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The Effects of Crystal Structure and Electronic Structure on Photocatalytic H₂ Evolution and CO₂ Reduction over Two Phases of Perovskite-Structured NaNbO₃

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ABSTRACT: Cubic and orthorhombic NaNbO₃ were fabricated to study the effects of crystal structure and electronic structure on the photocatalytic activities in detail. The samples were characterized by X-ray diffraction, field emission transmission electron microscopy, high-resolution transmission electron microscopy, UV–visible absorption spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic activities of the two phases of NaNbO₃ have been assessed by H₂ evolution from aqueous methanol solution and CO₂ photoreduction in gas phase. The photocatalytic H₂ evolution and CO₂ reduction activities over cubic NaNbO₃ were nearly twice of those over orthorhombic NaNbO₃. The first-principles calculation reveals that the higher activity over cubic NaNbO₃ can be attributed to its unique electronic structure, which is beneficial for electron excitation and transfer.

INTRODUCTION

As the fossil fuels have limitations in availability, a new source that can provide abundant and maintainable energy must be developed.1,2 For the past decades, photocatalysis has been developed as a candidate that can supply a renewable, unlimited, and environmentally friendly energy source to solve the energy crisis.3,4 The investigations on photocatalytic reaction mechanisms,5–7 energy-band structure engineering (including the optimization of crystal structure and the modulation of band energy levels),8–10 and morphology control11–15 have been carried out to enhance the photocatalytic efficiency. Generally, to study the relationship between crystal structure and electronic structure is helpful to understand the process of photogenerated carrier excitation and transfer. Up to now, the relevant studies have been performed on the TiO₂, CdS, BiVO₄, and AgGaO₂ with different crystal structures.16–19 Among intensively studied photocatalysts, the materials with perovskite and multilayered perovskite structures have received considerable attention.20–24 However, the report about the influence of crystallographic symmetry on photogenerated carrier excitation and transfer in the perovskite-structured photocatalysts is still limited.

NaNbO₃ is nontoxic, highly stable, and with a typical perovskite structure and thus attracts extensive attention in the field of photocatalysis. Many investigations have proved that NaNbO₃ is a high-efficient photocatalyst for H₂ generation.25–29 Under the irradiation of high-pressure mercury lamp, H₂O can be reduced into H₂ with quite high efficiency over NaNbO₃ nanoparticles.29 Nanofiber-structured NaNbO₃ was also verified to be useful to slit pure water and reduce CO₂ to CH₄.30 Moreover, NaNbO₃ normally belongs to the orthorhombic system at room temperature and exhibits an unusual complex sequence of temperature-, pressure-, and particle-size-driven phase transitions.31–35 When the temperature ranges from room temperature to 1000 K, there are several other phases of NaNbO₃ existing, such as tetragonal and cubic structures.36 All of them, cubic, tetragonal, and orthorhombic NaNbO₃, are constructed from a basic perovskite unit. However, to the best of our knowledge, all the reported photocatalytic measurements were carried out over the common orthorhombic NaNbO₃ and no measurement has been done over the other phases of NaNbO₃. Fabricating the NaNbO₃ with different crystal structures will help us to understand the influence of the crystallographic symmetry in the perovskite structure on the electronic structures and photocatalytic properties. Hence, in this work, cubic NaNbO₃ (c-NaNbO₃) and orthorhombic NaNbO₃ (o-NaNbO₃) were selectively synthesized.
The photocatalytic properties of these materials were characterized using the photocatalytic H₂ evolution and CO₂ photoreduction under UV–visible light irradiation. Detailed studies on the electronic structures were performed to understand the difference of photocatalytic activity between the c-NaNbO₃ and o-NaNbO₃.

## EXPERIMENTAL SECTION

**Material Preparation.** The c-NaNbO₃ was synthesized via a typical furfural alcohol derived polymerization–oxidation (FAPO) process. First, 1.0 g of (C₅H₄O₂)₃N and 0.24 g of C₅H₁₀ONa were added into 10 mL of 2-methoxyethanol and stirred at room temperature to form a clear colloid. After that, 2.5 g of P-123 (Mₜ = 5800) dissolved in 30 mL of furfuryl alcohol was added. Next, the mixture was stirred for 30 min and then heated to 95 °C with a rate of 1 °C·min⁻¹ and maintained at this temperature for 120 h in air to form a black solid polymer. Finally, the black solid was oxidized in air at 600 °C for 5 h, and a white powder product was obtained. To synthesize o-NaNbO₃ by a polymerized complex (PC) method, 1.0 g of NbCl₅ and 0.20 g of Na₂CO₃ were added into 10 mL of ethanol and stirred at room temperature to form a clear colloid. This colloid was then added into 50 mL of ethanol solution containing 12.0 g of critic acid and 2.0 mL of ethylene glycol. After it was stirred for 30 min, the mixture was heated to 120 °C with a rate of 1 °C·min⁻¹ and maintained at this temperature for 20 h in air for polymerization. Finally, the polymer was oxidized in air at 600 °C for 2 h, and a white powder product was obtained.

**Sample Characterization.** The crystal structure of NaNbO₃ powder was determined with an X-ray diffractometer (Rint-2000, Rigaku Co., Japan) with Cu Kα radiation. The diffuse reflection spectra were measured with an integrating sphere equipped UV–visible recording spectrophotometer (UV-2500PC, Shimadzu Co., Japan) using BaSO₄ as a reference, and the optical absorptions were converted from the reflection spectra according to the Kubelka–Munk equation. The specific surface areas were determined with a surface-area analyzer (BEL Sorp-II mini, BEL Japan Co., Japan) by the Brunauer–Emmett–Teller (BET) method. Transmission electron microscopy images and high-resolution images were recorded with a field emission transmission electron microscope (2100F, JEOL Co., Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) experiments were performed in type Theta probe (Thermo Fisher Co.) using monochromatized Al Kα at hv = 1486.6 eV, and the peak positions were internally referenced to the C 1s peak at 284.6 eV.

**Photocatalytic H₂ Evolution.** The H₂ evolution experiments were carried out in a gas closed circulation system. The NaNbO₃ powder (0.3 g) was dispersed by using a magnetic stirrer in CH₃OH aqueous solution (220 mL of distilled water + 50 mL of CH₃OH) in a Pyrex cell with a side window. The 0.5–1.5 wt % of Pt cocatalyst was photodeposited on the NaNbO₃ catalyst by adding a calculated amount of H₂PtCl₆ solution into the reaction solution. The light source was a 300 W Xe arc lamp without a filter (λ > 300 nm). The H₂ evolution was measured with an online gas chromatograph (GC-8A, Shimadzu) equipped with a flame ionization detector (FID) according to the standard curves. The H₂ evolution was measured with an online gas chromatograph (GC-14B, Shimadzu) equipped with a thermal conductivity detector (TCD) according to the standard curve.

**CO₂ Photoreduction.** The CO₂ photoreduction experiments were carried out in a gas closed circulation system with an upside window. The Pt-loaded catalyst powder (0.1 g) was dispersed on a small glass cell and then located in a Pyrex reaction cell. After that, 3 mL of distilled water was added into the gas closed reaction system. The whole system was then evacuated and filled with 80 kPa of pure CO₂ gas. The light source was a 300 W Xe arc lamp without a filter. The organic products were sampled and measured with a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector (FID) according to the standard curves. The H₂ evolution was measured with an online gas chromatograph (GC-8A, Shimadzu) with a TCD detector according to the standard curve.

**Theoretical Calculation.** The band structures, densities of state (DOS), and partial densities of state (PDOS) of cubic and orthorhombic NaNbO₃ were calculated using the plane-wave density functional theory (DFT) with the CASTEP program package. The core electrons were replaced by ultrasoft pseudopotentials with a plane-wave basis cutoff energy of 370 eV, and the interactions of exchange and correlation were treated within the framework of the local density approximation (LDA). The FFT grids of basis in all the models were 24 × 24 × 24 and 32 × 90 × 30 for c-NaNbO₃ and o-NaNbO₃, respectively. The k-point sets of 6 × 6 × 6 for c-NaNbO₃ and 5 × 2 × 5 for o-NaNbO₃ were used.

## RESULTS AND DISCUSSION

**Crystal Structure.** The basic perovskite NaNbO₃, which has a cubic structure with the space group of Pm₃m (Figure 1), is only stable at high temperature (>913 K). When cooling down from high temperature, NaNbO₃ undergoes a series of phase transitions from cubic to rhombohedral via intermediate tetragonal and orthorhombic phases. At room temperature, the common phase of NaNbO₃ is an antiferroelectric orthorhombic
phase, space group of $Pbcm$, $a = 5.506 \, \text{Å}$, $b = 5.566 \, \text{Å}$, and $c = 15.52 \, \text{Å}$ (Figure 1).\textsuperscript{39} This phase processes an “octahedral tilting” with three independent tilts as a $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 4a_0$ supercell of the basic cubic perovskite cell, where $a_0$ is the cubic lattice parameter, 3.906 Å.\textsuperscript{40}

The crystallographic phases of as-prepared NaNbO$_3$ were determined by X-ray diffraction (XRD) (Figure 2). The patterns show that the NaNbO$_3$ prepared through the FAPO route crystallized in a cubic system with the space group of $Pm\bar{3}m$, whereas the NaNbO$_3$ synthesized by a PC method was formed in an orthorhombic system with the space group of $Pbcm$. The diffraction peaks, of which $2\theta$ are about 32.5° and 46.5°, show the obvious difference between cubic and orthorhombic NaNbO$_3$. All peaks in these patterns could be indexed to the JCPDS database card (JCPDS-075-2102 for cubic and JCPDS-073-0803 for orthorhombic). Because the surface energy of c-NaNbO$_3$ is higher than that of o-NaNO$_3$ by common synthetic methods, the orthorhombic phase favors to form at room temperature.\textsuperscript{32,41} The formation of c-NaNbO$_3$ by a FAPO method is probably attributed to the addition of the surfactant P-123, which stabilized the surface of the c-NaNbO$_3$ crystal in solution. The study of the detailed mechanism of crystal growth is under way. The average crystallite sizes of c-NaNbO$_3$ and o-NaNbO$_3$ were calculated to be 18.5 and 23.1 nm using the Debye–Scherrer equation. The lattice parameters of NaNbO$_3$ were refined by the least-squares method (as listed in Table 1).

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) were further used to confirm the crystal structures of the as-prepared samples (Figure 3). The c-NaNbO$_3$ sample is constituted by particles with a uniform cuboid morphology. The cuboids are generally 40 nm in length. The o-NaNbO$_3$ sample contains irregular and cuboid particles. As exhibited in Figure 3b, the c-NaNbO$_3$ sample exhibits two mutually perpendicular fringes with the same $d$-spacing, 3.91 Å, which could be indexed to the phase $Pm\bar{3}m$.
and the orthorhombic fringes with lattice spacings of 5.52 and 5.59 Å are observed, corresponding to the \{010\} and \{100\} planes of o-NaNbO\(_3\) respectively. The insets of Figure 3b,d give the corresponding fast Fourier transform (FFT) patterns of two samples, which show the clear evidence to distinguish the two phases. The BET surface areas were measured to be 28.6 and 26.4 m\(^2\)g\(^{-1}\) for c-NaNbO\(_3\) and o-NaNbO\(_3\) respectively.

**Photophysical Property.** UV-visible absorption spectra of c-NaNbO\(_3\) and o-NaNbO\(_3\) powder samples are shown in Figure 4. Both the two samples have the only intense absorption with steep edges in the UV region. Compared with the absorption edge of o-NaNbO\(_3\) that of c-NaNbO\(_3\) has a slight red shift, suggesting that the c-NaNbO\(_3\) could absorb longer wavelength light. The band gaps \(E_g\) of c-NaNbO\(_3\) and o-NaNbO\(_3\) were determined according to the following equation

\[
(\alpha h \nu)^n = A (\nu - E_g)
\]

in which \(\alpha\), \(\nu\), \(A\), and \(E_g\) are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively.\(^ {42}\) The value of index \(n\) depends on the property of materials, where \(n = 2\) for the direct-band-gap semiconductor and \(n = 1/2\) for the indirect-band-gap semiconductor.\(^ {42}\) For both NaNbO\(_3\) samples, the \(n\) values were determined to be 1/2 according to the relationship between \(\log(\alpha h \nu)\) and \(\log(\nu - E_g)\). From the inset of Figure 4, the values of the band gaps for c-NaNbO\(_3\) and o-NaNbO\(_3\) are determined to be 3.29 and 3.45 eV, respectively. The c-NaNbO\(_3\) sample possesses a narrower band gap than o-NaNbO\(_3\).

**H\(_2\) Evolution Activity.** The H\(_2\) evolutions from CH\(_3\)OH aqueous solution (50 mL of CH\(_3\)OH + 220 mL of H\(_2\)O) over 0.5 wt % of Pt-loaded powder catalysts (0.3 g) under the irradiation of a Xe lamp (\(\lambda > 300\) nm) are presented in Figure 5a. As mentioned previously, both the cubic and the orthorhombic NaNbO\(_3\) are constructed of a basic perovskite structure. However, their photocatalytic activities are significantly different: c-NaNbO\(_3\) > o-NaNbO\(_3\). The H\(_2\) evolution amounts increased almost linearly in 8 h and were about 127 and 72.3 \(\mu\)molh\(^{-1}\) for c-NaNbO\(_3\) and o-NaNbO\(_3\), respectively. The difference in the photocatalytic activity between c-NaNbO\(_3\) and o-NaNbO\(_3\) is probably attributed to their different electronic structures and will be discussed in the following section.

For H\(_2\) evolution, the Pt serves as a cocatalyst to supply the reactive site where H\(_2\) could generate easily due to the low H\(_2\) overpotential on the Pt surface. The loaded Pt cocatalysts largely affect the H\(_2\) generation efficiency. The photocatalytic performance is influenced by the cover ratio and size of the cocatalyst that could be adjusted by the loading amount.\(^ {43}\) Since the c-NaNbO\(_3\) sample possessed a special morphology with a relatively high surface area, the optimization of the Pt cocatalyst was performed carefully in this study. The 0.5, 1.0, and 1.5 wt % of Pt cocatalyst were deposited on the c-NaNbO\(_3\) surface, and their corresponding photocatalytic H\(_2\) evolutions are plotted in Figure 5b. The H\(_2\) evolution rates over c-NaNbO\(_3\) were 127.4, 156.1, and 97.3 \(\mu\)molh\(^{-1}\) for 0.5, 1.0, and 1.5 wt % of Pt loading, respectively. The 1.0 wt % of loading amount supplied a proper cover ratio and size of cocatalyst and hence induced the highest H\(_2\) evolution rate for the c-NaNbO\(_3\) photocatalyst.

**CO\(_2\) Photoreduction Activity.** The photoreducible activity of NaNbO\(_3\) could also be applicable for converting CO\(_2\) into useful organic fuels, such as CH\(_4\). Figure 6a exhibits CH\(_4\) generation from CO\(_2\) photoreduction over c-NaNbO\(_3\) and o-NaNbO\(_3\) with a loading of 0.5 wt % Pt. The CH\(_4\) evolution rates over c-NaNbO\(_3\) and o-NaNbO\(_3\) were determined to be 0.486 and 0.245 \(\mu\)molh\(^{-1}\), respectively. The photoactivity order is the same as that of the H\(_2\) evolution reaction, c-NaNbO\(_3\) > o-NaNbO\(_3\). The optimization of the loading amount of Pt cocatalyst was also carried out for CO\(_2\) photoreduction. The 1.0 wt % of Pt-loaded c-NaNbO\(_3\) photocatalyst showed the best photocatalytic activity, which is in good agreement with the H\(_2\) evolution result (Figure 6b). These results reveal that the processes of electron excitation and transfer are similar in these two kinds of reactions.

It is well known that the CO\(_2\) photoreduction mainly undergoes two courses, including oxidation and reduction processes. In the oxidation process, H\(_2\)O is oxidized to O\(_2\) (2H\(_2\)O + 4h\(^+\) \(\rightarrow\) O\(_2\) + 4H\(^+\)). In the reduction course, there is a chain reaction to...
reduce CO$_2$ to CH$_4$ (CO$_2$ + 2H$^+$ + 2e$^-$ → HCOOH, HCOOH + 2H$^+$ + 2e$^-$ → HCHO + H$_2$O, HCHO + 2H$^+$ + 2e$^-$ → CH$_3$OH, CH$_3$OH + 2H$^+$ + 2e$^-$ → CH$_4$ + H$_2$O). To confirm that the CH$_4$ was generated from the photoreduction reaction, reference experiments were carried out over c-NaNbO$_3$ samples with 0.0, 0.5, 1.0, and 1.5 wt % Pt loaded. Figure 6c shows the concentration of CH$_4$ evolution when the reference experiments were carried out for 8 h. When the experiment was carried out in the absence of H$_2$O, only 0.1 ppm of CH$_4$ was detected. In the absence of catalyst or light irradiation, there were merely 0.33 and 0.15 ppm of CH$_4$, respectively. Since there is about 1 ppm of CH$_4$ in the natural air, the CH$_4$ in the above-mentioned experiments is considered as the contamination from air during samplings. Nevertheless, in the case that the CO$_2$ gas was replaced by Ar gas, 1.2 ppm of CH$_4$ was found. This value is obviously higher than that in natural air. As the sample was prepared from a carbon-containing precursor and NaNbO$_3$ possesses an alkaline surface, it is difficult to remove all the CO$_2$ from the sample surface even after a long calcination time. We once tested the CO$_2$ amount in the reaction system during the reference experiment without CO$_2$.
and found that about 300 ppm of CO₂ evolved from the sample surface. Therefore, a small amount of CH₄ should be generated from the photoreduction of the remaining CO₂ on the sample surface. Consequently, all the above-mentioned reference experiments prove that the H₂O supplies protons, CO₂ offers a carbon source, and the photocatalyst gives the redox potentials for the whole reaction to finally produce CH₄.

Besides CH₄, other hydrocarbon compounds (C₂H₄, C₂H₆, and C₃H₈) were also generated in the reaction. However, the productions of these organic compounds were much lower than that of CH₄. This results suggest that the long chain organic molecules are generated via photocatalytic reforming of CH₄, and CH₄ is the source of this reaction. 45,46 Inorganic by-products CO and H₂ were also detected, as shown in Figure 6d. CO is a common byproduct in the CO₂ reduction. Along with the CO₂ reduction over c-NaNbO₃, CO was produced with the rate of 0.082 μmol·h⁻¹. Although the reduction potential of H₂O to H₂ (−0.41 V vs NHE, pH = 7) is more negative than that of CO₂ to CH₄ (−0.24 V vs NHE, pH = 7),44 the evolution rate of H₂ (0.71 μmol·h⁻¹ catalyst) was higher than that of CH₄ (0.486 μmol·h⁻¹ catalyst). This could be attributed to that more electrons are consumed in CO₂ reduction (CO₂ + 6H₂O+8 e⁻ → CH₄ + 8OH⁻) than those in H₂O reduction (2H₂O + 2e⁻ → H₂ + 2OH⁻). Thus, the H₂ is easier to be generated dynamically.

Electronic Structure. The crystal structures of c-NaNbO₃ and o-NaNbO₃ are constructed of the same basic perovskite unit. Moreover, the band gap difference between the two materials is less than 0.2 eV. However, the photocatalytic H₂ generation and CO₂ reduction activities of c-NaNbO₃ are severely higher than those of o-NaNbO₃. Thus, the detailed investigation on band structure was carried out to understand this experimental phenomenon. The DFT calculation was used to investigate the electronic structures of c-NaNbO₃ and o-NaNbO₃. Figure 7a,b shows the calculated band structures of c-NaNbO₃ and o-NaNbO₃, respectively. The band structures indicate that both of them are typical indirect-band-gap semiconductors, which is consistent with the analysis of UV–visible absorption spectra. The theoretical band gaps of c-NaNbO₃ and o-NaNbO₃ are 1.63 and 2.33 eV, respectively, which are smaller than the values from experimental data. This difference is caused by the limitation of the LDA functional that underestimates the band gaps in semiconductor simulation. Besides the narrower band gap, the conduction band bottoms of c-NaNbO₃ and o-NaNbO₃ are significantly different. The energy level of the conduction band bottom in c-NaNbO₃ is lower than that in o-NaNbO₃. This difference is attributed to the variant octahedral ligand field of o-NaNbO₃ that changes Nb–O bond lengths and O–Nb–O

<table>
<thead>
<tr>
<th>Table 2. Optimized Bond Lengths and Bond Angles of NaNbO₃</th>
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<tr>
<td>Nb–O bond length (Å) O–Nb–O bond angle (degree)</td>
</tr>
<tr>
<td>c-NaNbO₃</td>
</tr>
<tr>
<td>1.966</td>
</tr>
<tr>
<td>90.00</td>
</tr>
<tr>
<td>o-NaNbO₃</td>
</tr>
<tr>
<td>1.971 (a–o)</td>
</tr>
<tr>
<td>86.13 (a–o–c)</td>
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<tr>
<td>93.65 (a–o–d)</td>
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<td>1.974 (b–o)</td>
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<tr>
<td>85.84 (a–o–c)</td>
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<tr>
<td>93.28 (a–o–f)</td>
</tr>
<tr>
<td>2.084 (c–o)</td>
</tr>
<tr>
<td>86.73 (b–o–c)</td>
</tr>
<tr>
<td>93.47 (b–o–d)</td>
</tr>
<tr>
<td>1.895 (d–o)</td>
</tr>
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<td>86.33 (b–o–c)</td>
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</tr>
<tr>
<td>96.20 (f–o–d)</td>
</tr>
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<td>89.71 (f–o–e)</td>
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Figure 8. Frontier orbital distributions of NaNbO₃: HOMO (a) and LUMO (b) of c-NaNbO₃; HOMO (c) and LUMO (d) of o-NaNbO₃.
bond angles (as listed in Table 2) of the basic cubic crystal structure. When the crystal structure of NaNbO₃ changes from cubic to orthorhombic style, the tilts of Nb–O bonds and the shifts of bond lengths contribute to lowering the energy; however, the Nb–O bond lengths in the z direction are nearly the same. Moreover, the frontier orbital distributions also supply the explanation for the photocatalytic activity difference (Figure 8). As the conduction band bottom of c-NaNbO₃ possesses a delocalized orbital covering Nb and O atoms, the photogenerated electrons could transfer along the x, y, and z directions. Nevertheless, for o-NaNbO₃ that possesses a localized conduction band bottom, the frontier orbital distributions exhibit a nonisotropy figure, inducing that the photogenerated electrons favor the migration along the z direction other than the x and y directions. Therefore, the high symmetry in the crystal structure of c-NaNbO₃ is beneficial for the transfer of photogenerated electrons and, subsequently, the better photo-reduction activity.

CONCLUSIONS
In conclusion, cubic and orthorhombic NaNbO₃ were synthesized to study the effect of crystallographic style on the electronic structure and photocatalytic activity in the perovskite structure in detail. This c-NaNbO₃ shows a narrower band gap (3.29 eV) than the common o-NaNbO₃ (3.45 eV). In photocatalytic H₂ generation, c-NaNbO₃ (127 μmol·h⁻¹) shows higher activity than o-NaNbO₃ (72.3 μmol·h⁻¹). For CO₂ photo-reduction in the gas phase, the CH₄ evolution rate over c-NaNbO₃ (0.486 μmol·h⁻¹) is about twice that over o-NaNbO₃ (0.245 μmol·h⁻¹). Theoretical calculation demonstrated that the band gap difference between the two phases of NaNbO₃ is caused by the variant octahedral ligand field. Furthermore, the high symmetry in c-NaNbO₃ results in its unique electronic structure that is beneficial for the electron excitation and transfer and thus contributes to its higher photocatalytic activity compared with o-NaNbO₃. The present study evidences that reforming the crystal structure of the perovskite semiconductor toward a higher symmetry can improve the photoelectron excitation and transfer. Therefore, it offers a new idea to enhance the photocatalytic efficiency in other perovskite or multilayered perovskite photocatalysts.

ASSOCIATED CONTENT
Supporting Information
XPS spectra of as-prepared NaNbO₃, XRD patterns and UV-visible absorption spectra of original catalysts and the catalysts after H₂ evolution and CO₂ reduction, and PDOS of Nb 3d and Na 1s orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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