as the reference electrode, Pt wire acted as the counter electrode, and the synthesized photoanode functioned as the working electrode. All potential measurements, were reported against the reversible hydrogen electrode (RHE) using the equation,  $E_{(vs RHE)} = E_{(vs Ag/AgCl)} + 0.1976 + (0.059 \times pH)$ . The current density–potential curves were measured both in the dark and with a 300 W Xe lamp (calibrated with a standard Si solar cell to simulate AM 1.5 illuminations) at a light intensity of 100 mW/cm<sup>2</sup> and an electrolyte solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH ~ 9.5). The linear sweep voltammetry scan rate was 20 mV s<sup>-1</sup>.

The Electrochemical Impedance Spectroscopy experiments were carried out in a one-compartment three-electrode cell by using the Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) at 10 mV amplitude AC signal and at the frequency 1 KHz in 0.1 M Na<sub>2</sub>SO<sub>3</sub> solution with a 100 mW/  $\rm cm^2$  irradiation. Mott-Schottky experiments were carried out in a one-compartment three-electrode cell by using the Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) at 10 mV amplitude AC signal and at the frequency 1 KHz in 10 mV amplitude AC signal and at the frequency 1 KHz in light condition.

#### 3. Results and discussion

### 3.1. Morphological and structural analysis (SEM, TEM and, EDX)

A schematic illustration of the synthesis and fabrication of TNTA-Ag/  $Sb_2S_3$  photoanode is given in Fig. 1 and the details were given in experimental section.



Fig. 3. (a) A FETEM image of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> and (b)–(f) elemental mapping of Ti, O, S, Sb and Ag respectively, (g) HRTEM of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> and, (h) SADE pattern of TNTA-Ag.

The surface morphologies of the synthesized TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanodes were analyzed by FESEM, and the surface and cross-section views of the TNTA and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes are shown in Fig. 2(a)–(c). As shown in the Supplementary Fig. S1, the distribution of pore diameter of TiO<sub>2</sub> NTs which are range from 5 to 37.5 nm, with an estimated average pore diameter of 18.5 nm and a length of  $\sim$ 3 µm.

Meanwhile, the surface SEM image of the Sb<sub>2</sub>S<sub>3</sub> coated TNTA

displayed in Fig. 2(c) and Fig. S2(a) confirms the conformal coating of  $Sb_2S_3$  on TiO<sub>2</sub> NTs. Furthermore, the high surface area provided by the porous and curved nature of the Ti mesh substrate (Supplementary Fig. S2) enable the formation of tilted TiO<sub>2</sub> NT enabling light to trap efficiently as shown in Fig. 1. Furthermore, the absence of an over layer of  $Sb_2S_3$  on the TNTA array allowing light to pass to the TNTA increasing the light absorption properties and hence the device performance as



Fig. 4. (a) XRD pattern of annealed Ti substrate, TNTA and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub>, and (b) the Raman shift of TNTA, TNTA-Ag, TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub>.



Fig. 5. High resolution XPS spectra (a) Ti 2p, (b) O 1s of TNTA, (c) Ti 2p, (d) O 1s of TNTA-Ag and (e) Ag 3d, and (f) Sb 3d of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode.

discussed later. The EDX analysis of the TNTA-Ag/Sb $_2$ S $_3$  photoanode shown in Fig. 2(d), confirms the presence of Ti, O, Sb, and S.

Notably, as shown in Fig. 2(d), no Ag species were found in the SEM/ EDX mapping, indicating either a homogenous distribution of Ag species across the TNTA or a lower concentration of Ag species convincing the effective fabrication of the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode. As the conformal coating of Sb<sub>2</sub>S<sub>3</sub> on TiO<sub>2</sub> NT is critical for efficient light harvesting as well as charge separation, FETEM and FETEM-EDX analysis of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> were performed. The FETEM image of a TiO<sub>2</sub> NT and corresponding FETEM-EDX images of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> are shown in Fig. 3(a)–(h) further confirm the homogeneous distribution of Sb<sub>2</sub>S<sub>3</sub> over the TiO<sub>2</sub> NT. On the other hand, as shown in Fig. 3(f), the sporadic distribution of Ag species in the EDX mapping indicates either a homogenous distribution and low concentration of Ag<sup>+</sup> ions in TNTA. Hence, the FETEM/EDX (sporadic distribution of Ag species) and SEM/ EDX (surface Ag is not seen in SEM/EDX) analysis of Ag shown in Figs. 3 (f) and 2(d) respectively is strong evidence of confirming the successful doping of Ag  $^+$  ions into the TiO<sub>2</sub> lattice.

As shown in Fig. 3(g), the HRTEM analysis revealed the lattice fringes with interplanar spacings of 0.35 and 0.24 nm which can be attributed to the (101) plane of anatase  $TiO_2$  and to the (101) plane of rutile  $TiO_2$  respectively [23]. The average d-spacing of 0.19 nm can be attributed to the (530) plane of  $Sb_2S_3$ , [24] at the same time it could also be due to the (200) plane of anatase  $TiO_2$  since both crystallographic planes are having almost the similar d-spacing values. Furthermore, SADE analysis of TNTA-Ag is shown in Fig. 3(h), further confirm the mixed phase of  $TiO_2$  as evident by the XRD analysis [25]. On the other hand, no diffraction pattern for Ag in XRD and together with SADE and the HRTEM image, reinforce the absence of metallic Ag or its oxides confirming the possible inclusion of Ag  $^+$  ion into the  $TiO_2$  and/or lower

concentration and homogeneous distribution of Ag ions over the TNTA.

X-ray diffraction (XRD) analysis was conducted to examine the material properties of photoanodes. Fig. 4(a) shows the XRD patterns of Ti mesh, anodized/annealed Ti mesh, and Sb<sub>2</sub>S<sub>3</sub> coated on the anodized/ annealed TNTA-Ag. As it can be seen in Fig. 4(a), diffraction peaks at  $38.4^{\circ}$ ,  $40.2^{\circ}$ ,  $53.0^{\circ}$  and  $70.6^{\circ}$  correspond to (0 0 2), (1 0 1), (1 0 2) and (1 0 3) planes of the Ti (JCPDS no. 89–5009) substrate [26]. In the XRD pattern of anodized Ti metal (TNTA), while Ti metal peaks can be clearly seen but the intensity of the TiO<sub>2</sub> peaks appears relatively low which is not due to the amorphous nature of the TiO<sub>2</sub> as confirmed by the FETEM analysis but mainly due to the porous nature of the surface and the non-flat fracture of the surface under investigation, which reduces the area analyzed by the X-rays [18]. However, weak peaks observed at  $25.54^{\circ}$  corresponds to the (101) crystal planes of the anatase phase of TiO<sub>2</sub> while the peaks at 39.26 and 48.09 can be attributed to the (004) and (200) planes of anatase TiO<sub>2</sub> [27].

Additionally, the weak peak observed at  $36.30^{\circ}$  can be assigned to the (101) plane, confirming the presence of the rutile phase of TiO<sub>2</sub> [27], confirming the mixed phase in TNTA. On the other hand, no diffraction peaks for Ag or Ag oxides, suggesting a homogeneous dispersion of Ag<sup>+</sup> ions/or a lower doping concentration confirming the potential fabrication of Ag<sup>+</sup> ions doped TiO<sub>2</sub> nanotubes. In contrast, the weak peaks at 29.65°,  $35.17^{\circ}$  (which is overlapped with the (101) plane of Ti substrate, see Fig. S3 in supplementary), and  $47.17^{\circ}$  can be attributed to the (2,1, 1), (4,2,0), and (5,3,0) crystal planes of Sb<sub>2</sub>S<sub>3</sub> indicating the polycrystalline nature of Sb<sub>2</sub>S<sub>3</sub> [28].

As Raman spectroscopy is known for its sensitivity to the crystallinity and microstructures of materials, for further confirmation of the crystalline nature and the phase of TiO<sub>2</sub>, Raman spectroscopic analysis was performed and depicted in Fig. 4(b). In all samples, characteristic anatase vibration modes, specifically A1g, B1g and Eg, were detected at 143, 395, 515, and 639 cm<sup>-1</sup>. Additionally, the observation a weak peak at 448  $\text{cm}^{-1}$ , corresponding to the  $\text{E}_{g}$  mode, confirmed the presence of the rutile phase of TiO<sub>2</sub>. Following group theory, the two sharp and intense bands at 282 cm<sup>-1</sup> and 306 cm<sup>-1</sup> were attributed to the antisymmetric Sb–S stretching modes Ag and B1g, respectively, while the band at 241 cm<sup>-1</sup> corresponded to the symmetric S–Sb–S bending mode (B<sub>1g</sub>) [29]. The shift of the peak towards higher frequencies is noticeable in the main peak, $E_{g(1)}$  (shown in the inset) when substituting Ag<sup>+</sup> ions in place of Ti<sup>+4</sup>. Furthermore, no peaks associated with Sb<sub>2</sub>O<sub>3</sub> or Sb<sub>2</sub>O<sub>5</sub> species were observed in RAMAN analysis, providing further confirmation of the successful fabrication of the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode. Furthermore, the primary peak observed in both TNTA and Ag<sup>+</sup> ion-doped TNTA exhibits a decrease in intensity and broadening from 13.06 to 15.57 cm<sup>-1</sup> (Supplementary Fig. S4). This phenomenon suggests a reduction in the O-Ti-O bonds [30], indicating the substitution of  $Ag^+$  ions for  $Ti^{+4}$  ions within the  $TiO_2$  lattice. As a result, oxygen vacancies are formed which was confirmed by the XPS analysis and these oxygen vacancies create new defect energy levels within the band gap of TiO<sub>2</sub> and leads to a reduction in the band gap, resulting in enhanced absorption of visible light and enhanced charge separation [31,32].

#### 3.2. Chemical analysis (XPS results)

X-ray photoelectron spectroscopy (XPS) analysis was conducted to gain insights into the chemical states of silver and its interaction with the  $TiO_2$  lattice and the high-resolution XPS spectra of Ti 2p and O 1s of TNTA is shown in Fig. 5(a) and (b) respectively while, XPS spectra of Ti 2p and O 1s of TNTA/Ag is shown in Fig. 5(c) and (d) respectively. In Fig. 5(e) and (f), the XPS spectra of Ag 3d and Sb 3d of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode are shown respectively. A carbon correction at 284.5eV was performed on each high-resolution scan. As shown in Fig. 5(a), typical binding energies of 457.8 and 463.4 (The peaks Ti  $2p_{1/2}$  and Ti $(2p_{3/2})$  shows the energy separation of 5.63 eV) in the XPS spectra of TNTA correspond to the peaks of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ , respectively, which are

assigned to the binding energy of Ti(IV) ion in titanium lattice in TiO<sub>2</sub> [33]. Furthermore, the observed small increase in the binding energies of Ti 2p of TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> to 458.5 and 464.3 eV when compared to the binding energy of Ti 2p of TiO<sub>2</sub> (supplementary Figure S5 and Fig. 6(a)) which might be due to the lowering of the electron density of Ti as a result of an electronic interaction between TiO<sub>2</sub> and Sb<sub>2</sub>S<sub>3</sub> [33,34]. However it has been reported, that in the crystal structure of Sb<sub>2</sub>S<sub>3</sub>, each [Sb<sub>4</sub>S<sub>6</sub>]n chain has five nonequivalent atomic sites, including two nonequivalent Sb sites (Sb1 and Sb2) and three nonequivalent S sites (S1, S2, and S3). As a result, the [hk0] orientation of Sb<sub>2</sub>S<sub>3</sub> ribbons just stand on a TiO<sub>2</sub> nanoparticle substrate, whereas the [001] orientation of Sb<sub>2</sub>S<sub>3</sub> can either stand on mismatched crystalline TiO<sub>2</sub> or chemically link with the crystalline [101] surface [35]. In Fig. 5(a), typical binding energy separation of 5.75 eV is observed confirming the presence of Ti<sup>+4</sup> valence state [36]. Importantly, the absence of shoulders on the lower binding energy side of the peaks indicate the absence of titanium in an oxidation state lower than +4, implying that only  $\mathrm{Ti}^{+4}$  exists within the TiO<sub>2</sub> structure. Similarly, the peaks detected at 528.9, 529.3 and 530.7 eV in the high-resolution scanning spectra of O 1s of TNTA can be attributable to TiO<sub>2</sub> lattice oxygen (O<sub>L</sub>), oxygen vacancies (O<sub>V</sub>), and chemisorbed or dissociated oxygen [36].

In Ag doped TNTA, the binding energy of Ti element is split into two spin orbits with energies of 458.5 and 464.2 eV that correspond to Ti<sup>4+</sup>  $2p_{3/2}$  and Ti<sup>4+</sup>  $2p_{1/2}$ , respectively. When compared to TNTA without Ag doping samples, the Ti 2p lattice peaks shift to a higher binding energy, and the increase in the binding energy of Ti 2p bands on silver ion impregnation could be due to a decrease in Ti electron density caused by Ag ion interaction with TiO<sub>2</sub> surface [37,38]. Furthermore, as shown in Fig. 5(c), the doping of Ag into the  $TiO_2$  also resulted in the formation of  $Ti^{3+}$  peaks at 458.0 and 463.5 eV that correspond to  $Ti^{3+} 2p_{3/2}$  and  $Ti^{3+}$  $2p_{1/2}$ , respectively, which could be the result of Ti<sup>4+</sup> reduction by Ag <sup>+</sup> ions to yield Ti<sup>3+</sup>state in TNTA-Ag [39]. Further, the formation of Ti<sup>3+</sup> states in TNTA by the doping of Ag ion into TiO<sub>2</sub> lattice is associated with the shift of the binding energies of O 1s. High-resolution XPS analysis for O 1s was conducted for Ag<sup>+</sup> ion-doped TNTA as shown in Fig. 5(d). In Ag<sup>+</sup> ion-doped TNTA, the peaks observed at 529.9, 531.2 and 532.5 eV can be attributed to the TiO<sub>2</sub> lattice oxygen (O<sub>1</sub>), oxygen vacancies (O<sub>V</sub>), and chemisorbed or dissociated oxygen species (O<sub>C</sub>), respectively [33,40] and in contrast to pure TNTA, there is an increase in the binding energy of O<sub>L</sub>, O<sub>V</sub>, and O<sub>C</sub> in Ag <sup>+</sup> ion-doped TNTA. This shift indicates that the doping of Ag<sup>+</sup> ions into the TiO<sub>2</sub> lattice has enhanced the structural stability, confirming the successful integration of Ag<sup>+</sup> ions into the  $TiO_2$  lattice [41]. In addition, the increased charge carrier density in Ag<sup>+</sup> ion doped TNTA may control and regulate the charge dynamics in TNTA enhancing the charge carrier separation and improving the PEC performance It is shown that the Vo can be generated by annealing TiO<sub>2</sub> in an elevated temperature (>400 °C) in an oxygen deficient environment [42], which is well align with the XPS studies of TNTA shown in Fig. 5(b). Furthermore, as observed by Takata et al., [43]. enhanced Vo in TNTA-Ag photoelectrode (by 15%) can be related to the reduction of  $\mathrm{Ti}^{+4}$  species to  $\mathrm{Ti}^{+3}$  and the subsequent creation of Vo for charge compensation due to the insertion of Ag  $^+$  ions into the TiO<sub>2</sub>.

Overall, the formation of electronic states below the  $TiO_2$  conduction band as a result of  $Ag^{n}$  <sup>+</sup> ions induced formation of oxygen vacancies  $(Ti^{3+}$  centers) may cause a decrease in the optical band gap energy as well as act as an electron trapping site may enhance visible light absorption and possibly decrease the electron-hole recombination rate [44]. Furthermore, oxygen vacancies can act as electron donors, improving electric conductivity and so enhancing the separation and transfer of photogenerated charge carriers [44–46]. As a result, the inclusion of Ag <sup>+</sup> ions into the  $TiO_2$  lattice may result in a decrease in the optical band gap energy of the TNTs as well as charge recombination rates, which could improve device performance. Meantime, excess oxygen vacancies should be avoided since they can act as recombination centers for photogenerated charges, which is detrimental to the PEC water splitting activity.



Fig. 6. (a) DRS and Tauc plot for TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes.



**Fig. 7.** (a) Linear sweep voltammetry (LSV) plot of the as prepared photoanode vs. RHE under chopped light illumination (b) ABPE of TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes (c) Chronoamperometric (I-t curve) analysis and (d) temporal evolution of Hydrogen gas of TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes.

In Fig. 5(e), the Ag 3d spectrum of the as-synthesized photoanode is presented. Two distinct peaks are observed at 367.9 and 373.9 eV, corresponding to Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ , respectively and we propose that these peaks can be attributed to the  $3d_{5/2}$  and  $3d_{3/2}$  states of Ag<sup>+</sup> within the TiO<sub>2</sub> lattice [33]. Fig. 5(f) exhibits the Sb 3d spectrum of Sb<sub>2</sub>S<sub>3</sub>, revealing two prominent peaks corresponding to Sb  $3d_{5/2}$  and Sb  $3d_{3/2}$  at 529.7 and 539.2 eV, respectively. These binding energy values

align well with the expected values for Sb<sup>+3</sup>, confirmation of the presence of Sb<sub>2</sub>S<sub>3</sub> [47,48]. However, it is important to note that the peak observed at 529.4 eV can be attributed to the O 1s signal originating from the TiO<sub>2</sub> lattice [37,49]. This observation is complicated by the overlapping of the O 1s and Sb 3d binding energy regions, making it challenging to differentiate between the contributions of O 1s and Sb 3d signals.



**Fig. 8.** (a) Nyquist plots with the equivalent circuit and (b) Mott Schottky plots of pristine TNTA, TNTA-Ag, TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes. Inset in Fig. 8(a) shows the enlarged Nyquist plot.

#### 3.3. Optical properties

The Diffuse Reflectance Spectroscopy (DRS) analysis was performed for TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoelectrodes and shown in Fig. 6(a) and the optical band gap were determined by using the Tauc's relation;  $\alpha h \upsilon = A (h \upsilon - Eg)^n$  where  $\alpha$  is the absorption coefficient, A is a constant and n is 1/2 for direct or 2 for indirect allowed transitions, hu is the photon energy and Eg is the optical band gap. Here we calculate the direct band gap by plotting the  $(\alpha h \upsilon)^2$  vs photon energy, hu and extrapolating the linear region to x axis [18,25,50]. Using Tauc plot, the calculated band gaps of the TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub>, and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> are 3.14, 2.75, and 2.62 eV, respectively (Fig. 6(b)). The TNTA showed absorption edge  $\sim 400$  nm and TNTA/Sb<sub>2</sub>S<sub>3</sub> and TNTA/Ag/Sb<sub>2</sub>S<sub>3</sub> absorb the visible light from 700 nm extending the photo-response of the Sb<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub> in the visible region. The inclusion of Ag <sup>+</sup> ions into TNTA has resulted in a red shift due to the contribution of oxygen vacancies created due to the considerable difference in the valence states of Ti<sup>+4</sup> and Ag <sup>+</sup> which could result in improved TNTA conductivity [44,45].

#### 3.4. Photoelectrochemical performance

To investigate the performance of the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode in a photoelectrochemical (PEC) context, PEC measurements were performed using linear sweep voltammetry with a chopped on/off simulated (AM 1.5 G, 100 mW/cm<sup>2</sup>) sunlight illumination at 20 mV  $^{-1}$  in Na<sub>2</sub>SO<sub>4</sub> (0.1 M) solution. As shown in Fig. 7(a), instant positive transient photocurrents for photoanodes TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub>, and TNTA/Ag/ Sb<sub>2</sub>S<sub>3</sub> were observed, whereas no current was observed when the illumination was turned off. At 0.80 V vs RHE, the photoanodic current densities for TNTA, TNTA/Sb $_2S_3$ , and TNTA/Ag/Sb $_2S_3$  electrodes are 0.27, 3.6, and up to 6.5 mA cm<sup>-2</sup>, respectively. These rapid photocurrent responses imply that photogenerated electrons are efficiently injected into the conduction band (CB) of TNTA, and then to the Ti metal, enabling the water reduction reaction at the counter electrode. Simultaneously, holes are left in the Sb<sub>2</sub>S<sub>3</sub> valence band (VB), increasing the oxygen evolution reaction (OER) and eventually resulting in higher photocurrent density. The PEC measurements provide useful information, demonstrating that the conduction band (CB) of Sb<sub>2</sub>S<sub>3</sub> has a higher positive potential than TiO2 NTs when compared to the vacuum level. Notably, the addition of Ag<sup>+</sup> ions (the optimum Ag ion concentration is 0.14 mM) to the TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanode resulted in a photocurrent density that was 24 times that of the pristine TNTA and 1.8 times that of the TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanode. These findings highlight the critical

function of Ag  $^+$  ions in boosting the PEC water splitting activity of the ternary photoanode. The insertion of Ag  $^+$  ions in place of Ti $^{+4}$  is claimed to improve the development of oxygen vacancies and hence the conductivity of TiO<sub>2</sub> nanotubes, which may facilitate in the separation of photogenerated charge carriers from Sb<sub>2</sub>S<sub>3</sub> to TNTA. This mechanism significantly contributes to the observed enhanced performance of the Ag  $^+$  incorporated TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanode.

Furthermore, the efficiency of the photoanode was also assessed in terms of Applied Bias solar-to-Current Efficiency (ABPE) using linear sweep voltammetry (LSV) measurements. The photoconversion efficiency of a photoanode can be calculated using LSV data and the following equation [26], ABPE =  $J_p \times (1.23 - V)/P_{light} \times 100\%$ . Where  $J_p$ represents the photocurrent density (mA cm<sup>-2</sup>) under light irradiation, V denotes the applied voltage (V) relative to the reversible hydrogen electrode (RHE), and P<sub>light</sub> corresponds to the light intensity (100 mW/cm<sup>2</sup>) incident on the photoanode. The calculated ABPE% versus the applied bias potentials (vs. RHE) for the TNTA, TNTA/Sb<sub>2</sub>S<sub>3</sub>, and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoelectrodes are shown in Fig. 7(b). Clearly, the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode has a much higher photoconversion efficiency than the pure TNTA and TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanodes across the full bias voltage range. This improvement is due to the improved charge transfer and conductivity enabled by the inclusion of Ag<sup>+</sup> ions into TiO<sub>2</sub>. The ternary photoanode reaches a maximum ABPE of 3.36% at a bias voltage of 0.65 V vs. RHE, which is 30 times more than that of pristine TNTA and 1.9 times greater than that of TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanodes, respectively. Furthermore, the calculated ABPE% as a function of Ag ion concentration showed that ABPE% increased from 2.4% to 3.6% when Ag ion concentration increased from 0.7 mM to 1.4 mM, and ABPE% remained constant as Ag ion concentration increased to 2.4 mM.

The PEC stability of the synthesized photoelectrode was evaluated through chronoamperometric (I-t) experiments for 120 min. The photocurrent stabilities of TNTA/Sb<sub>2</sub>S<sub>3</sub>, and TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> were tested at 0.65 V vs RHE under illumination for 2 h, and the results are presented in Fig. 7(c). Interestingly, the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode demonstrates constant photocurrent stability at ~3.5mAcm<sup>-2</sup> after 40 min which almost doubled than that of the TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanode. This indicates that the photoanode maintains a steady photocurrent output over the testing period of more than 2 h. However, despite the noteworthy photocurrent stability of the photoanode. Further, the significant decay of the photocurrent during the first 20 min, may be due to the reduction of Ag<sup>+</sup> species into metallic Ag, which may hinder the charge transfer mechanism. Therefore, additional studies are required to address this aspect and improve the long-term performance and

#### Table 2

VFB and ND values for the synthesized photoanodes.

Photoanode	V <sub>FB</sub> (vs. Ag/AgCl)/V	Carrier density (N_D) $\times  10^{19}/\text{cm}^{-3}$
TNTA	-0.37	9.33
TNTA-Ag	-0.45	11.3
TNTA/Sb <sub>2</sub> S <sub>3</sub>	-0.31	7.95
TNTA-Ag/Sb <sub>2</sub> S <sub>3</sub>	-0.38	9.52

durability of the photoanode. Hydrogen evolution was quantified with the gas chromatography and Fig. 7(d) depicts the evolved amount of  $H_2$  against 1V vs. RHE. Ag  $^+$  ion incorporated TNTA/Sb<sub>2</sub>S<sub>3</sub> provides a total of over 25 µmol of  $H_2$  gas over 2 h which is in good agreement with the photocurrent densities.

#### 3.5. Electrochemical impedance spectroscopy

It is a fact that the charge transfer properties of the Ag<sup>+</sup> ion incorporated TNTA photoanode are important for efficient photo-water splitting, and thus to confirm the promoted charge carrier separation upon Ag<sup>+</sup> ion doping into TNTA, and thus to gain insight into the charge transfer kinetics, EIS measurements of the photoanodes were carried out at the photoanode/electrolyte interface with the frequency ranging from 100 mHz to 500 kHz under light illumination. The Nyquist plots of TNTA, TNTA/Ag, TNTA/Sb<sub>2</sub>S<sub>3</sub> TNTA/Ag/Sb<sub>2</sub>S<sub>3</sub> are shown in Fig. 8(a) and the equivalent circuit is shown in the inset in Fig. 8(a), where in equivalent circuit, R<sub>S</sub> is the external series resistance, R<sub>t</sub> and C<sub>t</sub> are the surface state resistance related to the charge transfer from the valence band or conduction band to the surface of semiconductor electrode and capacitance at the depletion region of TNTA (TNTA/Ag), and  $R_{ct}$  and  $C_{ct}$ are the space charge separation resistance and the constant phase elements for the electrolyte/electrode interface and electrode surface, respectively. Table S1 in the supplementary materials shows the fitted Rs, Rt, and Rct for parameters for TNTA, TNTA/Ag, TNTA/Sb<sub>2</sub>S<sub>3</sub>, and TNTA/Ag/Sb<sub>2</sub>S<sub>3</sub>. The R<sub>S</sub> for all is in the 4–5 $\Omega$  range. The R<sub>t</sub> values of TNTA, TNTA/Ag, TNTA/Sb<sub>2</sub>S<sub>3</sub> TNTA/Ag/Sb<sub>2</sub>S<sub>3</sub> are 1281, 44, 436 and 207  $\Omega$  respectively while respective R<sub>CT</sub> values are 339, 257, 42 and 8  $\Omega$ . The EIS results show that the TNTA/Ag and TNTA/Ag/Sb<sub>2</sub>S<sub>3</sub> films exhibit faster interfacial charge transfer and separation rates during PEC water oxidation than those without Ag, which could be related to the creation of oxygen vacancies, which results in increased conductivity and hence observed PEC performance can be justified.

As shown in Fig. 8(b), Mott-Schottky measurements were carried out in 0.1 M Na<sub>2</sub>SO<sub>3</sub> under light at a constant frequency of 1 kHz to establish the role of Ag <sup>+</sup> ion doping in carrier density and to calculate the flat band potentials (V<sub>FB</sub>) of TNTA. The V<sub>FB</sub> and, the carrier concentration (N<sub>D</sub>) of the photoanodes were determined by the help of Mott-Schottky equation,  $1/C^2 = (2/\epsilon\epsilon_0 A^2 N_D)$  [V - (V<sub>FB</sub> + k<sub>B</sub> T/e)] where e is the electron charge,  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon$  is the dielectric constant of the substance, N<sub>D</sub> is the carrier concentration, V is the electrode potential,  $V_{FB}$  is the flat-band potential,  $k_B$  is the Boltzmann's constant and T is the temperature (see supplementary for values). The  $V_{FB}$  was calculated from the intercept by extrapolating the linear part of the M-S plot to the voltage axis. The M-S curve is shown in Fig. 8(b), and Table 2 gives the  $V_{FB}$  and carrier concentration  $(N_D)$  of TNTA, TNTA-Ag, TNTA/Sb\_2S\_3 and TNTA-Ag/Sb\_2S\_3 photoanodes. The n-type behavior of the photoanodes is demonstrated by the positive slop of MS plot. These results show that  $Ag^+$  ion doping in TNTA causes a negative shift in the VB of TNTA/Ag compared to TNTA while increasing the  $N_D$  of TNTA/Ag by a factor of 1.2 compared to TNTA. The increase in  $N_D$  can be related to the introduction of oxygen vacancies caused by Ag  $^+$  ion doping in TNTA [51], as demonstrated by XPS experiments.

Despite the observed negative shift in the V<sub>FB</sub> of TNTA/Ag, which would raise the over-potential for PEC water splitting [11], a large increase in the carrier concentration following doping of Ag<sup>+</sup> ions in TNTA resulted in TNTA/Ag outperforming TNTA in the PEC water oxidation reaction. As the N<sub>D</sub> increases, so does the conductivity, which may contribute to an increase in charge transportation and photocurrent density. The contribution of the metallic Ti substrate may be attributed to a modest increase in the predicted carrier concentration from the M -S plot for all TNTA electrodes when compared to literature values. Furthermore, the N<sub>D</sub> of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> is significantly higher than that of the TNTA/Sb<sub>2</sub>S<sub>3</sub> electrode. As the N<sub>D</sub> of TNTA-Ag is higher than that of TNTA, hence increased charge carrier density and reduced charge recombination upon Ag doping together with efficient light harvesting of Sb<sub>2</sub>S<sub>3</sub> coated TNTA-Ag and light scattering are the major contributing factors for the photocurrent enhancement of TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> which is shown schematically in Fig. 9.

#### 4. Conclusion

As per our knowledge, for the first time we have successfully designed and fabricated Ag<sup>+</sup> ion doped TNTA and the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanodes on porous Ti mesh for water splitting reaction using a simple electrochemical and spin coating technique. We were able to achieve a photocurrent density of  $6.5 \text{ mA cm}^{-2}$  vs. RHE which is 1.8 and 24 times compared to the TNTA/Sb<sub>2</sub>S<sub>3</sub> and bare TNTA photoanodes respectively. While 3.6% of ABPE was achieved for the Ag ion incorporated TNTA/Sb<sub>2</sub>S<sub>3</sub> photoanode at 0.65 V vs RHE. The enhanced PEC performance is dependent on the increased electrical conductivity of Ag ion-doped TNTA/Sb<sub>2</sub>S<sub>3</sub> which promotes photoelectrochemical water splitting by maintaining a favorable environment for charge carrier separation and transfer which is results in the formation of high density of surface oxygen vacancies, allowing for the efficient trapping of photogenerated charge carriers and promoting charge carrier separation, thereby increasing charge transfer kinetics, as well as light harvesting. Furthermore, the TiO2 NT produced in the porous of curved Ti metal mesh might improve light harvesting by effective light trapping as well as enhanced catalytic active sites. Overall, the improved PEC



Fig. 9. Schematic diagram showing the synergistic effect of Ag<sup>+</sup> and Sb<sub>2</sub>S<sub>3</sub> on the PEC performance (a) TNTA and (b)TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub>.

performance can be attributed to the synergistic effects of increased electrical conductivity and enhanced excited charge carrier separation of Ag<sup>+</sup> ion-doped TNTA, increased light trapping, and high optical activity of stibnite (Sb<sub>2</sub>S<sub>3</sub>). Moreover, despite of the significant photostability of the TNTA-Ag/Sb<sub>2</sub>S<sub>3</sub> photoanode, more long-term research is required to assess the stability of the photoanode. This study emphasizes the promise of this innovative composite material for improved energy conversion applications.

#### CRediT authorship contribution statement

**Chathuranga N. Wijerathna:** Writing – original draft, Methodology, Investigation. **Hong-yi Tan:** Writing – review & editing, Methodology, Investigation. **Chang-Feng Yan:** Writing – review & editing, Writing – original draft, Funding acquisition. **Jayasundera Bandara:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interest sor personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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