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Harnessing of low-energy IR photons via oxygenvacancies in SrTiO₃ nanocrystals for photocatalytic hydrogen production

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- High-temperature treatment with NaBH₄, oxygen vacancies (Ov) were formed in SrTiO₃.
- Presence of Ovs extend the light absorption to near-IR region.
- Photocatalytic water splitting of SrTiO₃ was demonstrated with IR photons.

GRAPHICAL ABSTRACT



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ABSTRACT

The surface-oxygen vacancies were generated to enhance the near-IR light response of the SrTiO₃ photocatalyst by heating SrTiO₃ in a highly reducing environment. The UV–visible diffuse reflectance spectra of SrTiO₃-Ov revealed strong absorption between 400 and 800 nm, while IPCE response was extended beyond 800 nm, confirming the near-IR light response of SrTiO₃-Ov. The hydrogen production rates for SrTiO₃-Ov at pH 3.0 under full solar spectrum, visible and IR radiation were 100, 25 and 10 μ lg⁻¹h⁻¹, respectively. The respective normalized hydrogen with respect to light intensity were found to be 100, 50 and 33 μ lg⁻¹h⁻¹ while hydrogen production of pristine SrTiO₃-Ov are key factors in the origin of the near-IR responses of the catalyst and the feasibility of using low-photonic-energy IR light to produce hydrogen by water splitting was demonstrated.

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Introduction

A possible fuel shortage in the near future is imminent due to short supply of fossil fuel making it critical to find a clean, cheap, and sustainable energy source to meet the future energy demand. The hydrogen energy can be regarded as the ideal solution for meeting future energy demands among alternative renewable energies because it can be used as a regenerative and environmentally friendly energy carrier [1,2]. The steam reforming method used to produce hydrogen from fossil fuels is both environmentally and economically unsustainable and hence hydrogen must be generated from renewable sources [3,4]. Photoelectrochemical and photocatalytic as well as electrochemical water splitting, which are inexpensive and promising methods, can convert solar energy into chemical energy such as hydrogen [5-9]. The photocatalytic water splitting method, on the other hand, remains challenging because photocatalytic performance is highly dependent on material properties such as crystallinity, surface area, defect structure band gap energy, and electrochemical properties [10]. As the photoresonse of common photocatalysts such as TiO₂, ZnO, and SnO₂ is limited to UV light, the development of photocatalysts that are active in the visible and near infrared ranges is critical for the use of photocatalysts in the production of hydrogen from water splitting [11–14]. Several methods, have been attempted to improve the visible light photocatalytic performance of these photocatalytic materials by modifying the surface with nanoparticle co-catalysts and introducing dopants into the material matrix [15–17]. However, utilizing IR light, which accounts for nearly half of solar energy, remains a challenge in solar energy conversion research. The ability of IR light to penetrate deeper into the photocatalyst is advantageous, particularly for photocatalytic reactions.

The IR response of semiconductors has been reported by introducing impurity energy levels (i.e., intermediate-band) via the incorporation of impurities (i.e., dopants) in the semiconductor band gaps [18-20]. These dopants, however, act as recombination centers, reducing photocatalytic activity. Hydrogen plasma treatment was discovered to be an effective method for producing a photocatalyst with a high electron concentration and an efficient visible light response in the case of TiO₂ (as an example, H-doped black titania) [21]. Similarly, reducing TiO₂ in the presence of reluctant such as molten Al or NaBH4 is another promising method for improving visible and near-infrared light response in semiconductors due to the formation of mid-band gap energy levels [19,22]. During the reduction process, the oxygen atoms in the lattice are replaced with hydrogen or vacancies, resulting in two unpaired electron spins distributed among Ti atoms. The high concentration of oxygen vacancies (O_v) is electronically compensated by changes in the oxidation state of the Ti cations. Oxygen vacancies have also been introduced into other photocatalysts such as WO₃ [23], ZnO [24], and Fe₂O₃ [25].

The perovskite oxides such as $SrTiO_3$ is one of the most popular high-band gap photocatalysts for water splitting as well as the degradation of environmental pollutants due to its high reducing and oxidizing power, non-toxicity, and sufficient stability. The experimentally detected direct and indirect band gap values of the SrTiO₃perovskite are 3.75 and 3.25 eV respectively [26]. The introduction of metal, nonmetal, or oxygen vacancies caused the formation of new energy levels in SrTiO₃ as an intermediate band gap, resulting in a narrowing of the band-gap [18,27-29]. Among these methods, partial replacement of atomic O by H is a convenient strategy for increasing the valence band maxima, which is thought to be an effective strategy for improving light absorption and charge separation in wide band gap semiconductors. The treatment of the high band gap SrTiO₃ material (<3.2 eV) with a strong reducing environment results in the formation of Ti³⁺ cations and oxygen vacancies in SrTiO₃ as well as the formation of band gap local states [30-33]. The theoretical ab initio calculations of the oxygen vacancies in SrTiO₃ perovskite has been discussed by Eglitis et al. [34,35]. The presence of oxygen vacancies has a significant impact on the conductive behaviour of the perovskite SrTiO₃, increasing electron concentration and making grain boundaries highly conductive. Though the visible light activity of SrTiO₃ by introducing Ti³⁺ cations and oxygen vacancies has been reported, the IR response of SrTiO₃ with Ov has not been reported. Hence, incorporating Ti³⁺ cations and oxygen vacancies into SrTiO3 may be a promising method for increasing its photocatalytic activity in the near-IR regions. Therefore, to demonstrate the photocatalytic activity of SrTiO₃ in near IR radiation, we synthesized SrTiO_{3-x} and discovered that SrTiO_{3-x} produced more hydrogen than pristine SrTiO₃ due to the presence of mid-gap states and oxygen vacancies in SrTiO_{3-x}, which extends optical adsorption beyond the visible light region and into the near IR-region and decreases charge recombination. Finally, it was able to demonstrate hydrogen production using low-photonic-energy IR light.

Experimental

Preparation of the catalyst

The photocatalyst was prepared by mixing 500 mg of SrTiO₃ powder (Strem chemicals, 99%) and 450 mg of NaBH₄ (MRS scientific, 90%) in an agate mortar and the mixture was placed in a porcelain boat, and sintered at 550 °C for 1 h with a heating rate of 5 °C/min under Ar saturated environment in a tubular furnace and finally cooled to room temperature in the furnace. After sintering, the black SrTiO_{3-x} powder product was thoroughly washed with distilled water to remove the excess unreacted NaBH₄, and then dried at 100 °C under atmospheric conditions.

Preparation of the photoelectrode

A thin film of SrTiO₃ was fabricated for electrochemical analysis by doctor-blading a mixture containing finely ground 4 mg of SrTiO_{3-x}, 0.2 ml of PEG (Sigma Aldrich, 44%), and 0.2 ml of isopropyl alcohol (Sigma Aldrich, 95%) on the FTO (Dyesol, 15 Ω) conducting glass, and the deposited electrode was dried at 100 °C. The electrode with pristine SrTiO₃ was made using the same method.

Characterization of the catalyst

A powder X-ray diffractometer (X'Pert PRO MPD, PW3040/60) with Cu K α (λ = 0.154 nm) radiation and a scanning step of 10 (deg/min) was used to investigate the crystal structure and crystallite size of SrTiO₃ and SrTiO_{3-x} samples. Morphological information and crystallite structure details of SrTiO3 and SrTiO_{3-x} samples were obtained by SEM (Hitachi S-4800) and TEM (JEM-2100) analysis. The oxidation states of the SrTiO₃ and SrTiO_{3-x}photocatalysts were confirmed using XPS(ESCA-LAB 250XI). The diffuse reflectance UV-Visible spectroscopy was used to measure light absorption and band gaps (SHI-MADZU UV-2450). The specific surface area of the Brunauer Emmett Teller (BET) was measured using a Quantachrome QUADRASORB SI-MP-10 apparatus. The methodology is described in detail in the SI. A HORIBA JY, Lab RAM HR800 Raman Spectroscopy System with a 514 nm laser was used for Raman spectroscopy measurements.

Photocatalytic activity

Photocatalytic activity was quantified as a function of generated hydrogen yield using gas chromatography (SHIMADZU MODEL GC-9AM) with either a packed charcoal column or 5A°Molecular sieves and a thermal conductivity detector (TCD) with Argon as the carrier gas. Experiments were conducted in a 25 cm³ volumetric flask filled with distilled water at pH 7.5. The catalyst (48 mg) was dispersed in 24 ml of distilled water for the experiment, and photocatalytic experiments were performed to determine hydrogen production with different light sources such as UV light (SUNTEST PLUS), visible light irradiation (halogen lamp wavelength of 500–950 nm, 50 mW/cm²), photodiode (850 nm, 30 mW/cm²), and in the dark as the control.

Photoelectrochemical measurements

To demonstrate the IR response, the transient photocurrent of the SrTiO₃ photoelectrode was measured. The SrTiO_{3-x} electrode with an active area of 0.5 cm² were used as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode and illuminated with a diode with 850 nm (30 mW/cm²). To determine the quantum efficiency of the photocatalyst, an IPCE (Bentham PVE300 unit with a TMc300 monochromator-based IPCE with a Xenon arc lamp in the wavelength range 300-1200 nm) was used. Mott-Schottky plots were performed at 10 mV amplitude AC signal and 1 KHz frequency using a Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) under ambient light for the threecomponent system with platinum as counter, Ag/AgCl (0.01 M) as the reference, and $SrTiO_{3-x}$ working electrode and 0.5 M Na₂SO₃ as the electrolyte. To investigate the charge transfer process at SrTiO₃ samples and the electrolyte interface, EIS was performed with the Zahner Zannium electrochemical interface analysis instrument and Thalas software at 10 mV amplitude ac signal and in the frequency range from 0.1 Hz to 10 kHz under dark conditions in a standard three-electrode system with a Pt foil as the counter electrode, an Ag/AgCl electrode as the reference electrode. The transient

photocurrent responses of the reduced $SrTiO_{3-x}$ and pristine $SrTiO_3$ electrodes were tested under intermittent irradiation of 850 nm diode with a Keithley 2400 source meter in a three electrode system of a Pt foil as the counter electrode, an Ag/ AgCl reference electrode, and $SrTiO_3$ as the working electrode.

Results and discussion

Characterization of the catalyst

The structure type and cubic morphology of the SrTiO_{3-x} perovskite, which was synthesized by treating SrTiO₃ in a highly reducing environment in the presence of NaBH₄ and Ar gas were confirmed by PXRD and SEM analyses. As shown in Fig. 1, pristine SrTiO₃ has diffraction peaks at 22.7°, 32.3°, 39.9°, 46.4°, 52.3°, 57.7°, 67.8°, and 77.1°, corresponding to (100), (110), (111), (200), (210), (211),(220), and (310) cubic SrTiO₃ crystal planes (JCPDS card no: 35–0734). The XRD patterns of SrTiO_{3-x} samples prepared at 350, 450, and 550 °C were similar to the original cubic phase SrTiO₃, indicating that there were no structural changes and no impurity phases formed after NaBH₄ treatment of pristine SrTiO₃. The appearance of stronger peaks with increasing reaction temperature, on the other hand, implies that the crystallinity of the product increases with increasing temperature. As shown in Fig. 1b, the structural parameters of samples prepared at different temperatures were refined further using Rietveld's profile-fitting method, and the final structural parameters of Rietveld's analysis are summarized in Table 1. In the Rietveld's refinement, the scale and background parameters were adjusted first, then the unit cell parameters, then the peak asymmetry and preferred orientation corrections, and finally the positional parameters and individual isotropic parameters.

The presence of nearly the same cubic lattice parameter and unit cell volume (Table 1) for 350-550 °C heated samples demonstrates that a high-temperature NaBH₄ reduction treatment (up to 550 °C) does not fundamentally change the overall crystal structure of SrTiO₃. The absence of change in the Ti–O bond lengths and Ti–O–Ti bond angles of SrTiO₃ and SrTiO_{3-x} further demonstrates the intact crystal structures of SrTiO₃.

As shown in Fig. 2a, UV–Vis diffuse reflectance absorption spectra were used to investigate the change in optical properties of the SrTiO₃ catalyst during the sintering process under reducing conditions. The SrTiO_{3-x} sample absorbs light across the entire solar spectrum (near IR to UV), whereas pristine SrTiO₃ absorbs only in the UV region. Using absorption spectra, the calculated band gaps of pristine and reduced SrTiO₃ sintered at 550 $^{\circ}$ C are 3.1 and 2.7 eV, respectively. The white colour pristine SrTiO₃ turns slightly blue at 350-450 °C and black at 500-550 °C due to the reducing conditions that prevail during the sintering process of SrTiO₃, (Inset in Fig. 2a). The appearance in blue colour is due to the formation of O_v at mid-gap states between the valence band and the conduction band, forming new transitions in the visible portion of the spectrum where as black colour may appear due to localized Ti³⁺, which exhibits absorption in the far-visible and near-IR regions of the spectrum [36,37]. These O_v and localized Ti^{3+} states may form an extended continuum band edge,

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Fig. 1 – a: XRD diffraction patterns of SrTiO₃, SrTiO_{3-x}(350 °C), SrTiO_{3-x}(450 °C) and SrTiO_{3-x}(550 °C). bRietveld's refinement XRD diffraction patterns of SrTiO₃, SrTiO_{3-x}(350 °C), SrTiO_{3-x}(450 °C) and SrTiO_{3-x}(550 °C).

narrowing the band gap and thus extending the solar absorbance range to lower energy waves.

Raman spectroscopy was used for additional optical characterization because it is very sensitive to short-range distortions caused by microstructural defects. The Raman spectra of pristine $SrTiO_3$ and STO_{3-x} (550 °C) are shown in Fig. 2b. Because of its centrosymmetric cubic nature with the space group Pm-3m, the Raman spectra of $SrTiO_3$ is dominated by second-order scattering in the regions 250-400 cm⁻¹ and 600-800 cm⁻¹ due to its centrosymmetric cubic nature with the space group Pm-3m. As shown in Fig. 2b, $SrTiO_3$ and STO_{3-x} (550 °C) have two broad bands centered in the 200–500

Table 1 — Refined structural parameters for SrTiO _{3-x} prepared at 350, 450 and 550 °C.				
Crystal parameter	SrTiO ₃	SrTiO₃ (350 °C)	SrTiO₃ (450 °C)	SrTiO₃ (550 °C)
a (Å)	3.905646	3.904402	3.905590	3.906569
b (Å)	3.905646	3.904402	3.905590	3.906569
c (Å)	3.905646	3.904402	3.905590	3.906569
α	90.00000	90.00000	90.00000	90.00000
β	90.00000	90.00000	90.00000	90.00000
γ	90.00000	90.00000	90.00000	90.00000
Unit cell volume (ų)	59.5770	59.5201	59.5745	59.6192
Ti–O length (Å)	1.95282	1.95250	1.95280	1.95328
Ti−O−Ti angle(°)	180	180	180	180

and 600-800 cm⁻¹ region. Furthermore, the peaks at 174, 677, and 782 cm⁻¹ correspond to first-order Raman scattering caused by structural defects, such as oxygen vacancies or strain. The low Raman scattering intensity of SrTiO_{3-x} on the other hand, could be due to a disordered surface caused by NaBH₄ treatment. The black colour of SrTiO_{3-x} remains stable under air suggesting the formation of highly stable Ti³⁺ states and O_v in SrTiO_{3-x} [38]. According to XPS analysis results, the presence of these states just below the surface of SrTiO_{3-x} is responsible for the stability of Ti³⁺ states and Ov in SrTiO_{3-x}.

Surface oxygen defects, or O_v , play an important role in photocatalytic processes because they trap photogenerated carriers and reduce rapid charge carrier recombination. Furthermore, due to the accumulation of surface energy states in the band gap, Ov is known to narrow the band gap, extending the solar absorbance range to lower energy wavelengths [39]. The composition and elemental chemical states of Ti ions and oxygen vacancies in SrTiO₃ and SrTiO_{3-x}, were confirmed using X-ray photoelectron spectroscopy, and as shown in survey spectra of SrTiO₃, SrTiO_{3-x}(350 °C) and SrTiO₃₋ x(550 °C) in Fig. S1, the binding peaks of Ti, O, Sr can identified in all samples and the absence of binding peak that corresponds to the B confirms that B is not incorporated in to the lattice structure of SrTiO₃ during NaBH₄ reduction process. The composition and elemental chemical states of Ti ions and oxygen vacancies in SrTiO3 and SrTiO3-x, were confirmed using X-ray photoelectron spectroscopy, and Fig. 3 depicts high-resolution spectra of Sr 3d, Ti 2p, and O 1s from pristine $SrTiO_3$ and treated samples. The XPS peaks of 134.68 and 132.98 eV in the pristine SrTiO₃ sample correspond to Sr 3d3/2 (Sr-O) and Sr 3d5/2 (Sr) of the SrO crystal phase, respectively, which is consistent with previous work on SrTiO₃. Similarly, the Ti 2p spectrum of pristine SrTiO3 can be fitted into two peaks at 458.3 and 464.1 eV, corresponding to the Ti 2p3/2 and Ti 2p1/2 binding states, respectively, and the O 1s can be fitted into three peaks at 528.6 eV, 529.4 eV, and 531.7 eV, corresponding to the lattice oxygen ion, oxygen vacancy, and adsorbed oxygen [40]. In comparison to pristine SrTiO₃, the peaks of Sr, Ti, and O gradually shift with increasing reaction temperature in NaBH₄ treated SrTiO₃ samples, which may be caused by defects such as oxygen vacancies and/or Ti³⁺ (or/ and Ti²⁺). The formation of oxygen vacancies in SrTiO₃ caused by surface lattice oxygen diffusion into the surrounding environment and the subsequent formation of dangling bonds or oxygen vacancies on the surface of SrTiO₃ during the high temperature treatment of SrTiO₃ with NaBH₄ is responsible for the observed shift in Sr 3d5/2 peak positions of SrTiO3-x (350 °C) and SrTiO_{3-x} (550 °C) to lower binding energy (Fig. 3a).

As shown in Fig. 3b, peaks at 458.28 (Ti 2P3/2) and 463.98 (Ti 2P1/2) eV can be assigned to the Ti^{4+} chemical state of the pristine SrTiO₃. Similarly as shown in Fig. 3c, for both 450 and 550°C heated SrTiO_{3-x} samples, only Ti⁴⁺ state is present. However, in the XPS of the etched $SrTiO_{3-x}$ (550 °C) sample, two titanium ion XPS peaks centered at 456.53 and 458.29 eV can be assigned to the chemical states of Ti^{3+} and Ti^{4+} respectively indicating the formation of lower Ti³⁺ states just beneath the surface of the SrTiO₃. Furthermore, the O1s high resolution XPS spectra of SrTiO_{3-x} can be fitted into three peaks at 530.0 eV, 531.9 eV, and 533.4 eV, respectively. The concentration of oxygen vacancies on the SrTiO_{3-x} surface is related to the intensity of the peak at 531.9 eV, which is attributed to O_2^- in the oxygen defect of the SrTiO_{3-x} surface. The increase in the intensity of the peak at 531.9 eV in SrTiO_{3-x} over SrTiO₃indicates the increase of the oxygen vacancy concentration on the SrTiO_{3-x} surface when the NaBH₄ treatment process is carried out at higher temperatures [18].



Fig. 2 – (a) Diffuse reflectance spectra of SrTiO₃ and SrTiO_{3-x} (550 °C), (b) RAMAN spectra of SrTiO₃ and SrTiO_{3-x} (550 °C).

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Fig. 3 – XPS spectra of(a) Sr 3d, (b) Ti 2p and (c) O 1s. Inset in (SrTiO_{3-x} 550 °C) shows the XPS of etched SrTiO_{3-x}.

The incorporation of significant amount of Ovs is associated with an increase in electron density in SrTiO_{3-x} resulting in an upward shift in the Fermi level caused by an increase in the equilibrium electron density. The capacitance analysis, in which Mott-Schottky plots were collected at 1 kHz and shown in Fig. 4, confirmed the upward shift of the Fermi level of SrTiO₃. The observed flat-band potentials for pristine SrTiO₃ and SrTiO_{3-x}(550°C) in the dark, are -0.2 and -0.30 eV, respectively indicating that the higher donor state densities N_d in SrTiO_{3-x} than in pristine SrTiO₃ which is confirmed by the estimated charge densities of pristine SrTiO₃ (Nd - $6.12 \times 10^{17} \text{ cm}^{-3}$) and SrTiO_{3-x}(550°C) (Nd - $8.5 \times 10^{19} \text{ cm}^{-3}$). The

 $N_{\rm d}$ is calculated as $N_{\rm d}=[2/e_0 \epsilon \epsilon_0]/[d(1/C^2)/dV]$, where the relative permittivity $\epsilon=170,\,\epsilon_0$ is the permittivity in the vacuum, e is the elementary charge, C is the capacitance, and V is the potential from the Mott-Schottky plot. Although the absolute donor density values calculated from a flat-electrode model are subject to error, they do provide a qualitative comparison of the slopes.

As the photocatalyst morphology is closely related to light absorption and charge separation, SEM images of pristine and treated $SrTiO_3$ catalysts were taken to investigate their morphology, and Fig. 5 shows SEM images of pristine and $SrTiO_3$ samples prepared at different temperatures. The



Fig. 4 – Mott-Schottky plots of SrTiO₃ and SrTiO_{3-x}(550°C).

pristine SrTiO₃ particles have smooth surface and truncated cuboid shape and are 400-500 nm in size. The roughness of samples increased with heating temperature when treated with NaBH₄ at 350 and 550 °C, while retaining the original truncated cuboid shape of pristine SrTiO₃.

The morphologies of the SrTiO₃ samples were further examined using TEM, and Fig. 6 shows high-resolution transmission electron microscopy (HRTEM) images of pristine and SrTiO_{3-x} samples prepared at different temperatures, as well as a TEM image of the pristine SrTiO₃ samples. The pristine SrTiO3 has a crystalline nature and well-resolved lattice features throughout the particles as shown in the HRTEM image in Fig. 6a, with lattice fringes with spacing of 0.27 and 0.38 nm corresponding to [110] and [001] atomic planes of the cubic SrTiO₃, respectively [41]. Similarly, after NaBH₄ treatment of SrTiO₃, a well-resolved crystal lattice plane spacing of 0.27 nm, corresponding to the (110) crystal plane of cubic SrTiO₃, is clearly visible, indicating the crystalinity of SrTiO_{3-x}. Fig. 6b, d, and e show SAED patterns for pristine, 450, and 550 °C heated SrTiO3 nanoparticles that are well-crystallized with atomic planes. Furthermore, the SAED patterns of these SrTiO₃ nanoparticles show diffraction rings corresponding to the cubic SrTiO₃ planes (100), (110), (111), (211), (311), (321), and (331), confirming the HR-TEM and XRD results. Despite maintaining the same crystallinity, 450 and 550°C treated SrTiO₃ samples, a disordered layer with a thickness of 1.6 nm and 5-7 nm appears in 450 and 550°C treated samples, respectively. The appearance of a disordered layer indicates surface reconstruction of SrTiO₃, and its formation is greater at 550°C than at 450°C, which is consistent with SEM results. As shown in Fig. S2, the EDS analysis of pristine and 550°C heated samples reveals that the 550°C heated samples have an apparent oxygen deficiency, which is caused by the formation of oxygen deficientSrTiO_{3-x} with Ov (supported by the UV-Vis spectra). As a result, it is possible that the SrTiO₃ samples heated with NaBH₄ at 450-550 °C have a SrTiO₃@SrTiO_{3-x} core/shell structure.

The characterization results confirmed the formation of a core $(SrTiO_3)/shell (SrTiO_{3-x})$ structure as a result of the



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Fig. 5 – SEM images of (a) $SrTiO_3$, (b) $SrTiO_{3-x}$ (350 °C) and (c) SrTiO_{3-x} (550 °C).

treatment of SrTiO3 with NaBH4. SrTiO3-x is composed of Ov and Ti³⁺ states, which extends the optical absorption in the 300-900 nm range beyond its direct band gap excitation. As previously stated, the presence of O_v can facilitate excited charge carrier transfer, resulting in improved photocatalytic activity in the IR/near IR and visible regions of the solar spectrum, as demonstrated by photocatalytic studies.



Fig. 6 – HRTEM images of (a) SrTiO₃, (c) SrTiO_{3-x} (350 °C) and (c) SrTiO_{3-x} (550 °C) and SAED patterns of (b) SrTiO₃, (d) SrTiO_{3-x} (350 °C) and (e) SrTiO_{3-x} (550 °C).

Photocatalytic study

As shown in Fig. 7a, H₂ production from water was measured under the full solar spectrum (300-900 nm range, 100 mW/ cm²), visible light (halogen lamp, wavelength in the 500–900 nm region, 50 mW/cm²), photodiode (850 nm, 30 mW/ cm²), and dark conditions to assess the near IR photoactivity of SrTiO_{3-x}. The observed hydrogen production rates are 100, 25 and 10 μ l g⁻¹ h⁻¹, under full solar spectrum, visible light, and photodiode conditions, respectively, while no hydrogen production is observed in the dark. The respective normalized hydrogen production with respect to light intensity, as shown in Fig. 7b are 100, 50 and 33 $\mu l~g^{-1}~h^{-1}\!,$ indicating that the IR light-induced photocatalytic activity of SrTiO_{3-x} is only 30% less than the full solar spectrum. The hydrogen production of pristine SrTiO3 was less than 2 $\mu l~g^{-1}~h^{-1}$ under full solar spectrum while hydrogen production of SrTiO_{3-x}(350 °C) and SrTiO_{3-x}(450 °C) with a photodiode (850 nm, 30 mW/cm²) are ~1.5 and 4.0 μ l g⁻¹ h⁻¹ respectively.

The absence of hydrogen production in the absence of light confirms that hydrogen production is a light-initiated reaction. In the case of pristine SrTiO₃, hydrogen production was only observed using the entire solar spectrum, rather than visible or infrared light because SrTiO₃ has a band gap energy of 3.2 eV, photocatalytic activity can only be expected when the SrTiO₃ photocatalyst is exposed to UV light. However, when compared to SrTiO_{3-x}, the pristine SrTiO₃ has a negligible hydrogen production. The low hydrogen yield, on the other hand, indicates that pristine SrTiO₃ is not an active photocatalyst under normal conditions. These findings indicate that the photocatalytic activity of SrTiO3-x increased significantly when compared to pristine SrTiO₃, as did the visible and near-IR activity of the SrTiO_{3-x} catalyst, which may be related to the presence of oxygen defects in the $SrTiO_{3\text{-}x}$ catalyst. The effect of O_v on enhanced photocatalytic activity of SrTiO_{3-x} is easily understood because these sites act as electron donors and contribute to increasing donor density, thereby improving charge transport in SrTiO_{3-x} [42]. The observed lower photocatalytic activity



Figure 7 – (a) hydrogen production rates for SrTiO_{3-x}(550°C)with full solar spectrum, Xalogen lamp and IR diode. (b) Corresponding normalized hydrogen production with respect to light intensity.

of SrTiO_{3-x}(350 °C) and SrTiO_{3-x}(450 °C) samples compared to SrTiO_{3-x}(550 °C) sample also may be related to the effect of Ov, where the critical number of Ov may not be present in both SrTiO_{3-x}(350 °C) (Fig. 3, XPS results) and SrTiO_{3-x}(450 °C) samples, resulting in lower electron density and thus diminishing charge transport properties. Furthermore, the negative shift in SrTiO_{3-x}/electrolyte interface due to increased electron density, promoting band edge bending and thus facilitating charge separation at the SrTiO_{3-x}-water interface.

The intrinsic efficiency of the photocatalyst is determined by the ease of transport and transfer of photogenerated charge carriers, particularly electrons, during the photocatalytic process. As a result, electrochemical impedance spectroscopy (EIS) is used to explain the higher photocatalytic activity of SrTiO_{3-x}. EIS is regarded as one of the most appropriate techniques for estimating the material's resistance to photogenerated charge carriers. The radius of the semicircular portion of the Nyquist plots, in general, has a positive correlation with surface charge transfer resistance, with a smaller radius indicating lower charge transfer resistance.

In the photocatalytic process, the ease of transport and transfer of photogenerated charge carriers, particularly electrons, determines the intrinsic efficiency of the photocatalyst, hence to explain the higher photocatalytic activity of SrTiO_{3-x}, electrochemical impedance spectroscopy (EIS) is used. EIS is regarded as one of the most suitable techniques for estimating the resistance offered by the material to the photogenerated charge carriers. In general, the radius of the semicircular portion of the Nyquist plots has a positive correlation with surface charge transfer resistance, with a smaller radius indicating lower charge transfer resistance [43]. Hence, as shown in Fig. S3, the smaller arc radius observed on the EIS Nyquist plot of SrTiO3-x compared to SrTiO3 indicates an effective separation of photogenerated electron-hole pairs and a fast interfacial charge transfer process in SrTiO_{3-x}. Because the Rct and CPE values in SrTiO_{3-x} sintered at 550°C were greatly reduced, a fast charge separation and transport process could be greatly enhanced in SrTiO_{3-x}, which may be favorable for higher photocatalytic activity. Because the Rct and CPE values in SrTiO_{3-x} sintered at 550 °C were greatly reduced, a fast charge separation and transport process in SrTiO_{3-x} could be greatly enhanced, potentially favouring higher photocatalytic activity.

The visible and near-IR photocatalytic activity of SrTiO_{3-x} was clearly demonstrated by the photocatalytic results. IPCE measurements of pristine SrTiO₃ and SrTiO_{3-x} were performed from 300 to 900 nm to further investigate the visible and near-IR photocatalytic activity of SrTiO_{3-x}. As shown in Fig. 8a, the IPCE response of SrTiO_{3-x} is greater than that of SrTiO₃ in 300–400 nm regions, and a clear response in the IPCE spectrum of SrTiO_{3-x} around 700–900 nm and no response from SrTiO₃ in near IR regions (inset in Fig. 8a) further demonstrates the visible and near-IR response of the SrTiO_{3-x} catalyst. Furthermore, the transient photocurrent response of SrTiO₃ and SrTiO_{3-x} shown in Fig. 8b clearly demonstrated that when visible light was turned on and off sequentially, photocurrent signals could be detected for SrTiO_{3-x} but not for SrTiO₃ (a very feeble response can be observed).

The photocatalytic hydrogen production results clearly show that $SrTiO_{3-x}$ has higher photocatalytic activity and visible and near-IR activity thanSrTiO₃. The origin of near-IR photocatalytic activity SrTiO_{3-x} can be explained as follows: The formation of Ov in the SrTiO₃ lattice as a result of the dissociation of Ti-O bonds results in the formation of mid-gap states in SrTiO_{3-x} after NaBH₄ treatment [44,45]. To maintain charge neutrality, some reduced Ti sites, such as Ti³⁺, are formed. As shown in Fig. 9a and b, these mid-gap states can form a continuum near the conduction band edges or a discrete energy level below the conduction band, resulting in a wider solar absorbance range from visible to lower energy radiation. In the first case (Fig. 9a), electrons are excited by visible/near-IR radiation from the extended VB of SrTiO_{3-x} to the extended CB of SrTiO_{3-x} as well as by direct band-to-band UV excitations. In the latter case (Fig. 9b), in addition to electron transitions between the valence and conduction bands caused by UV radiation, electrons are excited from the VB to the local states



Fig. 8 – (a)IPCE spectra of SrTiO_{3-x}(550 °C) and SrTiO₃, (b) Transient current of SrTiO_{3-x}(550 °C) and SrTiO₃.



Fig. 9 – Schematic illustration of the DOS of $SrTiO_{3-x}$ and (I) VB to CB excitation (UV light), (ii) sub-band to CB gap excitation (Visible light) and (iii) CB to sub-band gap and sub-band gap to VB excitation (IR light), (b) Schematic illustration of the DOS of $SrTiO_{3-x}$ with discrete sub-band gap levels.

formed by Ti^{3+} and O_v , and then transferred to the CB of $SrTiO_{3-x}$ when $SrTiO_{3-x}$ is exposed to visible or near-IR light. The spectral response and thus photocatalytic activity are extended beyond the UV–Vis-near IR regions in either case. As a result, the increased photocatalytic activity of $SrTiO_{3-x}$ formed by NaBH₄ reduction can be attributed to increased light absorption from UV–Vis-near IR regions in comparison pristine $SrTiO_{3}$, which absorbs primarily in the UV region of the solar spectrum. Furthermore, oxygen vacancies in $SrTiO_{3-x}$ affect the separation and migration of photogenerated electron-hole pairs as surface O_v can provide trapping sites for photogenerated carriers and prevent them from rapid recombination, as evidenced by EIS measurements.

Finally, catalytic amount variation, pH of the reaction medium, and sample preparation temperatures were varied to optimize the catalytic activity of $SrTiO_{3-x}$. According to the optimization results, the highest hydrogen yield was obtained for $SrTiO_{3-x}$ sample prepared with the reaction of NaBH₄ at 550 °C and in the presence of 2 g/l of catalyst and at pH 3.0 in

the reaction medium. Under the optimized condition, i.e $SrTiO_3$ prepared at 550 °C, the long term catalytic activity was studied with 2 g/l catalyst at pH 3.0 with water under the illumination of visible light. As shown in Fig. S4, the hydrogen amount produced increases with the time up to 70 h of reaction indicating the long term stability of the catalyst.

Finally, the catalytic amount, pH of the reaction medium, and sample preparation temperatures were varied to optimize SrTiO_{3-x} catalytic activity. The highest hydrogen yield was obtained for SrTiO_{3-x} samples prepared with the NaBH₄ reaction at 550°C in the presence of 2 g/l of catalyst and at pH 3.0 in the reaction medium, according to the optimization results. The long-term catalytic activity of 2 g/l catalyst at pH 3.0 with water under visible light illumination was studied under optimized conditions, i.e. SrTiO₃ prepared at 550°C. As shown in Fig. S5, the stability of the SrTiO_{3-x}(550 °C) catalyst for hydrogen production with IR light was confirmed by using it more than five times, with each cycle containing 10 h of hydrogen production.

Conclusions

In conclusion, we demonstrated IR-driven water splitting via oxygen vacancy generation in a $SrTiO_{3-x}$ catalyst. After NaBH₄ treatment, the presence of mid-gap states in $SrTiO_{3-x}$ extends optical adsorption beyond the visible light region and into the near IR-region. The presence of oxygen vacancies contributes to enhanced light absorption and a decrease in charge recombination, which accounts for remarkably enhanced near-IR and visible light-initiated photocatalytic activity of $SrTiO_{3-x}$. In summary, this work demonstrates the feasibility of using low-photonic-energy IR light to produce hydrogen by water splitting, and the mid-gap Ov and Ti^{3+} states in $SrTiO_{3-x}$ -Ov are critical in the origin of the visible and near-IR responses of the catalyst.

Author contributions

The experiment and the manuscript were jointly done by J.B and C.R. SEM, TEM and RAMAN analyses were done by T.H. and $C \cdot Y$ and C.J contributed in the manuscript preparation. All authors contributed in writing the manuscript.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2023.01.146.

REFERENCES

- Maeda K. Photocatalytic water splitting using semiconductor particles: history and recent developments. J Photochem Photobiol C Photochem Rev 2011;12:237–68.
- [2] Martin A, Agnoletti M-F, Brangier E. Users in the design of hydrogen energy systems: a systematic review. Int J Hydrogen Energy 2020;45:11889–900.

- [3] Oliveira AM, Beswick RR, Yan Y. A green hydrogen economy for a renewable energy society. Curr Opin Chem Eng 2021;33:100701.
- [4] Dawood F, Anda M, Shafiullah GM. Hydrogen production for energy: an overview. Int J Hydrogen Energy 2020;45:3847–69.
- [5] De Silva NL, Jayasundera AC, Folger A, Kasian O, Zhang S, Yan C-F, et al. Superior solar-to-hydrogen energy conversion efficiency by visible light-driven hydrogen production via highly reduced Ti 2+/Ti 3+ states in a blue titanium dioxide photocatalyst. Catal Sci Technol 2018;8:4657–64.
- [6] Yang W, Prabhakar RR, Tan J, Tilley SD, Moon J. Strategies for enhancing the photocurrent, photovoltage, and stability of photoelectrodes for photoelectrochemical water splitting. Chem Soc Rev 2019;48:4979–5015.
- [7] Hota P, Das A, Maiti DK. A short review on generation of green fuel hydrogen through water splitting. Int J Hydrogen Energy 2022;48:523–41.
- [8] Li M, Wang L, Qian Y, Du J. Facile synthesis of MoS2/CuS nanoflakes as high performance electrocatalysts for hydrogen evolution reaction. Int J Hydrogen Energy 2022;47:5319–25.
- [9] Du J, Qian Y, Wang L, Yang H, Kang D. Facile synthesis of copper sulfides on copper foam as an efficient electrocatalyst for oxygen evolution reaction. Mater Today Commun 2020;25:101585.
- [10] Chowdhury FA, Trudeau ML, Guo H, Mi Z. A photochemical diode artificial photosynthesis system for unassisted high efficiency overall pure water splitting. Nat Commun 2018;9:1–9.
- [11] Villa K, Galán-Mascarós JR, López N, Palomares E. Photocatalytic water splitting: advantages and challenges. Sustain Energy Fuels 2021;5:4560–9.
- [12] Gannoruwa A, Ariyasinghe B, Bandara J. The mechanism and material aspects of a novel Ag 2 O/TiO 2 photocatalyst active in infrared radiation for water splitting. Catal Sci Technol 2016;6:479–87.
- [13] Jia D, Li X, Chi Q, Low J, Deng P, Wu W, et al. Direct electron transfer from upconversion Graphene quantum Dots to TiO2 Enabling infrared light-driven overall water splitting. Research 2022:2022.
- [14] Pratibha Kapoor A, Rajput JK. Nanostructured materials for the visible-light driven hydrogen evolution by water splitting: a review. Int J Hydrogen Energy 2022;47:17544–82.
- [15] Han K, Lin YC, Yang CM, Jong R, Mul G, Mei B. Promoting photocatalytic overall water splitting by controlled magnesium incorporation in SrTiO3 photocatalysts. ChemSusChem 2017;10:4510–6.
- [16] Zhao W, Zhao W, Zhu G, Lin T, Xu F, Huang F. Black strontium titanate nanocrystals of enhanced solar absorption for photocatalysis. CrystEngComm 2015;17:7528–34.
- [17] Higashi M, Kato Y, Iwase Y, Tomita O, Abe R. RhOx cocatalyst for efficient water oxidation over TaON photoanodes in wide pH range under visible-light irradiation. J Photochem Photobiol A: Chem 2021;419:113463.
- [18] Tan H, Zhao Z, Zhu W-b, Coker EN, Li B, Zheng M, et al. Oxygen vacancy enhanced photocatalytic activity of pervoskite SrTiO3. ACS Appl Mater Interfaces 2014;6:19184–90.
- [19] Tan X, Qin G, Cheng G, Song X, Chen X, Dai W, et al. Oxygen vacancies enhance photocatalytic removal of NO over an Ndoped TiO 2 catalyst. Catal Sci Technol 2020;10:6923–34.
- [20] Choudhury B, Bayan S, Choudhury A, Chakraborty P. Narrowing of band gap and effective charge carrier separation in oxygen deficient TiO2 nanotubes with improved visible light photocatalytic activity. J Colloid Interface Sci 2016;465:1–10.

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- [21] Wang Z, Yang C, Lin T, Yin H, Chen P, Wan D, et al. H-doped black titania with very high solar absorption and excellent photocatalysis enhanced by localized surface plasmon resonance. Adv Funct Mater 2013;23:5444–50.
- [22] Zhao Z, Goncalves RV, Barman SK, Willard EJ, Byle E, Perry R, et al. Electronic structure basis for enhanced overall water splitting photocatalysis with aluminum doped SrTiO 3 in natural sunlight. Energy Environ Sci 2019;12:1385–95.
- [23] Liu Q, Wang F, Lin H, Xie Y, Tong N, Lin J, et al. Surface oxygen vacancy and defect engineering of WO 3 for improved visible light photocatalytic performance. Catal Sci Technol 2018;8:4399–406.
- [24] Wang J, Chen R, Xiang L, Komarneni S. Synthesis, properties and applications of ZnO nanomaterials with oxygen vacancies: a review. Ceram Int 2018;44:7357–77.
- [26] Van Benthem K, Elsässer C, French R. Bulk electronic structure of SrTiO 3: experiment and theory. Appl Phys A APPL PHYS A-MATER 2001;90:6156–64.
- [27] Tan KH, Lee HW, Chen J-W, Dee CF, By Majlis, Soh AK, et al. Self-assembled heteroepitaxial AuNPs/SrTiO3: influence of AuNPs size on SrTiO3 band gap tuning for visible light-driven photocatalyst. J Phys Chem C 2017;121:13487–95.
- [28] Vento-Lujano E, González LA. Defect-induced modification of band structure by the insertion of Ce3+ and Ce4+ in SrTiO3: a high-performance sunlight-driven photocatalyst. Appl Surf Sci 2021;569:151044.
- [29] Yang G, Xiong J, Lu M, Wang W, Li W, Wen Z, et al. Coembedding oxygen vacancy and copper particles into titanium-based oxides (TiO2, BaTiO3, and SrTiO3) nanoassembly for enhanced CO2 photoreduction through surface/interface synergy. J Colloid Interface Sci 2022;624:348–61.
- [30] Steiner S, Heldt J, Sobol O, Unger W, Frömling T. Influence of oxygen vacancies on core-shell formation in solid solutions of (Na, Bi) TiO3 and SrTiO3. J Am Ceram Soc 2021;104:4341–50.
- [31] Li C-Q, Yi S-S, Liu Y, Niu Z-L, Yue X-Z, Liu Z-Y. In-situ constructing S-scheme/Schottky junction and oxygen vacancy on SrTiO3 to steer charge transfer for boosted photocatalytic H2 evolution. Chem Eng J (Lausanne) 2021;417:129231.
- [32] Liu J, Wei Z, Shangguan W. Enhanced photocatalytic water splitting with surface defective SrTiO3 nanocrystals. Front Energy 2021;15:700–9.
- [33] Patial S, Hasija V, Raizada P, Singh P, Khan Singh AAP, Asiri AM. Tunable photocatalytic activity of SrTiO3 for water

splitting: Strategies and future scenario. J Environ Chem Eng 2020;8:103791.

- [34] Eglitis RI, Purans J, Popov AI, Bocharov D, Chekhovska A, Jia R. Ab initio Computations of O and AO as well as ReO2, WO2 and BO2-Terminated ReO3, WO3, BaTiO3, SrTiO3 and BaZrO3 (001) surfaces. Symmetry 2022;14:1050.
- [35] Eglitis R, Popov AI, Purans J, Jia R. First principles hybrid Hartree-Fock-DFT calculations of bulk and (001) surface F centers in oxide perovskites and alkaline-earth fluorides. Low Temp Phys 2020;46:1206–12.
- [36] Orgiani P, Perucchi A, Knez D, Ciancio R, Bigi C, Chaluvadi SK, et al. Tuning the optical absorption of anatase thin films across the visible-to-near-infrared spectral region. Phy. Rev. Appl. 2020;13:044011.
- [37] Pasquale O, Daniel K, Regina C, Goran D, Bigi C, Chaluvadi SK, et al. Tuning optical absorption of anatase thin lms across the visible/near-infrared spectral region. 2020.
- [38] Shang M, Hu H, Lu G, Bi Y. Synergistic effects of SrTiO 3 nanocubes and Ti 3+ dual-doping for highly improved photoelectrochemical performance of TiO 2 nanotube arrays under visible light. J Math Chem A 2016;4:5849–53.
- [39] Naldoni A, Allieta M, Santangelo S, Marelli M, Fabbri F, Cappelli S, et al. Effect of nature and location of defects on bandgap narrowing in black TiO2 nanoparticles. J Am Chem Soc 2012;134:7600–3.
- [40] Baek J-Y, Lee SY, Seo H. Technology. Aluminum doping for optimization of ultrathin and high-k dielectric layer based on SrTiO3. J Mater Sci Technol 2020;42:28–37.
- [41] Tarsa E, Hachfeld E, Quinlan F, Speck J, Eddy M. Growthrelated stress and surface morphology in homoepitaxial SrTiO3 films. Appl Phys Lett 1996;68:490–2.
- [42] Cui H, Zhao W, Yang C, Yin H, Lin T, Shan Y, et al. Black TiO2 nanotube arrays for high-efficiency photoelectrochemical water-splitting. J Mater Chem 2014;2:8612–6.
- [43] Martinson AB, Góes MS, Fabregat-Santiago F, Bisquert J, Pellin MJ, Hupp JT. Electron transport in dye-sensitized solar cells based on ZnO nanotubes: evidence for highly efficient charge collection and exceptionally rapid dynamics. J Phys Chem 2009;113:4015–21.
- [44] Xu H, Yan C, Li R, Song L, Ouyang SJ. Synergetic modulation of surface alkali and oxygen vacancy over SrTiO3 for the CO2 photodissociation. Nanotechnology 2021;33:085401.
- [45] Yoshinobu J, Kawasaki S, Nakatsuji K, Yamamoto S, Matsuda I, Harada Y, et al. X-ray absorption and emission studies of the electronic states of visible-light semiconductor photocatalyst: Rh-doped SrTiO3. https://www.issp.u-tokyo. ac.jp/labs/sor/pdf/user/harima/yoshinobu/AR2011_ YoshinobuARev.pdf.