**Vertically aligned Nitrogen doped (Sn,Nb)O₂ nanotubes – robust photoanodes for
hydrogen generation by Photoelectrochemical Water Splitting**

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Article type: Full Paper

Abstract:

Hydrogen generation from photoelectrochemical (PEC) water splitting is on the forefront of clean energy generation landscape. The efficiency of PEC system is dependent on the engineering of semiconductors with tailored narrow band gap coupled with superior photoelectrochemical activity and desired stability vital for the commercialization of PEC water splitting cells. We report herein the study of vertically aligned Nb and N doped SnO₂ nanotubes (NTs), i.e., (Sn_{0.95}Nb_{0.05})O₂:N NTs for PEC water splitting. (Sn_{0.95}Nb_{0.05})O₂ NTs was selected for co-doping with nitrogen by systematic analysis of applied bias photon-to-current efficiency of various Nb doped SnO₂ (x=0-0.1) compositions. Consequently, excellent photoelectrochemical stability and the highest efficiency of 4.1% is obtained for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs never observed for other known TiO₂, ZnO, and Fe₂O₃ systems to date. Additionally, theoretical first principles study provides understanding of Nb and N co-doping on the electronic structure and band gap of SnO₂ semiconductor, further corroborating results of experimental study.

Keywords:

Photoelectrochemical water splitting, nanotubes, tin oxide, doped metal oxide, nitrogen doping

1. Introduction

Clean renewable energy generation is quintessential for the sustainable development of the energy famished industrial world. It is a known fact that the predominant energy sources fueling the present energy driven economy (primarily carbon based fuels) are expected to run out by the year 2200.[1] Thus the impetus for switching to non-carbon based renewable energy

sources. This motivation is further hastened by the seemingly irreversible anthropogenic alteration of the earth's climate resulting in the global eco-system alteration threatening the extinction of myriad species, amphibious, aerial as well as terrestrial.[2, 3] Currently, the global energy demand is being addressed on an industrial scale by the combustion of carbonaceous fossil fuels. However, this approach is not sustainable as it has deleterious effects on the environment unfortunately, due to excessive greenhouse gas emissions, which has necessitated the identification of non-carbonaceous fuel, capable of meeting the future global energy demand.[4-9] This fuel should be easy to store, handle, transport and more importantly, economical to produce. In consideration of all of these aspects, hydrogen has been identified as the most promising energy source replacing Gasoline, on the grounds of its high energy density (120 MJ kg^{-1} for H_2 higher than 44.4 MJ kg^{-1} for Gasoline) and environmentally benign nature (low carbon footprint).[6-8, 10-16] However, there are many roadblocks for commercializing hydrogen as a fuel. These include not only economic production and storage but also efficient distribution of hydrogen all of which pose major challenges.

At present, hydrogen is produced on an industrial scale by steam reforming of natural gas.[7, 10, 14] Other widely used methods for hydrogen production include partial oxidation of hydrocarbons and coal gasification. The drawbacks of these processes are the high operating temperature (700°C - 1000°C) and production of CO_2 -undesired greenhouse pollutant.[7, 10, 14] Hence, alternate technology involving the use of clean fuel (low carbon footprint), low operating temperature without any greenhouse gas emissions and toxic/corrosive byproduct should be employed for efficient and economic production of hydrogen.[13]

A promising and environmentally benign approach for the generation of hydrogen is the **splitting of water**. This approach has received significant attention, as it does not involve any greenhouse gas emissions and moreover, any corrosive byproduct.

However, splitting of water for H₂ production is associated with a major activation energy barrier, requiring external energy ($\Delta G^0=237.13 \text{ kJ mol}^{-1}$). [17] To overcome this activation barrier, the utilization of solar energy delivering an energy of 120,000 TW per year to the surface of the earth alone [18, 19] for splitting water has received special interest. [5, 13] The deconcentrated, ubiquitous, and illimitable solar energy has been thus considered as an economic and viable natural energy source for a long time now, and can be utilized as an external energy source for the water splitting. Solar energy induced water splitting, alternatively also known as photoelectrochemical water splitting, i.e., PEC water splitting is considered to be an attractive and environmentally benign approach primarily because it involves production of hydrogen driven by the electricity produced from the absorption of solar energy resulting in the production of mobile charge carriers by a suitable semiconductor material. [16] Fujishima and Honda's pioneering work on PEC water splitting using n-type TiO₂ semiconductor has demonstrated for the first time that PEC water splitting using semiconductor material is indeed a promising approach for the production of hydrogen in an environmentally friendly manner. [13, 20]

The commercialization of PEC water splitting systems as an industrial process for the production of hydrogen has been largely hindered by the scarcity of an ideal semiconductor material exhibiting excellent absorption of light in the visible region of interest, excellent PEC stability for long term operation and high photoelectrochemical activity. [21, 22] A major part of

the solar spectrum consists of visible light (~46%) and ~4% of UV radiation.[13] Hence, it is important to develop semiconductor materials with superior capability for visible light absorption. The ideal semiconductor material, which can be used as photoanode in PEC water splitting, should exhibit narrow band gap ($1.23 \text{ eV} < E_g < 3 \text{ eV}$), high electrical conductivity, and the correct band structure such that oxidation (1.23V) and reduction potential of water (0V) lie within the band gap of the material.[13] Thus far, extensive work has been conducted on metal oxide semiconductors such as TiO_2 , ZnO and Fe_2O_3 , mainly due to their low cost and ease of availability.[7, 12, 21, 23-32] The wide band gap of TiO_2 (~3.2 eV) is one of the major constraints for its use as a photoanode in the commercialization of PEC water splitting cells.[33-36] The photocatalytic activity of Fe_2O_3 is also limited by the short lifetime and diffusion length of the photogenerated carriers, high resistivity, low electron mobility and high recombination rate of photo-generated charge carriers [37, 38] Also, the photoelectrochemical activity of ZnO is limited by poor light absorption in the visible region of interest due to the wide band gap (~3.2 eV) and poor long term stability in the aqueous electrolyte solution.[39] Hence, there is a need to develop a novel semiconductor material, which will satisfy the criteria mentioned above for the ideal semiconductor material.

In addition to TiO_2 , ZnO and Fe_2O_3 , SnO_2 is also a promising semiconductor, widely explored in dye sensitized solar cells (DSSCs) and as a transparent conducting oxide (TCO). It has good electron mobility and is highly corrosion resistant in the acidic electrolyte solution.[40-42] The electron mobility of SnO_2 ($\sim 100\text{-}200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is also orders of magnitude higher than that of TiO_2 ($\sim 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).[43, 44] The superior electron mobility is expected to help in fast electron transport from the semiconductor material to the current collector for SnO_2 . [44] However, similar to ZnO , SnO_2 also has a wide band gap of ~3.5 eV[45], as a result of which

reports on the use of SnO_2 as a photoanode for PEC water splitting are scant apart from reports on band gap engineering of SnO_2 by design of heterostructures of $\text{SnO}_2/\text{TiO}_2/\text{CdS}$, SnO_2/CdS and $\text{SnO}_2/\text{TiO}_2$ [46-49]. Use of SnO_2 as a photoanode for PEC water splitting thus necessitates systematic band gap engineering by suitable doping for improving the photoelectrochemical activity of SnO_2 . This approach will help in lowering the band gap energy of SnO_2 offering improved light absorption, which is extremely important for its use as semiconductor material in PEC water splitting.

Niobium is a well-studied dopant for SnO_2 for use in TCO applications mainly to improve the electrical conductivity of SnO_2 . [50-53] Niobium is considered as an effective dopant due to its abundant electronic states and minor influence on SnO_2 lattice structure, due to the lower ionic radii of Nb^{4+} (69 pm) compared to Sn^{4+} (71 pm), resulting in minimum lattice strain. [54, 55] The doping of Nb in SnO_2 is expected to introduce additional electronic states of Nb in the band gap of SnO_2 , thus reducing the band gap of SnO_2 . The wide band gap of SnO_2 is mainly due to the deep location of the valence band position (O 2p orbital) at high potential. [17] This issue can be addressed by the systematic upward shift of the valence band, without affecting the position of the conduction band that can be achieved by the introduction of a suitable dopant modifying accordingly the SnO_2 electronic structure. In this study thus keeping in line with the above analysis, nitrogen is also used in combination with niobium as a co-dopant for SnO_2 . Since N 2p orbitals have higher potential energy than O 2p orbitals, introduction of N in SnO_2 can offer hybridization of substitutional N 2p states with O 2p states causing a shift in the valence band (i.e. highest occupied molecular orbital, HOMO) upwards, without affecting the conduction band (i.e. lowest unoccupied molecular orbital, LUMO) [7], thereby, reducing the band gap and improving the light absorption. [17, 56-59] The physical morphology and orientation of the

135 nanostructure of doped SnO_2 is important as it affects the charge transport in the oxide. The
136 vertical orientation of nanostructure has received special attention as it offers high surface area
137 which provides large area for electrolyte-electrode contact and an efficient path for transport of
138 photogenerated carriers in the material.[60-62]

139 In this context, we report herein the photoelectrochemical performance of vertically
140 aligned nanotubes of Nb and N doped SnO_2 , denoted as $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2:\text{N}$ VANTs, as potential
141 photoanodes or semiconductor materials. The identification of an optimized concentration of
142 dopants is important for tailoring the band structure of SnO_2 . Though a high concentration of
143 dopant is desired, as it is expected to offer reduction in the band gap and thus, improved light
144 absorption, the additional dopant induced electronic states introduced in SnO_2 can act as
145 recombination sites for the photogenerated electron-hole pairs, resulting in poor PEC
146 performance and low applied bias photon-to-current efficiency (ABPE), in comparison to pure
147 SnO_2 . [56, 63] Hence, in this study, first, various compositions of Nb doped SnO_2 VANTs, i.e.,
148 $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ VANTs ($x=0, 0.05, 0.1$) were synthesized using ZnO nanowires (NWs) as a
149 sacrificial template[64, 65] and their photoelectrochemical activity was assessed to select a
150 composition exhibiting superior ABPE. The photoelectrochemical activity of the selected
151 composition of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ VANTs was then further improved by N-doping, which was
152 achieved by heat treatment in NH_3 atmosphere at different temperatures of 400°C , 500°C , 600°C
153 and 700°C , respectively. The heat treatment was carried out at different temperatures, in order, to
154 study the effect of concentration of nitrogen co-doped into $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ VANTs on the
155 resultant optoelectronic and photoelectrochemical properties.[7, 66, 67]

156 The influence of Nb and N co-doping on the electronic structure and the band gap in
157 particular, is also studied by conducting theoretical first principles calculations in this study to

corroborate and support the experimental results. To the best of our knowledge, study of photoelectrochemical activity of vertically aligned $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2:\text{N}$ VANTs ($x=0.05$) as photoanodes for PEC water splitting has not yet been reported to date. Thus, the present report documents the theoretical and experimental studies conducted on evaluating the photoelectrochemical performance of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2:\text{N}$ VANTs ($x=0.05$) as potential photoanodes for PEC water splitting with the aim of achieving efficient hydrogen generation and high photon-to-current efficiency from PEC water splitting.

2. Results and discussion

The doping strategy executed in this study, primarily utilizing Nb and N, as potential dopants for SnO_2 , is expected to improve the photoelectrochemical activity of SnO_2 , due to a reduction in the optical band gap of SnO_2 and thus leading to improved light absorption. As mentioned earlier, beyond an optimum concentration of the dopant, the additional electronic levels contributed by the dopants can facilitate the recombination of photogenerated carriers, resulting in poor photoelectrochemical activity of doped SnO_2 NTs.[56, 63] In recognition of this phenomenon, $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ NTs ($x=0.05, 0.1$) were synthesized by hydrothermal approach and tested as a photoanode primarily to select an optimal composition of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ NTs exhibiting superior photoelectrochemical activity, in comparison to undoped SnO_2 NTs.

2.1. Characterization of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ NTs ($x=0, 0.05, 0.1$)

X-ray diffraction study

The XRD patterns of pure SnO₂ and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) are shown in **Fig. 1**. The XRD pattern of pure SnO₂ NTs reveals presence of pure SnO₂ with tetragonal structure (JCPDS 41-1445). The XRD patterns of (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) show peaks corresponding to SnO₂ with tetragonal structure without any peaks corresponding to niobium or niobium oxide, suggesting the formation of doped SnO₂ NTs. The values of molar volume and lattice parameters of (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1), calculated using least square refinement technique are shown in **Table 1**. The lattice parameter and molar volume of pure SnO₂ NTs is a=b=4.738Å, c=3.187Å and 21.54 cm³ mol⁻¹, respectively, which is similar to that reported earlier.[68] The decrease in lattice parameter and molar volume is observed with increase in niobium concentration. This suggests lattice contraction possibly due to the ionic radius of Nb⁴⁺ (69 pm) being smaller than Sn⁴⁺ (71 pm), facilitating easy replacement of Sn⁴⁺ with Nb⁴⁺ with minimum lattice distortion.[54, 55]

UV-vis absorption study and Tauc analysis of (Sn_{1-x}Nb_x)O₂ NTs (x=0, 0.05, 0.1)

The optical properties of pure SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) studied using UV-visible absorption spectra are shown in **Fig. 2a**. The UV-vis absorption spectrum of pure SnO₂ NTs shows the onset of light absorption at ~350 nm, which is similar to that reported earlier.[69, 70] The red-shift in light absorption to the visible region of interest is observed for (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) which increases with increase in Nb content. Improved light absorption with increase in Nb content suggests decrease in the band gap of (Sn_{1-x}Nb_x)O₂ NTs, with increase in Nb content. The band gap of pure SnO₂ and (Sn_{1-x}Nb_x)O₂ NTs is calculated from the Tauc analysis, shown in **Fig. 2b**, the band gap being estimated from the x-intercept of $(\alpha h\nu)^2$

vs $h\nu$ curves. The values of the band gap are shown in **Table 2**. The band gap of pure SnO₂ NTs is 3.53 eV, which is similar to that reported earlier.[71-73] The reduction in band gap is observed with increase in Nb content, which is primarily responsible for the improved light absorption for (Sn_{0.9}Nb_{0.1})O₂ NTs, compared to pure SnO₂ and (Sn_{0.95}Nb_{0.05})O₂ NTs. The improvement in light absorption is important since it results in more number of photogenerated electrons vital for the hydrogen evolution reaction (HER).

Mott-Schottky analysis of (Sn_{1-x}Nb_x)O₂ NTs (x=0, 0.05, 0.1)

The electronic properties of pure SnO₂ NTs and doped forms, (Sn_{1-x}Nb_x)O₂ NTs are studied using Mott-Schottky analysis, performed in 0.5 M H₂SO₄ as the electrolyte solution at 26°C under dark conditions. The carrier density and flat band potential at the nanotubes/electrolyte interface are determined by the Mott-Schottky equation[34]:

$$1/C^2 = (2/e_0\epsilon\epsilon_0N_d)[(V-V_{FB})-kT/e_0]$$

where, e_0 is the electron charge, ϵ is the dielectric constant of SnO₂ (taken as 13)[74, 75] ϵ_0 is the permittivity of vacuum, N_d is the dopant/carrier density, V is the applied electric potential, V_{FB} is the flat band potential, k is the Boltzmann constant, T is the absolute temperature (299 K). The Mott-Schottky plots of SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs are shown in **Fig. 2c**. The flat band potential (V_{FB}) of pure and doped SnO₂ NTs is found from the x-intercept in Mott-Schottky plots ($1/C^2$ vs V). For undoped SnO₂ NTs, V_{FB} is ~0.05 V (vs RHE), while V_{FB} for (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) are ~(-0.08 V) and ~(-0.1 V) (vs RHE), respectively. Thus, V_{FB} of (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) is more negative than the standard reduction potential of water (0 V), indicating that the band edge of (Sn_{1-x}Nb_x)O₂ NTs is more negative than the standard reduction potential of water. A more negative V_{FB} is thus expected to offer efficient separation of the

photogenerated carriers at the semiconductor-electrolyte interface due to improved band bending at the semiconductor surface.[76-78] This is expected to offer a large driving force to the photogenerated electrons resulting in improved photocurrent density.[76-78] The carrier density is calculated from the slope determined from the Mott-Schottky plot using the following equation:

$$N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1} \dots\dots\dots(1)$$

The positive slope obtained in Mott-Schottky plots indicate n-type behavior for pure SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs. The carrier density, determined from the slope of Mott-Schottky plot, for pure SnO₂ and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1), is 2.42×10¹⁸ cm⁻³, 4.2×10¹⁹ cm⁻³ and 5.52×10¹⁹ cm⁻³, respectively (**Table 2**). This shows that increase in Nb concentration in SnO₂ NTs leads to an almost one order increase in carrier density in comparison to undoped SnO₂ NTs.

Photoelectrochemical characterization of (Sn_{1-x}Nb_x)O₂ NTs (x=0, 0.05, 0.1)

The superior photoelectrochemical activity is expected for (Sn_{1-x}Nb_x)O₂ NTs (x=0.1) due to its lower band gap facilitating superior light absorption (as seen in UV-vis absorption spectra shown in **Fig. 2a** and Tauc analysis in **Fig. 2b**) and increased carrier density (determined from Mott-Schottky plots in **Fig. 2c**) than pure SnO₂ and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05) (**Table 1** and **Table 2**). The photoelectrochemical activity of pure SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) is studied in 0.5 M H₂SO₄ as the electrolyte solution using a 300 W xenon lamp (Model 6258, Newport) equipped with an AM1.5G filter (Model 81094, Newport) used to simulate the solar spectrum. **Fig. 2d** shows the uncorrected and iR_Ω linear scan voltammogram (LSV) curves [R_Ω, the ohmic resistance was determined from electrochemical impedance spectroscopy (EIS) analysis discussed in detail later] of SnO₂ and (Sn_{1-x}Nb_x)O₂ NTs, in the dark and with

illumination of 100 mW cm^{-2} obtained with a scan rate of 1 mV sec^{-1} . The LSV curve for pure SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs in the dark showed a small background current of $\sim 10^{-3}$ mA cm^{-2} . Pure SnO₂ NTs showed poor photoelectrochemical activity with onset potential of 0.28 V (vs RHE) and photocurrent density of ~ 0 mA cm^{-2} at 0.75 V mainly due to its wide band gap (3.53 eV as shown in **Table 2**). In comparison to pure SnO₂ NTs, (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) exhibit superior photoelectrochemical activity with an onset potential of 0.17 V (vs RHE) and showed improved photocurrent density of 0.17 mA cm^{-2} and 0.1 mA cm^{-2} at 0.75 V in iR_{Ω} corrected LSV plot, respectively (**Fig. 2d** and **Table 2**). The improved photocurrent density for (Sn_{1-x}Nb_x)O₂ NTs compared to SnO₂ NTs can be attributed to the lower band gap offering improved light absorption (as seen in the UV-vis absorption spectra shown in **Fig. 2a** and Tauc analysis in **Fig. 2b**) and increased carrier density (as found from Mott-Schottky plot in **Fig. 2c**). The LSV curves do not show saturation in photocurrent density possibly due to efficient separation of photogenerated carriers upon illumination at higher potential (**Fig. 2d**).[7, 34, 79-82] It is noteworthy that (Sn_{0.95}Nb_{0.05})O₂ NTs (0.17 mA cm^{-2}) exhibit 1.7 times higher photocurrent density than (Sn_{0.9}Nb_{0.1})O₂ NTs (0.1 mA cm^{-2}) at 0.75 V in the iR_{Ω} corrected LSV plot. This indicates that (Sn_{0.95}Nb_{0.05})O₂ NTs exhibit improved reaction kinetics compared to pure SnO₂ NTs and (Sn_{0.9}Nb_{0.1})O₂ NTs, which is confirmed from electrochemical impedance spectroscopy (EIS) (**Fig. 2f**). The low frequency EIS plots of SnO₂ and (Sn_{1-x}Nb_x)O₂ (x=0.05, 0.1), shown in **Fig. 2f**, show a well formed semicircle, which can be related to the water oxidation reaction. The diameter of the low frequency semicircle, which is a measure of the charge transfer resistance (R_{ct}) and thus, the photoelectrochemical activity of the semiconductor material of (Sn_{0.95}Nb_{0.05})O₂ NTs (68.2 $\Omega \cdot \text{cm}^2$) is lower than (Sn_{0.9}Nb_{0.1})O₂ NTs (84.2 $\Omega \cdot \text{cm}^2$) and pure SnO₂ NTs (92 $\Omega \cdot \text{cm}^2$) (**Table 3**) indicating improved reaction kinetics due to relatively

efficient separation and thus, minimum recombination of photogenerated carriers for (Sn_{0.95}Nb_{0.05})O₂ NTs than pure SnO₂ NTs and (Sn_{0.9}Nb_{0.1})O₂ NTs.[81, 82] As mentioned earlier, it is expected that (Sn_{0.9}Nb_{0.1})O₂ NTs will likely exhibit higher photocurrent density due to the lower band gap with improved light absorption and increased carrier density than SnO₂ and (Sn_{0.95}Nb_{0.05})O₂ NTs [Fig. 2 (a-c) and Table 2]. However, higher photocurrent density for (Sn_{0.95}Nb_{0.05})O₂ NTs is obtained compared to (Sn_{0.9}Nb_{0.1})O₂ NTs and this is likely as a result of the significantly lower charge-transfer resistance (i.e. more facile electron transfer kinetics) (Fig. 2f and Table 3).

Following the recently published paper by Coridan et al. [83] in accordance with IUPAC nomenclature, the solar-to-hydrogen efficiency (STH) of photoanode materials is defined as a term to be used in the absence of bias (for zero applied potential, V = 0) and in the presence of bias, the efficiency is considered as “applied bias photon-to-current efficiency (ABPE)”, which is calculated using the equation[83-85]:

$$ABPE = I(1.23 - V) \times 100 / J_{\text{light}} \dots \dots \dots (2)$$

where, I is the photocurrent density at the measured potential, V is the applied potential and J_{light} is the illumination intensity of 100 mW cm⁻². The variation of ABPE with the applied potential is shown in Fig. 2e. (Sn_{0.95}Nb_{0.05})O₂ NTs exhibit maximum ABPE of 0.088% at 0.82 V. The maximum ABPE obtained for (Sn_{0.95}Nb_{0.05})O₂ NTs is higher than that for SnO₂ (0.008% at 0.9 V) and even (Sn_{0.9}Nb_{0.1})O₂ NTs (0.051% at 0.82 V), respectively (Table 2). The lower ABPE for (Sn_{0.9}Nb_{0.1})O₂ NTs compared to (Sn_{0.95}Nb_{0.05})O₂ NTs as mentioned above is thus likely due to the inferior reaction kinetics compared to (Sn_{0.95}Nb_{0.05})O₂ NTs (Fig. 2f and Table 3).

Based on the above analysis, although (Sn_{0.95}Nb_{0.05})O₂ NTs offeres improved ABPE than pure SnO₂ and (Sn_{0.9}Nb_{0.1})O₂ NTs, the ABPE achieved for (Sn_{0.95}Nb_{0.05})O₂ NTs is still low and

far from the point of considering it in the commercialization range for PEC water splitting cell.[10, 86-90] Hence, it is necessary to improve the ABPE of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs with the aim of achieving efficient and economic production of hydrogen from PEC water splitting. This is achieved by co-doping $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs with nitrogen to lower the band gap further and thus achieve improved light absorption, which is expected to improve the ABPE due to increase in the photo-generated electrons available for HER.

2.2 Characterization of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2\text{:N}$ NTs ($x=0.05$)

X-ray diffraction study

The XRD patterns of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-500}$ NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs, shown in **Fig. 3 (a-b)**, show peaks corresponding to tetragonal SnO_2 without any peaks corresponding to Nb containing phase. The values of molar volume and lattice parameters of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, calculated using the least square refinement technique, are shown in **Table 1**. The increase in lattice parameter and molar volume is observed with increase in the temperature of heat treatment in NH_3 for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-500}$ NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs, suggesting incorporation of nitrogen into the $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs and also lattice expansion upon nitrogen doping (due to observed negative shift in **Fig. 3b**). [7, 91] However, the XRD pattern of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-700}$ NTs shows peaks corresponding to Sn and Nb, suggesting the reduction of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs possibly by the atomic hydrogen originating from the decomposition of NH_3 [34]. Hence, 600°C was used as the optimal temperature for ammonolysis.

SEM/EDAX and TEM study of (Sn_{1-x}Nb_x)O₂:N-600 NTs (x=0.05)

Scanning electron microscopy (SEM) has been carried out to study the morphology of the representative composition, (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs. SEM image showing top view and cross-sectional view of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs is shown in **Fig. 3c**, respectively. Cross-sectional view of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs show dense and vertically oriented nanotubes of diameter of 180-240 nm and length of ~14 μm. The SEM image of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs reveals well-spaced nanotubes with clean surface and without any particles at the top and bottom of nanotubes. Energy dispersive x-ray spectroscopy (EDAX) is conducted to confirm the presence of elements Sn, Nb and N and also, determine concentration of N in the (Sn_{0.95}Nb_{0.05})O₂:N NTs, heat-treated in NH₃ at different temperatures.[7, 92, 93] EDAX spectrum of representative composition, (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, shown in **Fig. 3c**, confirms the presence of elements Sn, Nb and N. Quantitative elemental composition analysis by EDAX of (Sn_{0.95}Nb_{0.05})O₂:N-400 NTs, (Sn_{0.95}Nb_{0.05})O₂:N-500 NTs and (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, shown in **Table 1**, shows increase in N concentration incorporated in (Sn_{0.95}Nb_{0.05})O₂ NTs with increase in temperature of heat treatment in NH₃. [7, 66, 67] TEM images of representative composition, (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, shown in **Fig. 3d** reveals the geometry of hollow nanotube with diameter of ~180-220 nm.

X-ray photoelectron spectroscopy study of (Sn_{1-x}Nb_x)O₂:N NTs (x=0.05)

To determine the oxidation state of Sn, Nb and N, x-ray photoelectron spectroscopy (XPS) was carried out on (Sn_{0.95}Nb_{0.05})O₂:N NTs of different N concentration and pure SnO₂

NTs. The XPS spectrum of Sn (**Fig. 4a**) of pure SnO₂ shows the presence of Sn 3d_{3/2} and 3d_{5/2} doublet centered at ~495.37 eV and ~486.95 eV, corresponding to Sn⁴⁺. [94] The negative shift in binding energy of Sn 3d_{3/2} and 3d_{5/2} doublet is observed for (Sn_{0.95}Nb_{0.05})O₂:N NTs, which increases with increase in N concentration, which is consistent with previously reported results for N-doped TiO₂ nanoparticles. [95] In accordance with the previously reported results on N-doped TiO₂ nanoparticles [95], the negative shift in Sn 3d_{3/2} and 3d_{5/2} doublet for (Sn_{0.95}Nb_{0.05})O₂:N NTs can be assigned to change in electron density around Sn⁴⁺ due to Nb and N co-doping and thus, indicates modification in the electronic structure of SnO₂ NTs by Nb and N co-doping. [7, 95] The XPS spectrum of N, shown in **Fig. 4b**, shows the presence of N 1s peak centered at ~398.3 eV for (Sn_{0.95}Nb_{0.05})O₂:N NTs of different N concentration. The N 1s peak at ~398.3 eV indicates the presence of oxynitride (O-Sn-N or O-Nb-N) for (Sn_{0.95}Nb_{0.05})O₂:N NTs. [7, 96, 97] This shows substitutional doping of N at O sites in the lattice of (Sn_{0.95}Nb_{0.05})O₂:N NTs. [7, 34] Furthermore, the N composition (determined by XPS) is ~14% for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, which is similar to that obtained from EDAX analysis. The XPS spectrum of Nb of (Sn_{0.95}Nb_{0.05})O₂:N NTs, shown in **Fig. 4c**, shows the presence of Nb 3d_{3/2} and Nb 3d_{5/2} doublet centered at ~210.4 and ~207.6 for (Sn_{0.95}Nb_{0.05})O₂:N-400 NTs, corresponding to Nb⁴⁺, respectively. [98, 99] The shift of Nb 3d_{3/2} and Nb 3d_{5/2} doublet to lower binding energy value by ~0.1 eV and ~0.2 eV is observed for both (Sn_{0.95}Nb_{0.05})O₂:N-500 NTs and (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, which suggests the presence of oxynitride (O-Nb-N) due to substitutional doping of N at the O sites. [7, 96]

UV-vis absorption study and Tauc analysis of (Sn_{1-x}Nb_x)O₂:N NTs (x=0.05)

The light absorption property of (Sn_{0.95}Nb_{0.05})O₂:N NTs corresponding to different N concentration is studied from the UV-vis absorption spectra, shown in **Fig. 5a**. The UV-vis

absorption spectra show excellent light absorption for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, compared to pure SnO_2 and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs. $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-500}$ NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs show superior light absorption than that of both pure SnO_2 and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs at 500 nm. 500 nm is chosen for comparison of the absorbance of semiconductor materials in this study, as it is closest to the wavelength at which maximum solar irradiance is reportedly obtained.[100] The light absorption in the visible region increases with increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, suggesting the reduction in the band gap due to N incorporation in $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs. Tauc analysis as conducted earlier for the non-nitrogen doped system is accordingly conducted to determine the band gap for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs. The values of the band gap determined from the Tauc analysis (**Fig. 5b**) are given in **Table 2**. As can be seen, reduction in the band gap is obtained with increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, as indicated in **Table 2**. Also, the band gap of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs is lower than that of pure SnO_2 NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs. It is thus noteworthy that the lowest band gap of 1.99 eV is achieved for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs, which is significantly lower than non-nitrogen containing $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs (3.1 eV) and SnO_2 NTs (3.53 eV), suggesting the beneficial role of Nb and N co-doping facilitating the reduction in the wide band gap of SnO_2 . This observed narrowing of the band gap for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs after N incorporation is mainly attributed to the hybridization of the substitutional N 2p states with O 2p states, which is expected to shift the valence band upwards, without affecting the conduction band thereby, reducing the band gap and improving the light absorption in the visible region of interest.[7, 17] The reduction in the band gap is important since it offers improved light absorption in the visible wavelength regime of use and thus creates the appropriate conditions providing more photogenerated carriers for HER.

Mott-Schottky analysis of (Sn_{1-x}Nb_x)O₂:N NTs (x=0.05)

The positive effect of incorporation of nitrogen in (Sn_{0.95}Nb_{0.05})O₂ NTs on the electronic properties is, as discussed earlier for the non-nitrogen containing systems, is again studied by Mott-Schottky analysis by performing EIS in the dark in 0.5 M H₂SO₄ electrolyte solution at 26°C. The Mott-Schottky plot of (Sn_{0.95}Nb_{0.05})O₂:N NTs for different N concentration is shown in **Fig. 5c**. The flat band potential (V_{FB}) for (Sn_{0.95}Nb_{0.05})O₂:N-400 NTs, (Sn_{0.95}Nb_{0.05})O₂:N-500 NTs and (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs determined from the x-intercept in Mott-Schottky plots ($1/C^2$ vs V) as obtained earlier for the non-nitrogen containing compositions, are $\sim(-0.2$ V), $\sim(-0.28$ V) and $\sim(-0.33$ V) (vs RHE), respectively. Thus, the values of V_{FB} of (Sn_{0.95}Nb_{0.05})O₂:N NTs for the different N concentration are more negative than the standard reduction potential of water (0 V), indicating more negative band edge position for the N containing compositions (Sn_{0.95}Nb_{0.05})O₂:N NTs than standard reduction potential of water (0 V). The positive slope obtained in the Mott-Schottky plots indicate n-type behavior for (Sn_{0.95}Nb_{0.05})O₂:N NTs. The carrier density is determined from the slope of Mott-Schottky plot using **Equation (1)** as before. The carrier density of (Sn_{0.95}Nb_{0.05})O₂:N-400 NTs, (Sn_{0.95}Nb_{0.05})O₂:N-500 NTs and (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs is 3.3×10^{22} cm⁻³, 4.05×10^{22} cm⁻³ and 4.7×10^{22} cm⁻³, which is 3-4 orders of magnitude higher than the carrier density for the identical non-nitrogen containing compositions, (Sn_{0.95}Nb_{0.05})O₂ NTs (4.2×10^{19} cm⁻³) and SnO₂ NTs (2.42×10^{18} cm⁻³) (**Table 2**). The carrier density of ($\sim 4.7 \times 10^{22}$ cm⁻³) obtained in this study for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs is in the range of that of hydrogen-treated TiO₂ nanowires ($\sim 2.1 \times 10^{22}$ cm⁻³)[77] which showed excellent photoelectrochemical activity with photoconversion efficiency of $\sim 1.63\%$ and WO₃ films with superior photoelectrochemical performance ($\sim 2.5 \times 10^{22}$ cm⁻³)[101, 102]. This result

therefore clearly demonstrates the potential of N doping in (Sn_{0.95}Nb_{0.05})O₂ NTs contributing to significantly enhancing the carrier density which is vital since this implies that a higher number of photogenerated electrons are available for HER (at cathode). The increased carrier density for (Sn_{0.95}Nb_{0.05})O₂:N NTs with increase in N concentration is expected to shift the Fermi level upwards towards the conduction band resulting in negative shift in V_{FB} (as discussed earlier) with increase in N concentration and thus resulting in increased degree of band bending with increase in N concentration.[7, 34, 76, 77, 79, 80, 103-107] This is expected to result in improved separation of photogenerated carriers at the interface between the (Sn_{0.95}Nb_{0.05})O₂:N NTs and the electrolyte solution, leading to improved photocurrent density and thus, superior ABPE for (Sn_{0.95}Nb_{0.05})O₂:N NTs, compared to pure SnO₂ NTs and Nb doped non-nitrogen containing composition, (Sn_{0.95}Nb_{0.05})O₂ NTs.[7, 34, 76, 77, 79, 80, 103-107]

IPCE of (Sn_{1-x}Nb_x)O₂:N NTs (x=0.05)

To study the effect of light absorption properties on the photoelectrochemical properties, incident photon to current efficiency (IPCE) was determined for (Sn_{0.95}Nb_{0.05})O₂:N NTs using different bandpass optical filters with wavelength centered at 350, 370, 400, 420, 450, 470, 500, 520, 550, 570 and 600 nm. The IPCE is calculated by the equation[108]:

$$\text{IPCE (\%)} = \frac{1240 \times J \times 100}{\lambda \times P}$$

where, J is the measured photocurrent density (mA cm⁻²), P is the incident light intensity (mW cm⁻²) at a specific wavelength (λ, nm). As shown in **Fig. 6a**, the IPCE value is observed to increase for (Sn_{0.95}Nb_{0.05})O₂:N NTs with increase in N concentration with the highest value obtained for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs at all the wavelengths considered. At 500 nm in fact, IPCE for (Sn_{0.95}Nb_{0.05})O₂:N-400 NTs, (Sn_{0.95}Nb_{0.05})O₂:N-500 NTs and (Sn_{0.95}Nb_{0.05})O₂:N-600

NTs is 2%, 7% and 10%, respectively. This relatively large increase in IPCE with increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs can be attributed to the lowering of the optical band gap which in turn leads to improved visible light absorption and increase in carrier density, thereby, resulting in enhanced charge separation, collection as well as conversion efficiency in the visible region of interest. Once again, it should be mentioned that the IPCE value of 10% obtained in this study for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs at 500 nm is indeed the highest IPCE value obtained for semiconductor materials explored so far for PEC water splitting to the best of our reported understanding.[21, 34, 77, 109] The analyses conducted thus far indeed shows that Nb and N co-doping together is a promising strategy for improving the photoelectrochemical activity of SnO_2 NT based systems.

Photoelectrochemical characterization of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2\text{:N}$ NTs ($x=0.05$)

The photoelectrochemical activity of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration is studied in 0.5 M H_2SO_4 as the electrolyte solution. **Fig. 6b** shows the uncorrected and iR_Ω (R_Ω , the ohmic resistance was determined from EIS analysis discussed in detail later) corrected linear scan voltammogram (LSV) curves of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs collected in the dark and with illumination of 100 mW cm^{-2} obtained at a scan rate of 1 mV sec^{-1} . The LSV curves generated in the dark showed a small current in the range of $\sim 10^{-3} \text{ mA cm}^{-2}$ for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs. However, an enhanced photocurrent density is observed for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs under illumination with onset potential of (-0.02V), (-0.02V) and (-0.14V) (*vs* RHE) for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -400 NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -500 NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs, respectively (**Table 2**). The onset potential for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs is lower than SnO_2 (0.28 V *vs* RHE), $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs (0.17 V *vs* RHE) (**Table 2**), indicating improvement in

455 photoelectrochemical activity due to N doping in $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs. Also, the decrease in the
 456 onset potential with increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs suggests the
 457 beneficial role of N in improving the photoelectrochemical activity. It is also again noteworthy to
 458 point out that the negative onset potential of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of (-0.14V vs RHE)
 459 obtained in this study for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs suggests that a very minimal bias would be
 460 required in converting solar energy to photocurrent density indicating superior utilization of solar
 461 energy in the production of hydrogen from water, an important aspect to be considered for
 462 commercialization of this novel system. The wide band gap of SnO_2 usually does not allow for
 463 such low onset potentials for water splitting under photo-chemical conditions. The tailoring of
 464 the band gap of SnO_2 by co-doping of Nb and N in this study thus results in this remarkable and
 465 highly attractive photo-electrochemical behavior. The photocurrent density at 0.75 V [chosen
 466 since the max. ABPE of 4.1% is obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs at 0.75 V discussed
 467 later] in the iR_Ω corrected LSV plot (**Fig. 6b**) for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs,
 468 $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-500}$ NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs is 6.76 mA cm^{-2} , 11.74 mA cm^{-2}
 469 and 25.39 mA cm^{-2} , respectively (**Table 2**). Thus, the photocurrent density at 0.75 V increases
 470 with progressive increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, with the maximum
 471 value obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs (25.39 mA cm^{-2}), which is $\sim 275\%$ and $\sim 116\%$
 472 higher than that obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs (6.76 mA cm^{-2}) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$
 473 500 NTs (11.74 mA cm^{-2}), respectively. This indicates the observed improved reaction kinetics
 474 and thus, photoelectrochemical activity with increase in N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$
 475 NTs. Hence, the reaction kinetics is further studied by determining charge transfer resistance
 476 (R_{ct}) from EIS of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs. R_{ct} is determined from the diameter of the low
 477 frequency semicircle and is shown in **Table 3**. As seen in **Fig. 2f**, R_{ct} for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs

decreases with increase in N concentration with the lowest R_{ct} obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs composition ($15.3 \text{ } \Omega\cdot\text{cm}^2$), indicating improved reaction kinetics with increase in N concentration. Also, R_{ct} for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs ($15.3 \text{ } \Omega\cdot\text{cm}^2$) is almost six-fold lower than pure SnO_2 ($92 \text{ } \Omega\cdot\text{cm}^2$) and $(\text{Sn}_{0.9}\text{Nb}_{0.1})\text{O}_2$ NTs ($84.2 \text{ } \Omega\cdot\text{cm}^2$) and five-fold lower than $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs ($68.2 \text{ } \Omega\cdot\text{cm}^2$) (**Table 3**). These results concomitantly show the excellent reaction kinetics and thus expectedly improved photoelectrochemical activity for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs, in comparison to SnO_2 NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs, $(\text{Sn}_{0.9}\text{Nb}_{0.1})\text{O}_2$ NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-400}$ NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-500}$ NTs. The lower R_{ct} obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs can be attributed to the efficient charge separation and thus, minimum recombination of photogenerated carriers, as seen in the IPCE analysis (**Fig. 6a**) [81, 82]. Interestingly, there was no saturation seen in photocurrent density at higher potential under illumination, possibly due to efficient separation of photogenerated carriers (**Fig. 6b**).[7, 34, 79-82]

The photocurrent density at 0.75 V in iR_{Ω} corrected LSV plot (**Fig. 6b**) for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs is significantly higher than that of pure SnO_2 NTs ($\sim 0 \text{ mA cm}^{-2}$) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs (0.17 mA cm^{-2}), suggesting remarkably improved photoelectrochemical activity of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs after N doping. Thus the excellent photoelectrochemical activity of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs which increases with increase in N concentration with maximum value obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs can be attributed to the decrease in the band gap (as seen in the Tauc analysis in **Fig. 5b** and **Table 2**) and thus, improved light absorption (as seen in the UV-vis absorption spectra in **Fig. 5a**), increase in carrier density (as perceived in the Mott-Schottky analysis in **Fig. 5c** and **Table 2**), improved charge separation, transport and collection (as observed in the IPCE analysis in **Fig. 6a**) and improved electrochemical charge transfer (as

witnessed in the EIS plots obtained under illumination in **Fig. 2f** and **Table 3**) with increase in N concentration.[7]

The variation of applied bias photon-to-current efficiency (ABPE) for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ NTs, calculated using **Equation (2)** with applied potential is shown in **Fig. 6c**. The maximum ABPE observed for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -400 NTs, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -500 NTs and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -600 NTs is 1.83%, 2.29% and 4.1% at 0.78 V, 0.78 V and 0.75 V, respectively. These results indicate that the ABPE obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ NTs is 100-1000 order of magnitude higher than that for SnO_2 NTs (0.008% at 0.9 V) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs (0.088% at 0.82 V) clearly pointing towards the beneficial role of Nb and N co-doping simultaneously leading to significant improvement in the ABPE of SnO_2 NTs. The impressive progression seen here can be gauged from the fact that the highest ABPE obtained in this study for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -600 NTs (4.1% at 0.75 V) is correspondingly ~124% and ~79% higher than that of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -400 NTs (1.83% at 0.78V) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -500 NTs (2.29% at 0.78V), respectively. These results therefore validate the implementation of N as a potential dopant in improving the photoelectrochemical activity of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$ NTs.

It is also important to note that the ABPE of 4.1% obtained in this study for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2:\text{N}$ -600 NTs (at 0.75 V) is the highest ABPE obtained so far compared to other semiconductor materials studied as photoanode for PEC water splitting such as TiO_2 , ZnO and Fe_2O_3 , to the best of our assessment of the widely reported literature to date.[7, 77, 110-112] These excellent and unprecedented results clearly show the potential of Nb and N co-doping leading to significantly improving the photoelectrochemical activity and ABPE of SnO_2 NTs, as evidenced in above studies.

Photoelectrochemical stability of (Sn_{1-x}Nb_x)O₂:N NTs (x=0.05)

It is important that in addition to the excellent photoelectrochemical activity discussed above, the semiconductor materials need to also exhibit adequate and acceptable long term photoelectrochemical stability for use of these systems in PEC water splitting cell. Hence, accordingly, chronoamperometry (CA) test has been carried out for 24 h to study the long term photoelectrochemical stability of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs under illumination in the electrolyte solution. The CA test is carried out at a constant potential of 0.75 V (at which the max. ABPE is obtained, as shown in **Fig. 6c** and **Table 2**) in 0.5 M H₂SO₄ solution by illuminating the photoanode for 24 h. The corresponding CA curve of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs is shown in **Fig. 7a**. A very minimal loss in photocurrent density is observed for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs indicating excellent photoelectrochemical stability of the co-doped system. In addition, the CA curve obtained under light ON/OFF cycles shows instantaneous photoresponse of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs under illumination and also, displays superior photoelectrochemical stability with negligible loss in photocurrent density (**Fig. S1** in **Supporting information**). After 24 h CA test, LSV is carried out (**Fig. 7b**) to study and determine any potential loss in photoelectrochemical activity of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs and accordingly, ensure that the system undergoes no degradation and exhibits similar photoelectrochemical activity prior to the start of the CA test. Accordingly, LSV collected after 24 h CA test shows negligible loss in photoelectrochemical activity of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, suggesting the excellent photoelectrochemical stability of the co-doped system obtained following ammonolysis at 600°C. The ICP analysis conducted on the electrolyte solution collected after CA test does not show the presence of Sn and Nb for the (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs. This result is a further testimonial affirming the excellent photoelectrochemical stability of

(Sn_{0.95}Nb_{0.05})O₂:N-600 NTs in the electrolyte solution under illumination of 100 mW cm⁻² indicating the ability of the system to be deployed for long term operation in PEC water splitting cell.

Measurement of H₂ and O₂ gases under illumination for (Sn_{1-x}Nb_x)O₂:N-600 NTs (x=0.05)

Measurement of the concentration of H₂ and O₂ gases generated at the cathode and photoanode, respectively serves as a measure of the efficiency of the system and is thus carried out to ensure that the photocurrent is indeed arising from water splitting. Hence, during CA test of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs at constant potential of 0.75 V, the concentration of the gases generated were measured after 1 h intervals by gas chromatography. Additionally, the theoretical concentration of H₂ gas is calculated from the measured photocurrent using the Faraday's law as under[108]:

$$\text{No. of moles of H}_2 = \frac{Q}{2F} = \frac{It}{2F} = \frac{\int_0^t I.d\tau}{2F}$$

where, I is the photocurrent density, t is time, F is the Faraday constant (96484.34 C mol⁻¹) and Q is the quantity of charge in coulomb. The concentration of H₂ and O₂ gases evolved is correspondingly shown in **Fig. S2 (Supporting information)**. As shown in **Fig. S2**, the theoretical amount of evolved H₂ gas is closer or comparable to the measured amount of H₂, suggesting ~100% Faradaic efficiency. If the decomposition of water is non-stoichiometric, there will be change in concentration of either H⁺ or OH⁻ ions. However, in this study, the ratio of concentration of generated H₂ and O₂ gases is ~2, as seen in **Fig. S2** and also, there was no change observed in the pH of the electrolyte solution (~0) before and after water splitting reaction, an extremely important aspect further confirming the efficiency of the novel system.

This result thus shows the expected stoichiometric decomposition of water into H₂ and O₂ in the present study for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs serving to demonstrate the promise of this uniquely engineered system.

2.3 Results of the computational study

Pure SnO₂

It should be noted that the electronic structure of pure SnO₂ is ubiquitously discussed in the literature[113-115] from a theoretical perspective. Nevertheless, in the context of the present work it is logical to describe the electronic structure of SnO₂. In addition the electronic structure of pure SnO₂ will be used for illustrating the combined Nb- and N-doping effects on the SnO₂ electronic structure.

The total and projected densities of electronic states calculated for pure SnO₂ are thus shown in **Fig. 8a**. The main energy band structure of SnO₂ consists of three bands, low energy oxygen 2s states (~-18.9 to -16.4 eV), wide valence band (-7.9 to 0.0 eV) consisting of hybridized O-2p – Sn-5s, -5p states (forming three sub-bands with O-2p – Sn-5s, O-2p – Sn-5p, and the non-hybridized O-2p states, respectively) and the conduction band consisting mainly of Sn-5s states (lower band) and Sn-5p states (upper band) with relatively small admixture of the oxygen 2s- and 2p- states. The energy gap separating the top of the valence band from the bottom of the conduction band of the Sn-5s character, is equal to 1.12 eV. Due to the well-known intrinsic characteristic limitation of DFT (on account of self-interaction effects and derivative discontinuities of the exchange correlation energy), the value of the forbidden gap is underestimated substantially in comparison to the experimental measured value of 3.53 eV (see **Table 4**). Since the goal of the current study is to compare the general trends of the electronic

structure modifications arising from the doping of SnO₂ (using Nb and N), a precise calculation of the band gap is however not critical. Hence this noted disadvantage of DFT will not significantly affect the results obtained and discussed in the current manuscript. Furthermore, the main parameters of the electronic structure for SnO₂ calculated in the present study agree well with the results obtained from previously published theoretical calculations.[113-115]

SnO₂ doped with Nb and N

The calculated total and projected densities of electronic states for (Sn_{0.94}Nb_{0.06})O₂ oxide composition are shown on **Fig. 8a**. One can see that the main band structure of the Nb-doped SnO₂ is similar to the undoped SnO₂. However, the main difference between the two is an appearance of the Nb-4d electronic states slightly hybridized with Sn-5s and O-2p states located at the bottom of the conduction band within the Fermi level vicinity. The valence band of Nb-doped SnO₂ remains virtually the same as that of pure SnO₂ and is separated from the hybridized conduction band by the energy gap of 1.08 eV. This optical band gap value is quite smaller than the E_{BG} calculated for the pure SnO₂ (1.12 eV) which agrees well with experimental observations demonstrating narrowing of the optical band gap observed with Nb-doping (**Table 4**). Of course, both values are significantly underestimated due to the limitation of DFT analysis (mentioned above). However the relative difference between these values is qualitatively the same as that experimentally observed. Since the impurity Nb-4d states locate at the Fermi level, it clearly indicates that Nb-doped SnO₂ is a n-type semiconductor, which is in accordance with the results of Mott-Schottky analysis (**Fig. 2c**). Also, the calculated electronic structure is very similar to other calculations reported previously.[115]

To study effect of nitrogen doping on electronic structure of SnO_2 the composition $\text{SnO}_{1.96875}\text{N}_{0.03125}$ has been considered. The projected density of electronic states for this composition is shown in **Fig. 8a**. One can see that the general picture is almost the same as for pure SnO_2 . The only difference between pure and N-doped SnO_2 oxide is the appearance of N-2p impurity states at the top of the valence band. The calculated band gap E_{BG} is 0.8 eV (**Table 4**) which is noticeably narrower than the corresponding calculated band gap of pure SnO_2 . Thus it can be seen that indeed the incorporation of N can help decrease the optical band gap and correspondingly extend the absorption of SnO_2 into the visible region.

Simultaneous co-doping of nitrogen together with niobium into SnO_2 significantly influences the electronic structure of the system within the Fermi level vicinity. **Fig. 8b** show the calculated projected density of electronic states for $(\text{Sn}_{0.94}\text{Nb}_{0.06})\text{O}_{1.97}\text{N}_{0.03}$, $(\text{Sn}_{0.94}\text{Nb}_{0.06})\text{O}_{1.94}\text{N}_{0.06}$, and $(\text{Sn}_{0.94}\text{Nb}_{0.06})\text{O}_{1.875}\text{N}_{0.125}$, respectively. One can see that the overall electronic structure results from the combination of Nb-doped SnO_2 and N-doped SnO_2 considered above. Compared to pure SnO_2 , there are N-2p electronic states located at the top of the valence band and Nb-4d electronic states located at the bottom of the conduction band, separated by the energy gap (E_{BG}). The value of this optical band gap gradually decreases with increase in the concentration of N in the compound (from 0.93 eV for 3 at% to 0.87 eV for 12.5 at% of N). Such a narrowing of the optical band gap originates from widening of the N-2p states at the top of the valence band with the corresponding increase in the N-concentration. Otherwise, the overall electronic structure is virtually the same for all the three different compositions containing 3, 6, and 12.5 at% of N shown in **Fig. 8b**. Thus, the present computational study is in qualitative agreement with the experimental observations reflecting a general trend of narrowing the optical band gap with co-doping of Nb and N into SnO_2 structure. The calculated and

experimentally measured optical band gaps for all the materials considered in the present study are shown in **Table 4**.

The present experimental and theoretical study clearly demonstrates the excellent photoelectrochemical performance and stability of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs with an unprecedented ABPE of 4.1% representing in fact, the highest ABPE obtained so far to the best of our analysis and assessment of the reported data to date compared to other well studied semiconductor materials used widely as photoanodes for PEC water splitting, such as TiO_2 , ZnO and Fe_2O_3 . [7, 77, 110-112] This superior photoelectrochemical performance of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs can be attributed to significant reduction in the band gap, as also validated by theoretical first principles calculations (**Fig. 8a-b**) and confirmed from the UV-vis absorption spectra and Tauc analysis (**Fig. 5a-b**), resulting in reduction in band gap of pure SnO_2 NTs from 3.53 eV to 1.99 eV for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs. The lowered optical band gap further facilitates excellent light absorption (**Fig. 5a-b**). In addition to improved light absorption property, excellent photoelectrochemical performance of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs compared to other materials in this study is observed which can be attributed to the significantly improved carrier density (**Fig. 5c and Table 2**), improved carrier separation and collection efficiency (**Fig. 6a**) and improved electrochemical charge transfer kinetics (**Fig. 2f**). Furthermore, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs exhibit excellent long term photoelectrochemical stability as witnessed by the CA test carried out under illumination for 24 h (**Fig. 7a-b**). A detailed study of effect of structural and synthesis parameters of nanotubes on fundamental photoelectrochemical properties of SnO_2 before and after doping will be reported in the future. All of the above results thus clearly show that $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs is indeed a promising semiconductor material with excellent photoelectrochemical performance and stability and an

outstanding ABPE of 4.1% truly demonstrating the outstanding promise of this engineered system. The results discussed herein are thus indeed important and provide a framework for gradually transforming the system further towards achieving efficient hydrogen production by utilizing solar energy in an environmental friendly manner thus solving global energy demand.

Conclusion

The photoelectrochemical activity of a carefully engineered and band gap tailored system $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs is reported in this study. The nanotubes were synthesized using ZnO NWs as sacrificial template followed by systematic heat treatment in NH_3 atmosphere. This work clearly demonstrates the potential of Nb and N co-doping to significantly reduce the optical band gap of SnO_2 NTs from 3.53 eV to 1.99 eV for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs leading to excellent light absorption characteristics. Accordingly, Nb and N co-doping results in 4-orders of magnitude improved carrier density, improved carrier separation and transport and collection efficiency as well as outstanding ABPE, along with negative onset potential (-0.02 V to -0.14 V) indicating superior photoelectrochemical activity. The optical band gap of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs is indeed the lowest reported for SnO_2 based materials combined with significantly improved carrier density which together opens up new ground for this material to be explored for different solar energy based applications. The ABPE of 4.1% obtained for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs at 0.75 V (*vs* RHE) is indeed the highest ABPE reported so far following careful assessment of the reports available in the literature to date compared to other well-known materials, ZnO, Fe_2O_3 and TiO_2 . Furthermore, $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ -600 NTs exhibit excellent long term photoelectrochemical stability in the electrolyte solution under illumination. Theoretical first principles calculations also revealed strong effects of Nb- and N-doping on

electronic structure of SnO₂ in general, and on the optical band gap width in particular. The computational study also sheds light to clearly demonstrate the favorable benefits of simultaneous doping of Nb and N to decrease substantially the optical band gap serving to move the absorption of SnO₂ into the visible region. Moreover, the theoretical results complement and agree well with the experimental observations conducted in the present study. The Nb and N co-doping strategy for SnO₂ thus results in excellent photoelectrochemical performance for (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs mainly due to (a) excellent light absorption properties, (b) increased carrier density, and (c) facile electrochemical charge transfer. This work will therefore be important in the pursuit of photoelectrochemically active and stable semiconductor materials for efficient and economical hydrogen generation from PEC water splitting.

Author contribution

P.P.P. and P.N.K. devised the original concept. P.P.P. designed the experiments, synthesized the materials, prepared the electrodes, performed structural and photoelectrochemical characterization and analyzed structural and photoelectrochemical data. O.I.V. conducted the theoretical analyses. J.P. and A.M. collected and analyzed the XPS data. P.P.P. performed SEM/EDAX. B.G. carried out TEM. M.K.D. and P.J. made important suggestions in the context of fundamental structural and photoelectrochemical characterization. P. P. P., P. J., O.I.V. and P.N.K. wrote the first draft of the paper; and all authors participated in the manuscript revision. The project is conceived and supervised by P.N.K.

Acknowledgment:

Research in part supported by the National Science Foundation, CBET – Grant 0933141. P.N.K acknowledges the Edward R. Weidlein Chair Professorship funds and the Center for Complex Engineered Multifunctional Materials (CCEMM), Swanson School of Engineering, University of Pittsburgh for support of this research and also for procurement of the electrochemical equipment and facilities used in this research work. P.N.K also acknowledges Mr. Matt Detzel (Chemical Engineering Undergraduate Laboratory Technician/Instructor, University of Pittsburgh) for allowing to use UV-vis spectrophotometer and gas chromatography (GC) system. Finally, P.N.K and O.I.V gratefully acknowledge the support of the Pittsburgh Supercomputing Center for allocating the computational units needed to complete the theoretical component of the present study.

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909 **Table 1. The lattice parameter and molar volume for SnO_2 , $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ ($x=0, 0.05, 0.1$)**
910 **and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs, along with N concentration for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs**
911 **(obtained from EDAX analysis)**

Composition	Lattice parameter (nm)	Molar volume ($\text{cm}^3 \text{mol}^{-1}$)	N concentration from EDAX analysis (at. %)
SnO_2	$a=b=0.4738$ $c=0.3187$	21.54	-
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$	$a=b=0.4735$ $c=0.3184$	21.49	-
$(\text{Sn}_{0.9}\text{Nb}_{0.1})\text{O}_2$	$a=b=0.4732$ $c=0.3180$	21.44	-
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 400 NTs	$a=b=0.4741$ $c=0.3190$	21.58	3.02
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 500 NTs	$a=b=0.4743$ $c=0.3193$	21.62	7.1
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 600 NTs	$a=b=0.4748$ $c=0.3196$	21.69	14.01

912

Table 2. Results of Tauc analysis, Mott-Schottky analysis and photoelectrochemical characterization of SnO₂, (Sn_{1-x}Nb_x)O₂ (x=0.05, 0.1) and (Sn_{0.95}Nb_{0.05})O₂:N NTs (performed in 0.5 M H₂SO₄ electrolyte solution under illumination of 100 mW cm⁻² at 26⁰C)

Composition	Band gap (eV)	Carrier density (cm ⁻³)	Onset potential (V, RHE)	Photocurrent density at 0.75 V (vs RHE) (mA cm ⁻²)	Max. applied bias photon-to-current efficiency (ABPE) (%)	Potential corresponding to max. ABPE (V vs RHE)	N concentration (from EDAX analysis) (at. %)
SnO ₂	3.53	2.42×(10 ¹⁸)	0.28	~0	0.008	0.9	-
(Sn _{0.95} Nb _{0.05})O ₂	3.1	4.2×(10 ¹⁹)	0.17	0.17	0.088	0.82	-
(Sn _{0.9} Nb _{0.1})O ₂	2.99	5.52×(10 ¹⁹)	0.17	0.1	0.051	0.82	-
(Sn _{0.95} Nb _{0.05})O ₂ :N-400 NTs	2.58	3.3×(10 ²²)	(-0.02)	6.76	1.83	0.78	3.02
(Sn _{0.95} Nb _{0.05})O ₂ :N-500 NTs	2.38	4.05×(10 ²²)	(-0.02)	11.74	2.29	0.78	7.1
(Sn _{0.95} Nb _{0.05})O ₂ :N-600 NTs	1.99	4.7×(10 ²²)	(-0.14)	25.39	4.1	0.75	14.01

918 **Table 3. Results of EIS analysis of SnO_2 , $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ ($x=0.05, 0.1$) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$**
919 **NTs performed at 0.75 V (RHE) in 0.5 M H_2SO_4 electrolyte solution in frequency range of**
920 **100 mHz-100 kHz under illumination (100 mW cm^{-2}) at 26°C**

Composition	$R_s (\Omega.\text{cm}^2)$	$R_e (\Omega.\text{cm}^2)$	$R_{ct} (\Omega.\text{cm}^2)$
SnO_2	15.16	6.49	92
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2$	15.18	6.47	68.2
$(\text{Sn}_{0.9}\text{Nb}_{0.1})\text{O}_2$	15.18	6.45	84.2
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 400 NTs	15.17	6.43	24.6
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 500 NTs	15.16	6.41	19.2
$(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-}$ 600 NTs	15.17	6.38	15.3

921
922 **Table 4. Calculated and experimental values of optical band gap (E_{BG}) of pure and doped**
923 **SnO_2**

Composition	Calculated E_{BG} (eV)	Experimental E_{BG} (eV)
SnO_2	1.12	3.53
$(\text{Sn}_{0.94}\text{Nb}_{0.06})\text{O}_2$	1.08	3.1
$\text{Sn}(\text{O}_{1.97}\text{N}_{0.03})$	0.80	-
$(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.97}\text{N}_{0.03})$	0.93	2.58
$(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.94}\text{N}_{0.06})$	0.91	2.38
$(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.875}\text{N}_{0.125})$	0.87	1.99

924 **Figure captions:**

925 **Figure 1.** The XRD patterns of pure SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) in wide
926 angle 2θ scan

927 **Figure 2.** (a) UV-vis absorption spectra of SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1), (b)
928 Tauc analysis of SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1), (c) Mott-Schottky plot of SnO₂
929 NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1), (d) The linear scan voltammogram (LSV) curves for
930 SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) in dark and under illumination of 100 mW cm⁻²
931 in 0.5 M H₂SO₄ at 26⁰C, before and after iR_Ω correction, (e) Applied bias photon-to-current
932 efficiency (ABPE) as a function of applied potential for SnO₂ NTs and (Sn_{1-x}Nb_x)O₂ NTs
933 (x=0.05, 0.1), (f) EIS spectra of SnO₂ NTs, (Sn_{1-x}Nb_x)O₂ NTs (x=0.05, 0.1) and
934 (Sn_{0.95}Nb_{0.05})O₂:N NTs of different N concentration obtained at 0.75 V (vs RHE) in 0.5 M H₂SO₄
935 at 26⁰C in the frequency range of 100 mHz to 100 kHz under illumination (100 mW cm⁻²) with
936 the circuit used for fitting experimental data

937 **Figure 3.** (a) The XRD patterns of pure SnO₂ NTs and (Sn_{0.95}Nb_{0.05})O₂:N NTs of different N
938 concentration in wide angle 2θ scan, (b) The magnified view of XRD patterns of pure SnO₂ NTs
939 and (Sn_{0.95}Nb_{0.05})O₂:N NTs of different N concentration, (c) SEM micrograph showing top
940 image, cross-sectional image and EDAX spectrum of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs, (d) The bright
941 field TEM images of (Sn_{0.95}Nb_{0.05})O₂:N-600 NTs showing hollow nanotubes of diameter ~180-
942 220 nm

943 **Figure 4.** The XPS spectra of (Sn_{0.95}Nb_{0.05})O₂:N NTs showing (a) Sn 3d_{3/2} and 3d_{5/2} doublet, (b)
944 N 1s peak and (c) Nb 3d_{3/2} and 3d_{5/2} doublet

Figure 5. (a) UV-vis absorption spectra of $(\text{Sn}_{1-x}\text{Nb}_x)\text{O}_2$ NTs ($x=0.05$) and $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration, (b) Tauc analysis of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration, (c) Mott-Schottky plots of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration

Figure 6. (a) IPCE spectra of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration measured at potential of $\sim 0\text{V}$ (vs RHE), (b) The linear scan voltammogram (LSV) curves for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration in dark and illumination of 100 mW cm^{-2} measured in $0.5\text{ M H}_2\text{SO}_4$ at 26°C , before and after iR_Ω correction, (c) Applied bias photon-to-current efficiency (ABPE) as a function of applied potential for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N}$ NTs of different N concentration

Figure 7. (a) The variation of photocurrent density vs time in the chronoamperometry test of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs, performed in $0.5\text{ M H}_2\text{SO}_4$ solution under a constant potential of 0.75 V (vs RHE) at 26°C for 24 h under illumination (100 mW cm^{-2}), (b) The linear scan voltammogram (LSV) curve for $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$ NTs in dark and under illumination of 100 mW cm^{-2} measured in $0.5\text{ M H}_2\text{SO}_4$ at 26°C , obtained before and after 24 h chronoamperometry test

Figure 8. (a) Projected density of states for pure SnO_2 , SnO_2 doped with $6.25\text{ at\%}$ of Nb, SnO_2 doped with $3.125\text{ at\%}$ of N. Fermi level is set for zero, (b) Projected density of states for $(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.97}\text{N}_{0.03})$, $(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.94}\text{N}_{0.06})$, $(\text{Sn}_{0.94}\text{Nb}_{0.06})(\text{O}_{1.875}\text{N}_{0.125})$. Fermi level is set for zero

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Figure 1

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Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 2e

Figure 2f

Figure 3a

Figure 3b

(c)

Figure 3c

1005
1006
1007
1008
1009

(d)

Figure 3d

1010

1011

1012

Figure 4a

Figure 4b

Figure 4c

Figure 5a

Figure 5b

Figure 5c

Figure 6a

Figure 6b

Figure 6c

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Graphical abstract

Vertically aligned nanotubes
of $(\text{Sn}_{0.95}\text{Nb}_{0.05})\text{O}_2\text{:N-600}$

Photoelectrochemical stability