

Insights into unlocking the latent photocatalytic H₂ production activity in the protonated Aurivillius-phase layered perovskite Na_{0.5}Bi_{2.5}Nb₂O₉

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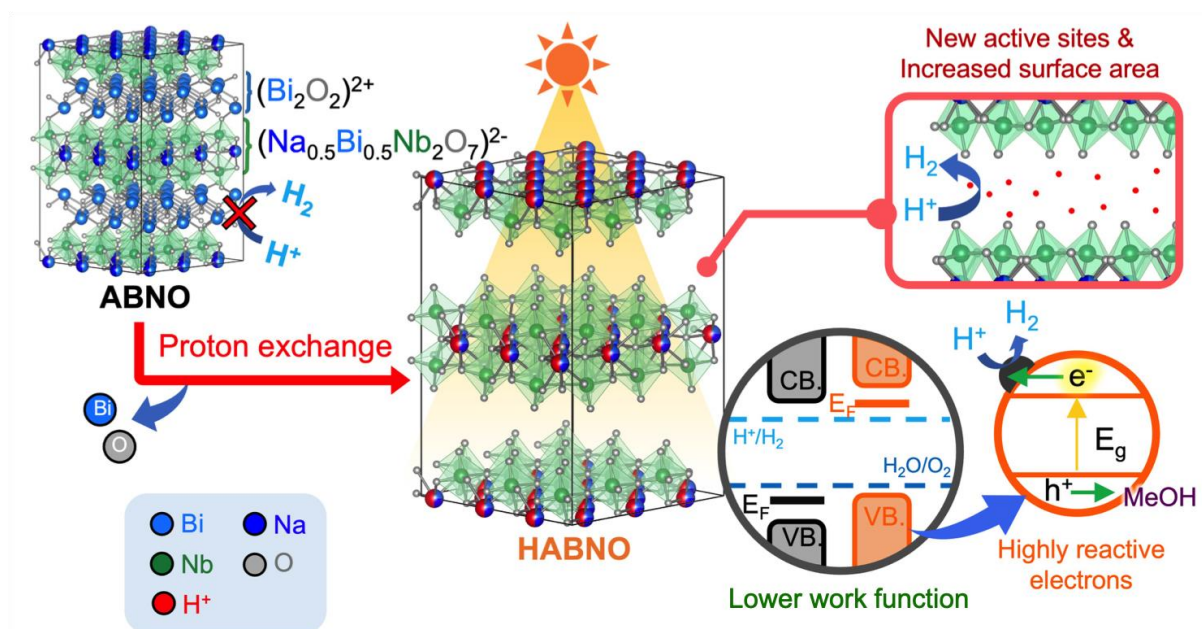
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Abstract

The introduction of protonated interlayers in layered perovskite compounds has already demonstrated promising results in terms of photocatalytic activity. However, the mechanisms behind the observed enhancements remain unexplored. Here, we report a rapid and efficient proton exchange process for $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ (ABNO), involving selective leaching of $(\text{Bi}_2\text{O}_2)^{2-}$ layers accompanied by the introduction of interlayer H^+ . This process, using acid treatment at room temperature is completed within only 24 hours, the fastest method to date for a layered perovskite. Protonation induces changes at the molecular and electronic level, investigated using Synchrotron-based techniques, diffused reflectance spectroscopy (DRS), DFT calculation, and transient absorption spectroscopy (TAS), influencing the electronic band structure, surface properties, and charge carrier dynamics of the compounds. After protonation, BET surface area increases by more than 20 times, to $156.19 \text{ m}^2/\text{g}$. These structural and surface modifications unlock the material's latent photocatalytic potential, enabling H^+ exchanged $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ (HABNO) to achieve a H_2 production rate of $242 \text{ }\mu\text{mol}/\text{h}/\text{g}$. This work delves into the photocatalytic mechanism, revealing how substitution by H^+ provides more active sites and enhances the ability of the material to generate more highly reactive electrons that can participate in H_2O reduction. This study highlights the promising strategy of altering the structure and electronic properties of layered materials through protonation to improve their performance for applications in photocatalysis for a cleaner and more sustainable future.

Graphical abstract



Research highlights

- Proton-exchanged $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ was prepared using the fastest process to date.
- Electronic band structures of $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ and its protonated form are reported.
- A lower work function unlocks the latent photocatalytic H_2 production activity.
- The first study of charge carrier dynamics reveals the photocatalytic mechanism.

Keywords: layered perovskite, proton exchange, photocatalysis, H_2 production, charge carrier dynamics

Introduction

The reliance on fossil fuels to support urbanization and industrial growth poses significant threats to the environment and human health. Alternative technologies like photocatalysis [1–3], which can convert solar energy to chemical energy, either for removing pollutants or producing energy carriers like clean H_2 fuel offer a promising solution [4]. The design of photocatalysts that efficiently convert solar energy into H_2 is an active field of research [5]. However, meeting all the necessary requirements remains challenging due to the many factors involved. The crystal structure of the photocatalyst is a critical factor in determining its activity because it affects orbital overlap and the resulting electronic band structure. This includes the energy of the bandgap and the position of the band edges, which influence the amount of solar energy the material can

absorb and its ability to drive redox reactions on its surface [6]. Layered perovskites are an appealing class of material increasingly studied for photocatalytic applications [7]. Their interlayer spaces serve as reaction sites and can generate intrinsic electric fields that help separate charge carriers [2,8,9]. In addition, the ability of reactants to penetrate the 2D layers of these perovskites shortens the distance charge carriers must travel, reducing recombination and enhancing activity [10,11]. Despite these advantages, some compounds with layered structures may not function efficiently as solar water splitting photocatalysts due to unfavorable electronic band structures [8,10]. However, substitution of ions in the lattice can create new active sites and modify the electronic band structures [10,12–15]. In line with this strategy, ion exchange, especially proton (H^+) exchange, has been shown to enhance photocatalytic activity for water splitting in layered perovskites [1,8,10].

Various studies have explored H^+ exchange in different layered-perovskite structure types, such as Ruddlesden-Popper and Dion-Jacobson [10,16]. Despite demonstrating significant improvements in photocatalytic H_2 production [17,18], layer perovskites based on the Aurivillius structure type, expressed with the general formula $Bi_2A_{n-1}B_nO_{3n+3}$ or $Bi_2O_2[A_{n-1}B_nO_{3n+1}]$, have been less studied for H^+ exchange. The understanding of photocatalytic properties in protonated Aurivillius-type structures has so far been limited to specific compounds. Studies on H^+ -exchanged $ABi_2Ta_2O_9$ ($A = Ca, Sr, Ba, K_{0.5}La_{0.5}$) indicate that H^+ intercalation enhances H_2O migration during water splitting reactions [11,19,20]. In $SrBi_2Nb_2O_9$ [21], proton exchange increases surface area, while the layered structure aids carrier separation. Similarly, changes in the conduction band edge potential following H^+ exchange have been linked to improved H_2 production activity in $K_{0.5}La_{0.5}Bi_2M_2O_9$ ($M = Nb, Ta$) [22] and $Bi_2SrNaNb_3O_{12}$ [23]. However, direct evidence supporting these claims remains lacking. Although the protonation strategy has shown promise, the mechanism underlying photocatalytic H_2 production in these protonated Aurivillius-type layered perovskites is still unclear. Furthermore, the acid treatment procedure often used typically takes several days to facilitate proton exchange [11,19,22,24,25].

In this work, we present the first report on the proton-exchange of $Na_{0.5}Bi_{2.5}Nb_2O_9$, an Aurivillius-phase layered perovskite compound. The materials were prepared through rapid acid treatment and completed within a 24-hour timeframe, representing the fastest process reported in the literature to date (Table S1). The proton exchange is shown to activate the ability of Aurivillius-type perovskite-layered compound to produce H_2 through

photocatalytic water reduction. By employing various investigation methods, this work provides a comprehensive understanding of the role of H^+ in the layered structure on the photocatalytic mechanism. **The key findings revealed the improved charge transfer efficiency in H^+ form as Synchrotron-based techniques, including X-ray photoelectron spectroscopy (XPS), Ultraviolet photoelectron spectroscopy (UPS), and diffused reflectance spectroscopy (DRS) expose reduced work function and Transient absorption spectroscopy (TAS) unveils enhanced electron reactivity.** This allowed us to gain unique insight on the reasons for the enhanced photocatalytic H_2 production activity seen in the proton-exchanged perovskite produced and studied herein, and could influence the rational design of more active perovskite structured materials.

Experimental

Materials.

Starting materials, including $Bi(NO_3)_3 \cdot 5H_2O$ ($\geq 99\%$, Sigma-Aldrich), $C_4H_4NNbO_9$ (99.99%, Sigma-Aldrich), NaOH ($\geq 98\%$, Sigma-Aldrich), HCl (37% fuming, Carl Roth), and HNO_3 (68-70%, Carl Roth) were used without further purification.

Sample preparation.

$Na_{0.5}Bi_{2.5}Nb_2O_9$ was synthesized using a method similar to a previously reported procedure [2]. In a typical synthesis, the precursors were dissolved in suitable solvents: 3 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 mL of 4 M HNO_3 solution and 2.88 mmol of $C_4H_4NNbO_9$ in 46 mL of DI water. The solutions were mixed through 5 minutes of stirring, after which 6 mL of a 30 w/w% NH_3 solution and 20 mL of 6 M NaOH solution were introduced. **The mixture was stirred for 30 minutes and then transferred to a Teflon-lined stainless-steel autoclave, heated at 180 °C for 36 hours. Subsequently, the resulting mixture was centrifuged, and the precipitate was washed three times with DI water before being dried at 80 °C overnight.** This resulting sample is identified herein as ABNO.

Proton exchange was performed using HCl treatment. In a typical procedure, 2 g of ABNO was dispersed in 400 mL of 3 M HCl and stirred for 24 hours at room temperature. Following this, the resulting precipitate was collected through centrifugation, washed three times with DI water and dried overnight at 80 °C. The obtained sample is denoted as HABNO. Moreover, optimization for acid treatment was conducted using 1 M HCl with different treatment durations, including 24, 48, and 72 hours. Subsequently, various HCl concentrations, including 1 M, 2 M, and 3 M, were studied with fixed treatment duration of 24 hours.

Sample characterizations.

X-ray diffraction (XRD) was conducted using a Bruker D2 Phaser with parallel beam optics equipped with a Lynx-Eye detector. Cu K α_1 ($\lambda = 1.54056 \text{ \AA}$) and Cu K α_2 radiation ($\lambda = 1.54439 \text{ \AA}$) were used (intensity ratio 2:1). High-quality XRD patterns were recorded between $5^\circ \leq 2\theta \leq 120^\circ$ with an increment of 0.02° and 2 s per step. Lattice parameters and the average crystallite size were determined using a least-squares refinement and the Scherrer equation. Scanning electron microscopy (SEM) images were acquired using a Zeiss AURIGA field emission gun scanning electron microscope (FEG-SEM) operating at an acceleration voltage of 5 kV. Additionally, a high-resolution transmission electron microscope (HRTEM) image and elemental composition were obtained using a Talos F200X Thermo Fisher Scientific field-emission transmission electron microscope (FE-TEM). Raman spectra were collected using a VERTEX 70 Bruker Fourier Transform Infrared Raman Spectrophotometer with a 1045 nm laser (220 mW light intensity). Thermogravimetric analysis (TGA) was performed under N $_2$ gas and from room temperature to 1000 °C at a heating rate of 10 °C/minute. The UV-visible diffuse reflectance spectra (DRS) were obtained using a Cary 60 Agilent UV-visible spectrophotometer with BaSO $_4$ as the reference. N $_2$ adsorption-desorption measurements were conducted using a Micromeritics ASAP 2420 porosimeter with the N $_2$ adsorbent. The BET method was used to determine specific surface areas. Prior to analysis, the samples were degassed at 150 °C for 3 hours.

Elemental composition and oxidation states of the samples were determined using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with Al K α monochromatic X-ray radiation (1486.6 eV). Adventitious carbon in the C 1s spectrum (284.8 eV) was used as a reference. The work function (Φ) was determined using monochromatic synchrotron light source ($h\nu = 60 \text{ eV}$) located at BL3.2a of the Synchrotron Light Research Institute (SLRI), Thailand. Φ can be calculated using the relation between $h\nu$, the cutoff edge (E_{cutoff}), and Fermi level (E_F) from the photoemission spectra with the equation $\Phi = h\nu - (E_{\text{cutoff}} - E_F)$. To separate the secondary electrons and acquire the local vacuum level of the sample, especially if it is more negative than that of the detector, the system was biased at -9.5 eV. The energy scale of the UPS spectrum was calibrated using gold (Au) as a reference, where E_F of Au was set to 0 eV. The E_F , valence band maximum (VBM), and E_{cutoff} of the samples were then determined relative to this calibration.

Transient absorption spectroscopy was measured from the microsecond to second timescale in diffuse reflection mode. A Nd:YAG laser (Litron Lasers, Stable Resonator Nano

S 120-20) was used as the excitation source, generating 355 nm UV light from the third harmonic ($\sim 725 \mu\text{J}\cdot\text{cm}^{-2}$ per pulse, repetition rate of 0.7 Hz, $\sim 4\text{--}7$ ns pulse width). A 100 W Bentham IL1 quartz halogen lamp was used to generate probe light. Long pass filters (Comar Instruments) were placed between the lamp and sample to minimize short wavelength irradiation of the sample. Transient change in diffuse reflectance from the sample was collected using a 2" diameter, 2" focal length lens and directed to a monochromator (Oriel Cornerstone 130). These changes were measured at wavelengths from 600 to 1100 nm, in 100 nm intervals. Time-resolved changes in diffuse reflectance were collected using a Si photodiode (Hamamatsu S3071). Data for times faster than 3.6 ms was recorded using an oscilloscope (Tektronics DPO3012) after passing through an amplifier box (Costronics), and data for times slower than 3.6 ms was recorded on a National Instrument DAQ card (NI USB-6251). Acquisitions were triggered by a photodiode (Thorlabs DET10A) from scattered laser light. Data was acquired and processed using home-built software written in Labview. Each kinetic trace was obtained from the average of between 100 and 350 laser pulses and measurements. Measurements were carried out in air. For each experiment, a few milligrams of each powder sample were pressed between two microscope slides, and held tight by tape, to make a homogeneous pressed powder sample. For chemical scavenger experiments, a few microliters of a chemical scavenger was placed on the surface of one side of the powder sample before being closed between the two microscope slides, with measurements carried out on the side of the sample where the scavenger was placed. Two chemical scavengers were studied, glycerol (Sigma-Aldrich, $\geq 99.0\%$) and an aqueous silver nitrate solution (Acros Chemicals, 99.99%, 20 mM).

Computational method.

The first-principles calculations were conducted using the projector augmented wave (PAW) method [26] within the Vienna ab initio simulation package (VASP) [27]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh (PBE) [28] functional was employed for the exchange-correlation energy. To optimize the crystal structures, electronic wave functions were expanded using a plane wave basis set with a cut-off energy of 520 eV. Brillouin zone integration was performed using a Monkhorst-Pack [29] mesh with a $7 \times 7 \times 1$ grid in primitive cells for both structures. The relaxation convergence criteria for energy and force were set to 0.001 eV/atom and 0.01 eV/Å, respectively. The calculated Local Density of States (LDOS) of the system utilized a Monkhorst-Pack mesh with a $13 \times 13 \times 2$ grid in primitive cells for both structures.

Photocatalytic test.

A suspension containing 50 mg of photocatalyst, 5.3 μL of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.25 M) and 120 mL of Milli-Q water/methanol (90/10 %v/v) was added to a photocatalytic reactor. The suspension was stirred under N_2 and a water-cooling bath was connected to the reactor to keep at constant temperature of 25 $^\circ\text{C}$. The suspension was purged with N_2 a flow rate of 20 $\text{mL} \cdot \text{min}^{-1}$ for 1 hour to remove residual O_2 . The solution was illuminated for 3 hours using a Xe lamp (1000 W), with light passed through an AM 1.5 and an IR filter to achieve 1 sun power (100 $\text{mW} \cdot \text{cm}^{-2}$ on the photocatalytic cell entrance). The reaction products were analyzed every 300 s by gas phase compact chromatograph.

Results and discussion

1. Material characterizations

Crystal structures.

The layered perovskite compound, $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ (ABNO), and its proton-exchange form (HABNO), were successfully synthesized, with their XRD patterns depicted in Figure 1a. The diffraction peaks confirm a single phase Aurivillius-type structure with orthorhombic symmetry (space group $A2_1am$), as per the standard database (PDF42-0397). As illustrated in Figure 2a, the crystal structure comprises $(\text{Bi}_2\text{O}_2)^{2+}$ layers interleaved with pseudo-perovskite $(\text{Na}_{0.5}\text{Bi}_{0.5}\text{Nb}_2\text{O}_7)^{2-}$ layers [30]. Sharp XRD peaks observed in the ABNO sample indicate high crystallinity. The crystallite size obtained using Scherrer's equation for the (115) peak was 31.58 nm. Notably, the intensities of the XRD peak corresponding to the (200) and (020) diffractions are approximately two times higher than the standard pattern. This suggests preferential crystal evolution along the [200] and [020] directions, promoting anisotropic development for the (001) plane and causing nanosheet growth [31]. Such variations in relative peak intensity are common in anisotropic nanomaterials [32–34].

Proton-exchanged HABNO was prepared via acid treatment, where H^+ interacts with oxygen atoms in the perovskite oxide, replacing cations through protonation [16,25]. However, acid treatment can dissolve the layered perovskite structure or introduce impurities like Ruddlesden-Popper phases and BiOCl . Therefore, conditions were optimized to achieve a pure H^+ substituted phase. Figure S1 illustrates XRD patterns of samples treated with different acids, concentrations, and durations. After 24 hours of treatment with 3 M HCl , the XRD peaks aligned with the parent ABNO phase, indicating preserved long-range order. However, broader and weaker diffraction peaks suggest reduced crystallinity and a smaller crystallite size of 7.56 nm. The unit cell parameters of

HABNO were determined using a least-squares refinement method and found to be smaller than those of ABNO, confirming successful proton exchange. The cell parameters a , b , and c for ABNO are 5.4690(8) Å, 5.4784(12) Å, and 25.3581(51) Å, respectively. In comparison, the corresponding parameters for HABNO are 5.4378(8) Å, 5.4488(12) Å, and 25.3367(51) Å. As a consequence, the unit cell volume is also smaller for HABNO, refined as 750.70(18) Å³ compared to 759.76(19) Å³ for ABNO.

The TEM image of ABNO (Figure 1b) shows lattice fringes with d-spacings of 0.272 nm and 0.269 nm, corresponding to the (200) and (020) planes, respectively. Considering the orthorhombic crystal system and growth mechanism, these findings suggest the exposure of the {001} crystal planes on the surface of the crystals. The SAED pattern of the ABNO sample (Figure 1d) reveals high crystallinity, with the angle between (200) and (020) planes matching the theoretical value of 90°. The same d-spacing is observed in the HABNO sample (Figure 1c), indicating that H⁺ was introduced into the interlayers perpendicular to [001] direction without affecting the exposed {001} crystal plane. Moreover, the SAED pattern of HABNO (Figure 1e) shows a diffused ring pattern, confirming a partial amorphization of the sample.

The Raman spectra are shown in Figure 1f to provide insights into the lattice structures. For ABNO, all observed Raman bands correspond to the vibrational modes of the Na_{0.5}Bi_{2.5}Nb₂O₉ lattice [35,36]. Significant changes were observed in the Raman spectrum of HABNO. A reduction in the intensities of bands (1), (2), and (4), assigned to the Bi³⁺ vibration in the (Bi₂O₂)²⁺ layer, indicates the disappearance of the (Bi₂O₂)²⁺ component. The band (3), related to the Nb⁵⁺ vibration, disappeared entirely. The band (5), associated with the vibration of the Bi–O bond corresponding to Bi³⁺ located at the A-site in the perovskite layer, was also absent, suggesting that Bi³⁺ in this position was replaced by H⁺. The band (6), attributed to Nb–O stretching, shifted to a higher frequency (blue shift), while band (8), corresponding to symmetric Nb–O stretching, disappeared. This indicates that only an asymmetric Nb–O environment remained due to the substitution of Bi³⁺ at the A-site with a much smaller cation like H⁺. The band (7) is likely related to lattice distortion or internal stress caused by proton exchange.

With evidence from XRD, TEM, and Raman, formations of ABNO and HBNO are summarized in Figure 1g-i. Due to its intrinsic layer structure and the higher chemical potential of (200) and (020) planes, the crystal exhibits anisotropic growth along [200] and [020] direction [2,31]. Consequently, the nanosheets with a (001) surface are obtained under hydrothermal conditions. Acid treatment causes ion-exchange reactions in the

296 layered structures of ABNO, selectively leaching the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and introducing H^+
297 ions into the lattice between the interlayers [16,24,25]. Interestingly, cell parameter c of
298 the sample changes only slightly after proton exchange, indicating that the interlayer
299 spacing is preserved despite the removal of the $(\text{Bi}_2\text{O}_2)^{2+}$ layers. This suggests that the
300 ABNO crystal structure includes large void spaces between the layers, facilitating water
301 diffusion during catalytic reactions.

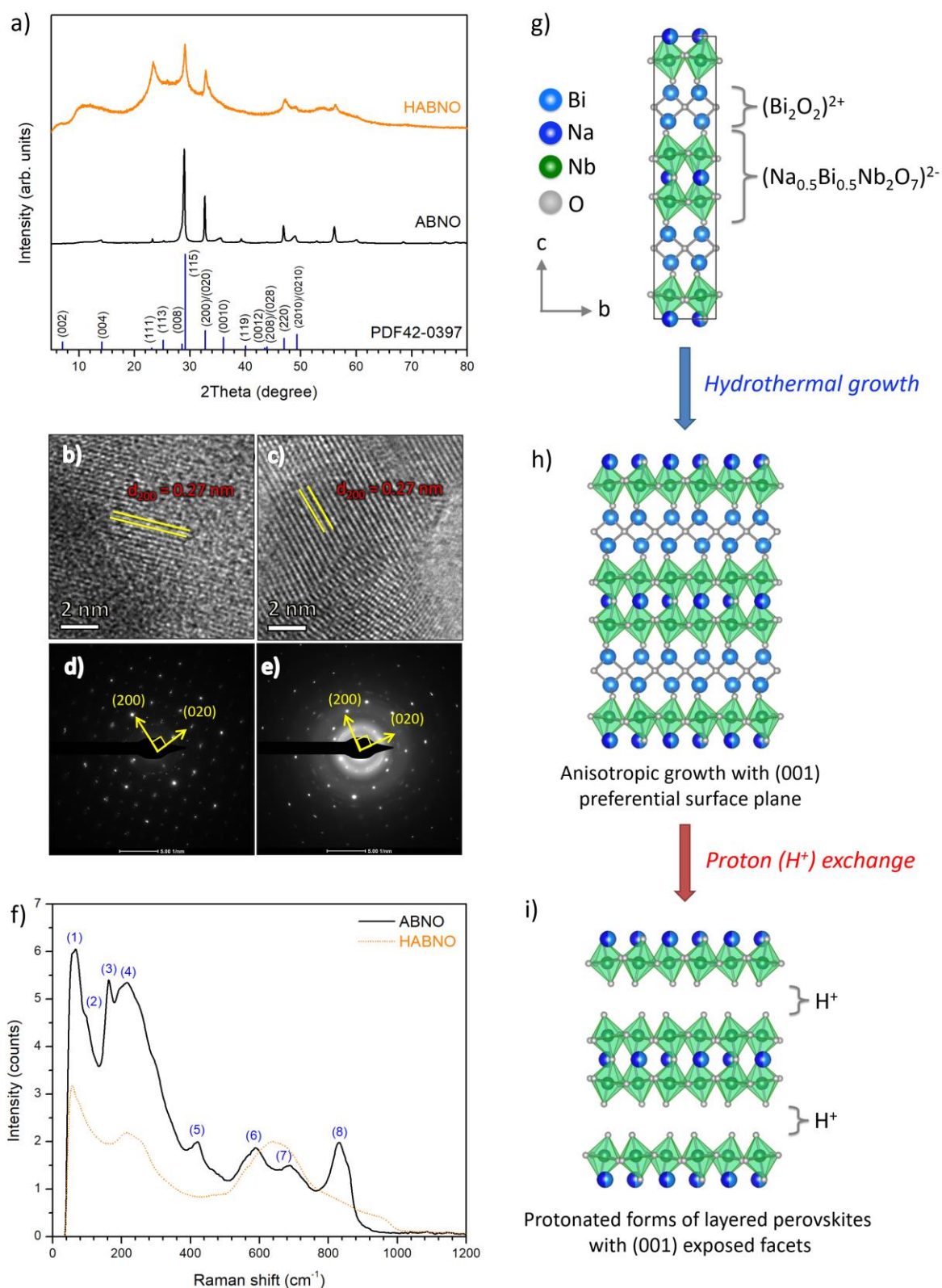


Figure 1. XRD patterns of ABNO and HABNO (a). HRTEM images and SAED patterns of ABNO (b, c), and HABNO (d, e). Raman spectra of ABNO and HABNO (f). Schematic illustration of crystal structures from the origin (g), after hydrothermal synthesis (h), and after proton exchange (i).

Chemical composition.

EDS analysis confirmed the chemical composition of the prepared compounds. As shown in Figure 2, TEM-EDS mappings illustrate an even distribution of Na, Bi, Nb, and O in the ABNO sample, with a metal ratio of $\text{Na}_{0.48}\text{Bi}_{2.78}\text{Nb}_2$ for ABNO, close to the expected ratios of $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2$. After proton exchange, significant reductions in Na and Bi were observed, resulting in a ratio of $\text{Na}_{0.12}\text{Bi}_{0.43}\text{Nb}_2$ for HABNO. These decreases indicate the replacement of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and some Na in the perovskite layer with protons [11,16,25]. While H^+ content, likely in the form of H_3O^+ , cannot be measured by EDS, TGA analysis (Figure S2) of HABNO shows approximately 10 w/w% loss of tightly bound H_3O^+ (around 100-400 °C). This value aligns with the expected 9.96 w/w% if all $(\text{Bi}_2\text{O}_2)^{2+}$ layers and 0.4 Na^+ are exchanged [22].

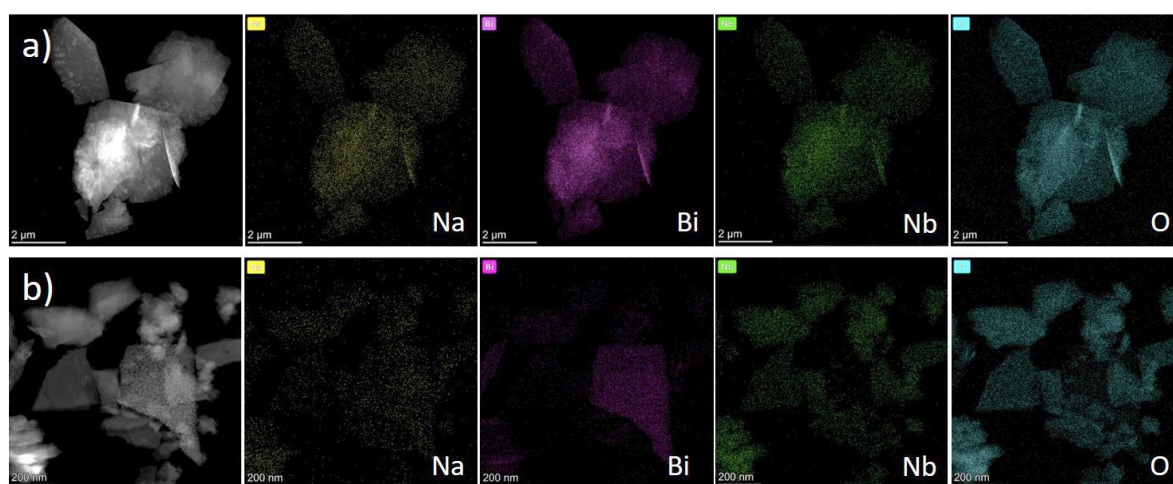


Figure 2. EDS mappings from transmission electron microscopy (TEM) techniques of ABNO (a) and HABNO (b).

XPS survey spectra confirm the presence of all expected elements in ABNO and HABNO, with no impurity elements detected (see Figure S3). Core-level XPS spectra for Na 1s, Bi 4f, Nb 3d, and O 1s, are presented in Figure 3. The binding energies of the deconvoluted peaks are reported in Table S2, and were identified as Bi^{3+} , Nb^{5+} , and Na^+ [2,3]. For O 1s spectra, two types of oxygen environments are observed in ABNO: oxygen bonded with cations in the lattice and oxygen bonded with adventitious C [2]. The additional peak in O 1s spectra of HABNO corresponds to adsorbed water molecules [2,37]. Upon H^+ introduction, the binding energies of Bi 4f and Nb 3d shifted higher by ~0.5 to 0.7 eV, indicating an electron-deficient local structure due to proton incorporation. Notably, Na 1s signals were insufficiently resolved in HABNO, indirectly confirming H^+ substitution at Na^+ sites in the structure.

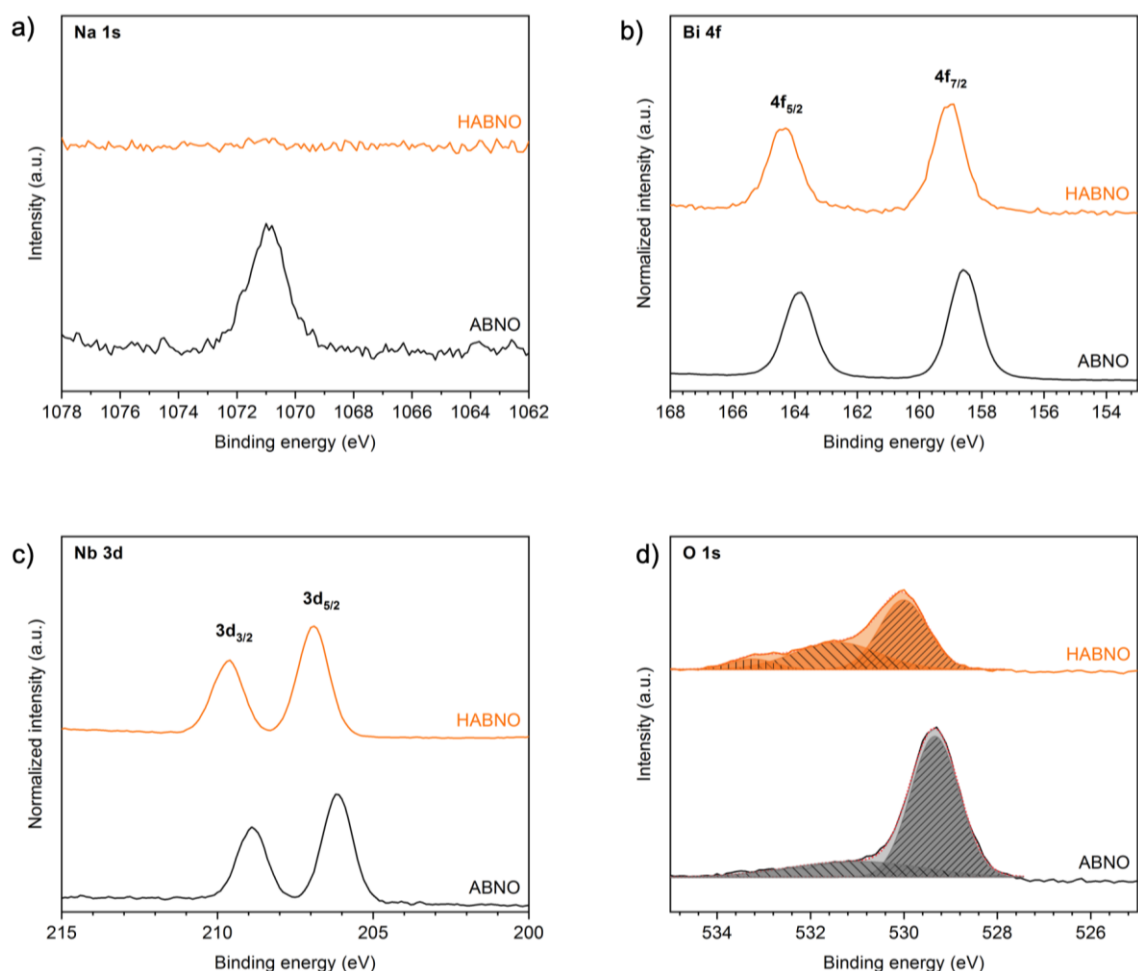


Figure 3. XPS spectra of core-level orbitals in ABNO and HABNO including Na 1s (a), Bi 4f (b), Nb 3d (c), and O 1s (d).

Physical properties.

The particle morphologies are shown in SEM and TEM images (Figure 4a-4h). Under hydrothermal synthesis conditions, these compounds typically form nanosheets due to their layered structure [2,31]. The ABNO sample consists of nanosheets with the size ranging from 1.9 to 4.8 μm and the thickness of 31.5 ± 11.4 nm, with smaller granular structures (39.7 ± 9.4 nm) distributed on their surface. After proton exchange, HABNO nanosheets are smaller (82.7 nm to 1.2 μm) and thicker (57.5 ± 21.4 nm). Particle size histograms of ABNO and HABNO are shown in Figure 4i. Furthermore, the proton exchange enhances the surface area from 7.08 m^2/g for ABNO to 156.19 m^2/g for HABNO. The increase in surface area through proton exchange can be attributed to structural changes induced by the process. Proton exchange replaces the larger, positively charged $(\text{Bi}_2\text{O}_2)^{2+}$ groups in the material's framework with smaller H^+ ions (protons). This

substitution loosens the parent layered structure, increasing the surface area available as active sites for adsorption of reactant and photocatalytic processes [23]. N₂ adsorption-desorption isotherms of all samples (Figure S4) can be classified as a non-porous or mesoporous material with weak adsorbent-adsorbate interaction. Both samples exhibit a primary pore size distribution around 50 nm, indicative of particle porosity. However, the total pore volume is significantly higher in HABNO, confirming that acid treatment enhances porosity, as evidenced by the increased BET surface area. HABNO also features smaller pores (<5 nm) attributed to H⁺ interlayers, which are less prominent in samples treated with 2 M HCl for 72 hours. This highlights the importance of treatment conditions, as complete proton exchange is necessary to improve porosity and surface area, underscoring the role of interlayer space in enhancing material properties.

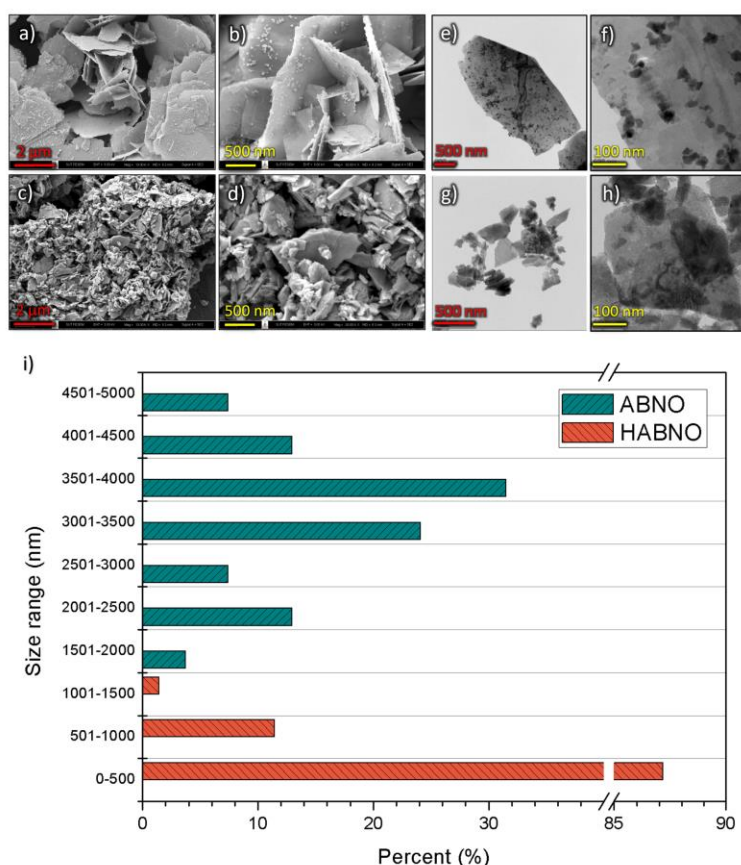


Figure 4. SEM images of ABNO (a, b) and HABNO (e, f). TEM images of ABNO (c, d) and HABNO (g, h). Particle size histogram of ABNO and HABNO (i).

2. Photocatalytic properties

For the photocatalytic H₂ production test, all samples were loaded with 0.5 w/w% Pt as a cocatalyst [22]. The XRD patterns of samples after 0.5 w/w% Pt loading showed no differences from the parent compounds (Figure S5a). Methanol (10 v/v%) was added as a sacrificial agent to prevent the back reaction (i.e. recombination of H₂ with OH and

photogenerated holes to form H₂O). Figure 5 illustrates the cumulative H₂ production of the photocatalysts during 3 hours of simulated solar light irradiation. The 0.5 w/w% Pt/ABNO showed minimal H₂ production (10 μmol/h/g), while 0.5 w/w% Pt/HABNO demonstrated a significantly enhanced H₂ production rate of 242 μmol/h/g. However, the prepared HABNO photocatalyst could not be reused for the subsequent cycle. The deactivation was suggested by the significant increase in BET surface area to 437.0 m²/g and the agglomeration of catalyst particles (Figure S5b-f). These changes are related to surface properties where the photocatalytic reaction takes place. While directly comparing H₂ production rates across different reports is challenging, the efficiency of the HABNO photocatalyst in this study is comparable to other proton-exchanged Aurivillius oxides (see Table S3 in the Supporting Information) [11,19,21–23]. Notably, the improvement after H⁺ incorporation relative to the pristine phase is evident.

A result from the acid-treat sample using 2 M HCl for 72 hours is also added in the plot, which exhibited a H₂ production rate of 22 μmol/h/g for its platinized form, which is only slightly higher than the one of pristine ABNO. This result suggests the importance of optimized conditions for proton exchange. It should be noted that the BET surface area of this sample (99.77 m²/g) is only 37% lower than that of HABNO, while its photocatalytic H₂ production is 10 times lower. The much lower photocatalytic efficiency in this sample could then be due to its higher amorphosity, illustrated by lower signal to noise ratio detected for XRD pattern (Figure S1).

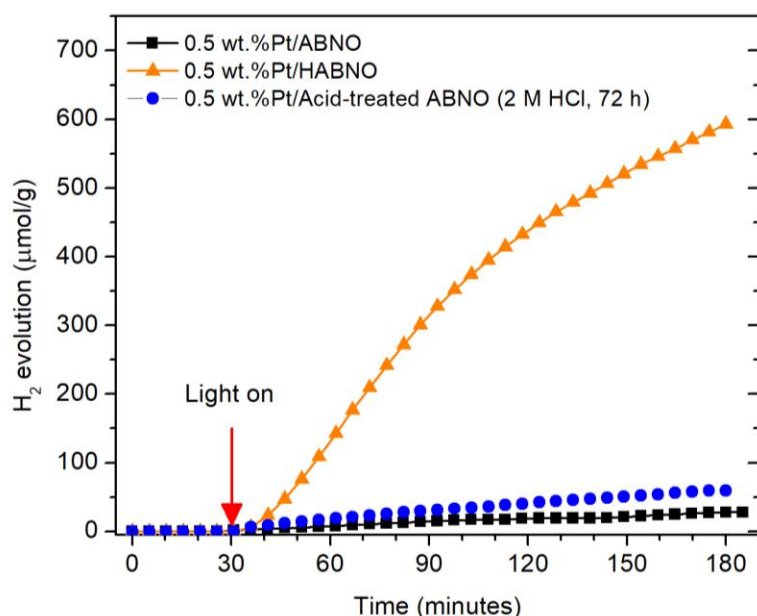


Figure 5. Photocatalytic H₂ production (μmol/g) under solar simulated light irradiation at 1 sun irradiance (Xe lamp, AM 1.5 and IR filter, 100 mW.cm⁻²) for platinized ABNO, HABNO (3M HCl, 24h), and the acid-treated ABNO using 2 M HCl for 72 hours.

3. Electronic band structures

While earlier works reports the photocatalytic efficiency enhancement in some proton-exchanged Aurivillius oxides, detail investigations on the exact roles of proton in the lattice and its correlation to the observed properties are still missing. To investigate this in detail, we experimentally determined the band edge positions and calculated the electronic band structure (EBS) of the compounds. Figure 6a presents the band edge positions of ABNO and HABNO. The ϕ values, representing the energy difference between the vacuum level and E_F , were determined using the aforementioned equation and validated through the measured valence band and cut-off spectra shown in Figure S6. The ϕ values for ABNO and HABNO were found to be 5.8 eV and 4.1 eV, respectively, enabling the determination of the E_F positions. The valence band maximum (E_{VBM}) was obtained by extrapolating the valence states for each sample, yielding values of 1.1 eV and 2.4 eV below E_F for ABNO and HABNO, respectively (Figure S6b). The conduction band minimum (E_{CBM}) was then calculated using the relationship $E_g = E_{CBM} - E_{VBM}$, where E_g is the band gap energy. Finally, the energy levels relative to the vacuum level (E_{vac}) were converted to the normal hydrogen electrode (NHE) scale using the equation: $E_{NHE} (V) = (E_{vac} + 4.44 \text{ eV})/e$, where e is the electrical charge of an electron [39,40].

The band gap energies of ABNO and HABNO determined from the Tauc plots (Figure S6a) are 3.05 eV and 3.30 eV, respectively. The larger band gap in proton-exchanged sample is attributed to a distortion in the layered perovskite structure, resulting in a change in the bond angle between metal and oxygen (M-O-M, where M represents metals) [41]. Figure 6a shows that both ABNO and HABNO have an E_{CBM} below 0 V relative to NHE, indicating theoretical feasibility for photocatalytic H₂ production. On the other hand, ϕ represents the minimum energy required for electrons to be removed into the vacuum. In our case, E_F relatively to the NHE scale, is 1.5 V for ABNO and -0.5 V for HABNO, indicating that electrons in HABNO could be more easily transferred. Particularly, a work function of lower than E_{NHE} suggests the lower energy barrier for photocatalytic hydrogen production in HABNO [42–44].

The EBS and local density of states (LDOS) shown in Figure 6b-f are obtained using the fully relaxed lattice parameters of $a = 5.49370 \text{ \AA}$, $b = 5.45710 \text{ \AA}$, $c = 24.91690 \text{ \AA}$, and $V = 747.00 \text{ \AA}^3$ for Na_{0.5}Bi_{2.5}Nb₂O₉ and $a = 5.61281 \text{ \AA}$, $b = 5.26052 \text{ \AA}$, $c = 19.21597 \text{ \AA}$,

and $V = 567.30 \text{ \AA}^3$ for the system after proton exchange, where $(\text{Bi}_2\text{O}_2)^{2+}$ layers are substituted with two H^+ . The results reveal that the VBM primarily consists of O p states, while the CBM primarily comprises Nb d states, resulting in an indirect band gap energy of 2.58 eV in ABNO. After proton exchange, a similar distribution of O and Nb states is observed in the valence band region across the same energy range. However, a decrease in Bi p states is noticeable due to $(\text{Bi}_2\text{O}_2)^{2+}$ leaching. It is noted that H s states are primarily detected at deep levels of around -6 eV due to their hybridization with O and Nb states. Interestingly, a mid-gap state is present at around 1 eV in HABNO, suggesting small alterations from the environment of O and Bi atoms, related to their p and s states, respectively. The calculated band gap of 2.78 eV for the HABNO sample agrees well with the trend observed from DRS.

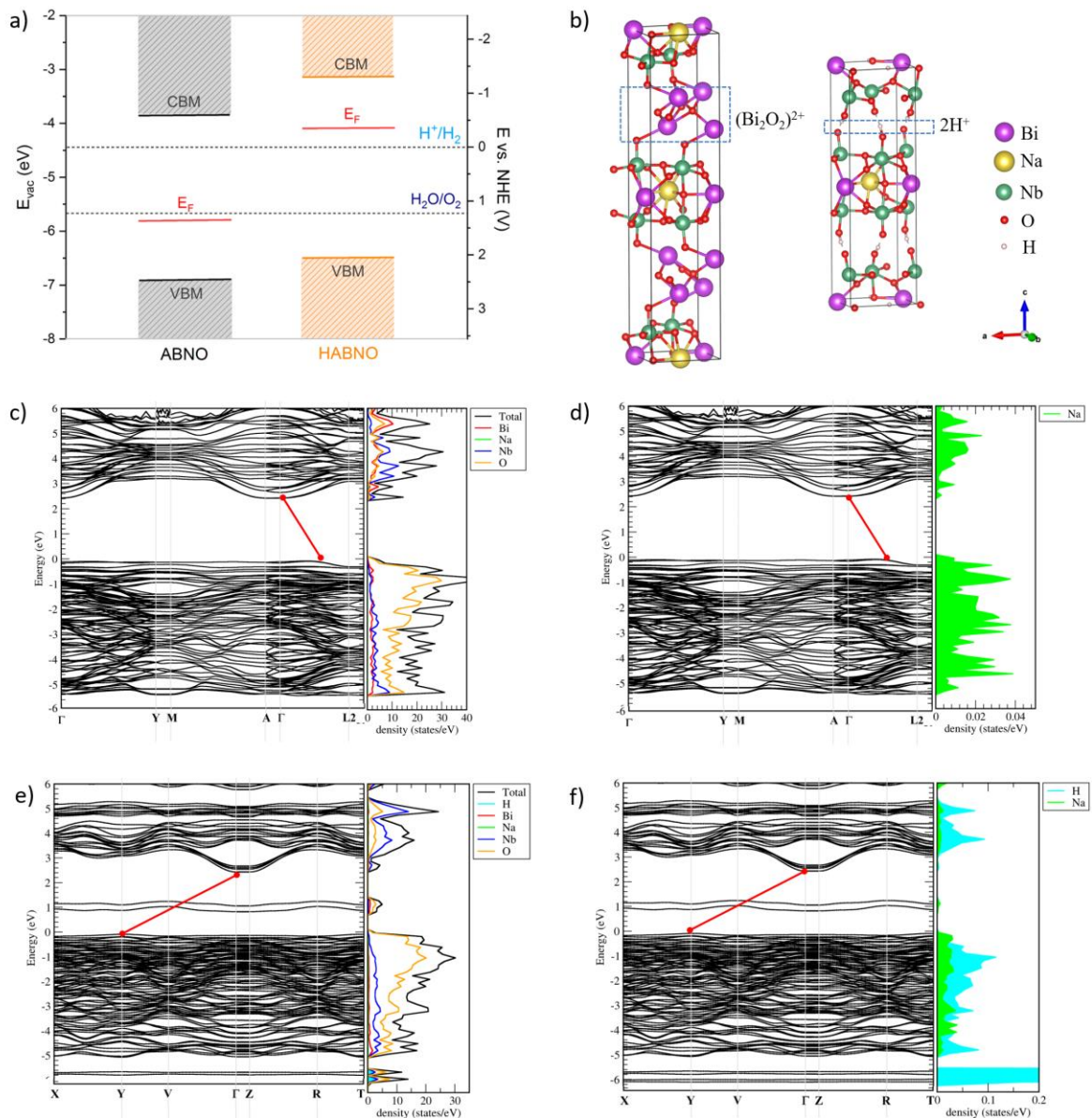


Figure 6. Band alignment of ABNO and HABNO samples as a function of vacuum level and NHE potential ($E_{\text{NHE}} = -(E_{\text{vac}} + 4.44)$) (a). Structural models (b) used for calculating DFT band structures and local density of states (LDOS) for ABNO (c, d) and HABNO (e, f).

4. Charge carrier dynamics

Transient absorption spectroscopy (TAS) was employed to investigate the intrinsic lifetime and reactivity of photogenerated charge carriers in ABNO, HABNO, and their platinized forms [45]. To our knowledge, the time-resolved charge carrier behavior of these materials has not previously been studied.

The recombination dynamics of ABNO and HABNO (Figure S7) followed a power-law function:

$$f(t) = A t^{-\alpha} \quad (\text{Equation 1})$$

where $f(t)$ is the charge carrier concentration at time t , and A and α are constants. Such behavior arises when ideal bimolecular recombination (seen for $\alpha = 1$) is disrupted by multiple trapping processes, in which a carrier is repeatedly thermally excited to the band-edge in order to move through the crystal [46,47]. Both materials exhibited similar initial transient absorption ($\sim 1 \Delta\text{O.D.}\%$ at $10 \mu\text{s}$), which assuming a similar extinction coefficient of photogenerated charge carriers in both ABNO and HABNO, indicates a similar initial population of photogenerated charge carriers. For ABNO, charge carrier recombination was faster at NIR wavelengths, indicating that there is a distribution of trap states in the material (Figure S7a). At 800 nm , a fit to the power law model (Equation 1) revealed an α of ~ 0.31 and a $t_{50\%}$ (i.e. the time taken for half the population of charges seen to decay from the start of the measurement, $10 \mu\text{s}$) of $\sim 110 \mu\text{s}$. For HABNO (Figure S7b), charge carrier recombination was faster, with an α of ~ 0.63 and a $t_{50\%}$ of $\sim 32 \mu\text{s}$. The intrinsic transient absorption spectra (Figure S8) of both materials showed broad transient absorption across the blue to NIR. ABNO consistently absorbed stronger in the blue (Figure S8a), while HABNO initially showed stronger NIR absorption (i.e. at $10 \mu\text{s}$) (Figure S8b), shifting to blue at longer times, suggesting similar trap state variations.

Upon platinization, the recombination kinetics in both systems were substantially slowed, with $t_{50\%}$ increasing to $\sim 300 \mu\text{s}$ for ABNO-Pt and $\sim 195 \mu\text{s}$ for HABNO-Pt (Figure S9). The near-linear decay on a logarithmic timescale indicates tunneling-mediated recombination [47] Also, after their platinization, the degree of initial transient absorption decreased in both materials ($\sim 90\%$ and $\sim 60\%$ lower transient absorption for HABNO and ABNO, respectively), which we attribute to parasitic light absorption losses by Pt. Both platinized materials showed broad visible-to-NIR absorption, with stronger absorption in the blue region (Figure S10).

For ABNO, the transient absorption decays and spectra in the presence of electron and hole scavengers are shown in Figure S11, and the decay kinetics at 800 nm and transient absorption spectra at 1 ms in the absence and presence of these scavengers are shown in Figure S12. In the presence of the electron scavenger, the photogenerated charge lifetime increased ($t_{50\%}$ of ~ 510 μs is observed), while the hole scavenger caused no significant change (Figure S12b). This suggests photogenerated electrons in ABNO are more mobile and reactive than holes. The transient absorption spectra (Figure S12d) show that hole carrier signals absorb more strongly in the blue region. Also, the transient absorption spectra of ABNO in the presence of an electron scavenger are similar to spectra measured in the absence of scavengers (Figure S12d).

For HABNO (Figures S13 and S14), scavenging effects were observed for both hole and electron scavengers. The hole scavenger increased the charge carrier lifetime ($t_{50\%}$ of ~ 370 μs at 800 nm) while the electron scavenger has much smaller effects ($t_{50\%}$ of ~ 51 μs at 800 nm) (Figure S14b). This was the reverse of what was seen in ABNO, and indicate that photogenerated holes in HABNO are more mobile and reactive than photogenerated electrons. The transient absorption spectra indicate that photogenerated electrons absorb more strongly in the NIR and photogenerated holes absorb more strongly in the blue (Figure S14d), which is similar to the prominent semiconductor photocatalyst, TiO_2 [48,49].

For ABNO-Pt (Figures S15 and S16), the electron scavenger significantly extended the charge carrier lifetime ($t_{50\%}$ ~ 810 μs at 800 nm), but not the hole scavenger ($t_{50\%}$ ~ 32 μs at 800 nm) (Figure S16b). For HABNO-Pt (Figures S17 and S18), the hole scavenger had a reduced effect, indicating lower mobility/reactivity of photogenerated holes after platinization. However, the activity in the presence of the electron scavenger was significantly enhanced ($t_{50\%}$ $\sim 57,200$ μs at 800 nm) more so than any of the other materials examined herein, which indicated that photogenerated electrons were more reactive and/or mobile after platinization of this system.

The charge carrier behavior of ABNO and HABNO, and its platinized forms, ABNO-Pt and HABNO-Pt, are compared in Figure 7. The carrier lifetime of ABNO is intrinsically higher than that of HABNO. Despite the smaller particle size and shorter diffusion distance in HABNO, its lower crystallinity adversely impacts carrier mobility, leading to reduced overall charge transport efficiency. After platinization, the initial populations of photogenerated charge carriers at 800 nm decreased due to parasitic light absorption, more prominent in HABNO (Figure 7a). Platinization significantly enhanced the intrinsic lifetimes of charge carriers, especially in HABNO ($t_{50\%}$ increased from ~ 32 to ~ 220 μs) compared to ABNO ($t_{50\%}$

increased from ~ 115 to ~ 330 μs) (**Figure 7b**). At 1 ms after the laser pulse, the timescale where water splitting processes typically occur, [50] both materials exhibited $\sim 50\%$ lower transient absorption, with a similar spectral shape favoring blue over NIR regions (Figure 7c). Despite reduced charge populations, platinization markedly improved charge carrier reactivity. In ABNO, carrier lifetimes roughly doubled in the presence of both electron and hole scavengers. In HABNO, electron scavenging increased carrier lifetimes by nearly three orders of magnitude (Figure 7d).

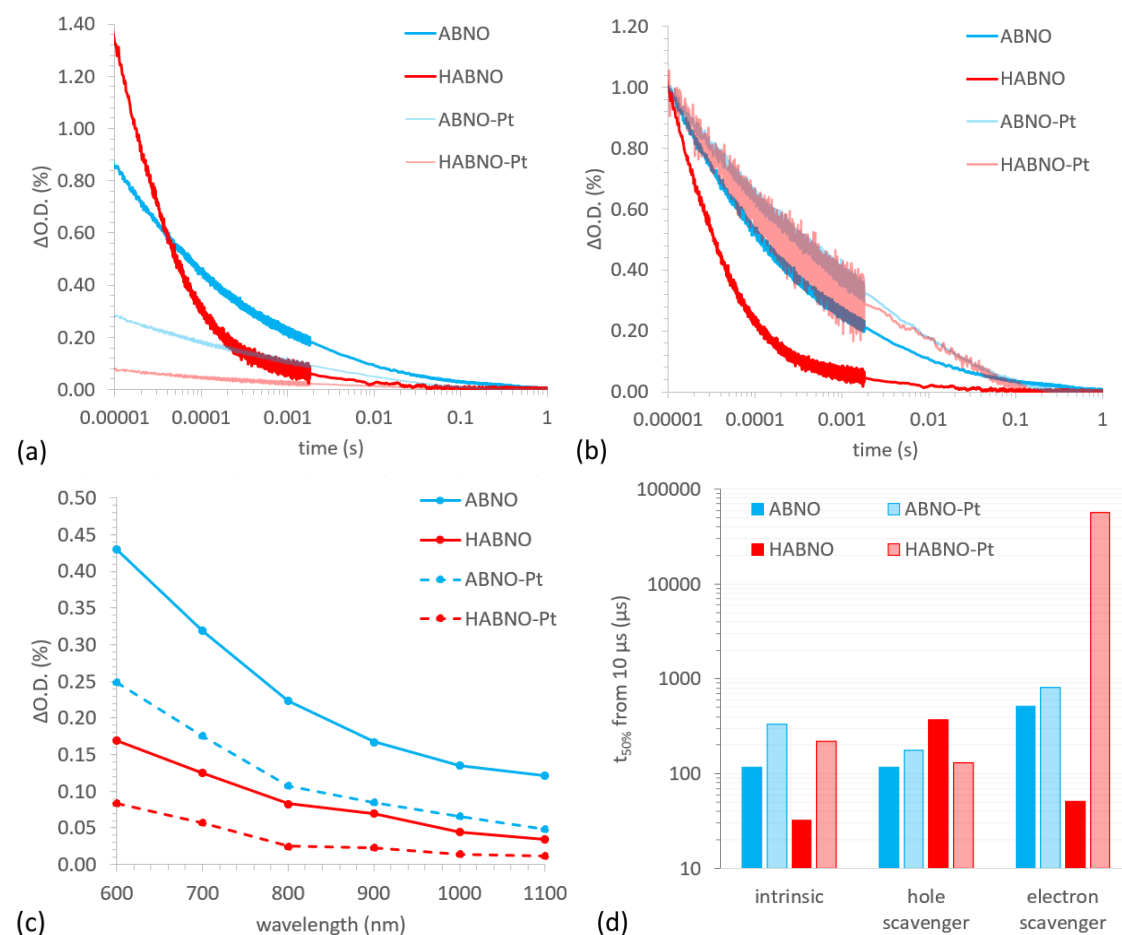


Figure 7. Comparisons of transient absorption behavior of ABNO and HABNO, and its platinized forms ABNO-Pt and HABNO-Pt (355 nm laser excitation pulse, $\sim 725 \mu\text{J}\cdot\text{cm}^{-2}$ per pulse, repetition rate of 0.7 Hz, $\sim 4\text{--}7$ ns pulse width). Non-normalized (a) and normalized (b) transient absorption decays measured in the absence of chemical scavengers at a probe wavelength of 800 nm. Transient absorption decays 1 ms after the laser pulse measured in the absence of chemical scavengers (c). Charge carrier lifetime ($t_{50\%}$ from 10 μs) of decays measured at a probe wavelength of 800 nm in the presence and absence of chemical scavengers (hole scavenger = glycerol, electron scavenger = aqueous silver nitrate solution) (d).

Discussion

The significant difference in photocatalytic H_2 production of ABNO and HABNO arise from differences in their chemical and physical properties, which can be rationalized as

follows: 1) HABNO possesses a more suitable EBS, having a higher CBM than ABNO, thus having a larger thermodynamic driving force to drive proton reduction [42,51,52]. **Additionally, the Fermi level of HABNO is also more negative than the proton reduction potential and the Fermi level of Pt. Thus, electron transfer from HABNO to Pt cocatalyst is more feasible and the enhanced carrier activity is more pronounced for platinized HABNO [11,20].** 2) Proton substitution in the $(\text{Bi}_2\text{O}_2)^{2+}$ layers creates large interlayer space, promoting hydration and water intercalation. This facilitates the transport of H_2O and methanol, into the interlayer and creates additional active sites for the oxidation and reduction reactions [12,13,53,54]; 3) It is evident that the proton-exchanged forms have significantly increased BET surface areas, indicating more active sites to facilitate reactions [10,55,56]. Even though the photo-generated electrons and holes possess thermodynamically sufficient potentials for water splitting, they will recombine if active sites for redox reactions are not present on the surface. Furthermore, larger surface areas also suggest that Pt deposition might be more effective on HABNO, increasing the positive effects of Pt cocatalyst as evidenced from TAS results.

Conclusion

The Aurivillius phase, double-layered perovskite $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ (ABNO) was proton-exchanged to form HABNO using a simple 3 M HCl treatment at room temperature for 24 hours. Our samples were characterized by various physical characterization methods. XRD revealed a single-phase HABNO material, with symmetry consistent with ABNO phase. As suggested by TEM-EDS, Raman, and TGA results, H^+ was introduced into the crystal lattices at the interlayers perpendicular to [001] direction. The elemental composition measured by EDS and XPS techniques revealed the leaching and replacement of $(\text{Bi}_2\text{O}_2)^{2+}$ layers with protons. Importantly, Photocatalytic H^+ production showed over a tenfold increase in activity for platinized HABNO compared to the platinized ABNO. The remarkable improvement of the photocatalytic activity was attributed to a dramatic increase in BET surface area, new active sites created by H^+ interlayers, smaller work function, and higher electron activity. **The proton exchange process unlocked the latent photocatalytic potential of ABNO, enabling H_2O reactant to access interlayer spaces and facilitating efficient transfer of photogenerated electrons and holes to H_2O for effective H_2 evolution. Additionally, the reduced work function and enhanced electron reactivity improved charge transfer efficiency. This work highlights the potential of proton exchange as a general strategy to enhance the electronic**

and physicochemical properties of layered semiconductor materials, providing a pathway to significantly improve photocatalytic H⁺ production in various systems.

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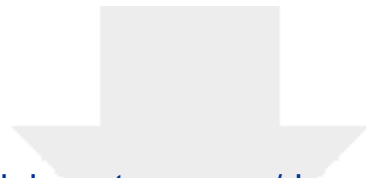
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Declaration of interests

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

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