Topological synthesis of crystalline Ag/T-Nb₂O₅ nanobelts with enhanced solar photoelectrochemical properties for splitting water

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Abstract
The tetragonal phase Nb₂O₅ (T-Nb₂O₅) nanobelts with preferentially exposed the (010) facet have been successfully prepared for the first time by in situ topological reaction using the KNb₃O₈ nanobelts as the precursor. Meanwhile, the transformation mechanism of the crystal structure and morphology from the layered KNb₃O₈ nanobelt to the T-Nb₂O₅ nanobelt was revealed in detail by using XRD, FE-SEM, TEM, HRTEM, SAED, UV-vis DRS, EDX, XPS, and Raman spectra. In addition, Ag deposited T-Nb₂O₅ (Ag/T-Nb₂O₅) nanobelts were prepared by photo-reduction reaction. The photoelectrochemical properties of the T-Nb₂O₅ nanobelts and Ag/T-Nb₂O₅ nanobelts as a photocatalyst were evaluated by splitting water under simulated sunlight. The results show that the photocurrent density generated by the prepared Ag/T-Nb₂O₅ sample is 48.1 µA cm⁻², which is 2.3 times that of the T-Nb₂O₅ sample, and the prepared tetragonal phase T-Nb₂O₅ nanobelts produce a photocurrent value 1.5 times that of the contrast orthogonal phase O-Nb₂O₅ nanosheets. It indicates that the (010) facet of the tetragonal phase Nb₂O₅ is one of the highest photocatalytic active surfaces, and the visible light utilization efficiency of the T-Nb₂O₅ nanobelt with Ag deposited on the surface has been significantly improved, which implies that it has potential applications in the field of photocatalysis.

KEYWORDS
Ag/T-Nb₂O₅ nanobelts, crystal structure evolution, photoelectrochemical properties, topological hydrothermal synthesis

1 | INTRODUCTION

Nowadays, human beings are facing the problems of global environmental pollution and fossil resource depletion, and it is urgent to develop renewable and clean energy. Photocatalysis, as a new science, can be used in environmental purification, photolysis water to produce hydrogen, solar photovoltaic cells, and carbon dioxide energy. In addition, photocatalyst has the advantages of low price, easy batch production, no secondary pollution,
and so on. Therefore, it has very attractive application prospects, especially using solar energy to decompose water in order to produce hydrogen, which will become a valuable and important technology for sustainable development in the future.\textsuperscript{[1,2]} Due to the different nature of semiconductor photocatalysts, their photocatalytic activity is also different. The energy level structure of a semiconductor has a close relationship with its band gap ($E_g$). Different semiconductors have different electronic energy level structures, and their valence band (VB) and conduction band (CB) positions are also different. As a result, different semiconductor photocatalysts have different photocatalytic activities. Even the same kind of photocatalyst shows different photocatalytic activities in the process of photocatalytic reaction due to its crystal type, crystallinity, exposed crystal facet, morphology, particle size and other properties.\textsuperscript{[3–5]} Among them, inorganic semiconductor materials are the most widely used photocatalytic active materials. In order to improve the utilization rate of solar energy and separation efficiency of photoelectrons, a lot of researches focus on the lattice structure (including lattice distortion, defect modulation, etc.), surface/interface chemistry, electronic structure, and morphological structure of semiconductor, and it has been found that these inherent properties have a great influence on the photocatalytic activity of semiconductor.\textsuperscript{[6]} This is very important to design and develop high efficient semiconductor photocatalytic materials.

In recent years, niobium oxide materials have been widely used in many fields, that is, catalysis, ferroelectricity, microelectronics, light refraction, nonlinear optics, piezoelectricity, and Li-ion batteries.\textsuperscript{[7–14]} Among niobium oxide materials, the most typical type is niobium pentoxide ($\text{Nb}_2\text{O}_5$), which is an important n-type semiconductor functional material. The most common crystalline phases are hexagonal $\text{Nb}_2\text{O}_5$, orthorhombic $\text{Nb}_2\text{O}_5$, monoclinic $\text{Nb}_2\text{O}_5$, and tetragonal $\text{Nb}_2\text{O}_5$.\textsuperscript{[15–17]} $\text{Nb}_2\text{O}_5$ has excellent optical properties, electrochemical response, chemical stability, corrosion resistance, and color changes. And it is widely used in many fields of optoelectronic devices, catalysts, high-performance dye-sensitized solar cells,\textsuperscript{[18–20]} selective oxidation of organic compounds,\textsuperscript{[21–28]} optical sensors,\textsuperscript{[29–31]} biological sensor,\textsuperscript{[32]} etc. Because the photocatalytic reaction takes place on the surface of the photocatalyst, the crystal structure on the surface of the catalyst has a great influence on its photocatalytic activity. However, in terms of photocatalysis, the research of niobium pentoxide is based on direct preparation or doping with various non-metals, metals, and forming heterojunctions to study its photocatalytic activity. For the different crystal phases of $\text{Nb}_2\text{O}_5$, in addition to the orthogonal phase and the hexagonal phase, the other crystal phases have relatively little research on photocatalysis. Since it is difficult to control the exposed crystal facets of the particles, there is very little research on the photocatalytic activity of each crystal facet. In order to obtain $\text{Nb}_2\text{O}_5$ photocatalysts with high photocatalytic activity, it is necessary to study its crystal phase (such as tetragonal and monoclinic phase) and exposed crystal facets. It is expected to replace $\text{TiO}_2$\textsuperscript{[33,34]} and provide a reference for the development of new photocatalysts.

In recent years, we have developed a new hydrothermal topological synthesis process, that is, firstly synthesizing the oxylate precursor with layered structure, then conducting acid exchange, and then preparing the oxide exposed the specific crystal facet related to the morphology of the precursor through hydrothermal topological synthesis. First, we have prepared the anatase $\text{TiO}_2$ nanocrystals exposed dominantly (010) facet with high photocatalytic activity from titanate nanosheets precursors,\textsuperscript{[35–37]} and the orthorhombic $\text{Nb}_2\text{O}_5$ nanosheets exposed dominantly (010) facet with high photocatalytic activity from $\text{K}_4\text{Nb}_6\text{O}_{17} \cdot 4.5\text{H}_2\text{O}$ nanosheets precursors under hydrothermal condition.\textsuperscript{[38]} Then, the monoclinic $\text{WO}_3$ nanosheets exposed dominantly the (100) facet have been prepared using $\text{H}_2\text{WO}_4$ disk particles as precursors by an in situ hydrothermal topological reaction.\textsuperscript{[39]} In this study, we first hydrothermally synthesized niobate $\text{KNb}_3\text{O}_8$ nanobelts with layered structure and uniform particle size by adding sodium oleate ($\text{C}_{17}\text{H}_{33}\text{CO}_2\text{Na}$). Then, the tetragonal phase $\text{Nb}_2\text{O}_5$ (T-$\text{Nb}_2\text{O}_5$) nanobelts were prepared by the in situ photocatalytic reduced reaction between the prepared $\text{Nb}_2\text{O}_5$ nanobelts and AgNO$_3$ aqueous solution. The photoelectrochemical properties of the obtained Ag/T-$\text{Nb}_2\text{O}_5$ nanobelts are evaluated by decomposing water into H$_2$ under simulated sunlight. We find that the prepared Ag/T-$\text{Nb}_2\text{O}_5$ nanobelts have high solar photocatalytic activity and high photoelectric conversion efficiency, indicating that it has potential application value in the preparation of photocatalysts and clean energies.

2 | RESULTS AND DISCUSSION

2.1 | Characterization of $\text{KNb}_3\text{O}_8$ samples synthesized by hydrothermal method

In order to prepare $\text{KNb}_3\text{O}_8$ nanocrystalline with layered structure, whose morphology and particle size meet the
requirements of the precursor, the synthesis conditions of KNb$_3$O$_8$ nanocrystalline prepared by hydrothermal method were investigated. Figure 1 shows the XRD patterns of the samples obtained by hydrothermal treatment at 200°C for 24 hours at different C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ molar ratio. When the molar ratio of C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ is 0, there is no diffraction peak of KNb$_3$O$_8$ in the pattern, as shown in Figure 1A, indicating that there is no crystallization of KNb$_3$O$_8$ in the obtained sample. As the molar ratio of C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ increases, it is found that KNb$_3$O$_8$ samples with good crystallinity can be obtained, as shown in Figure 1A to 1E. As shown in Figure 1C, when the molar ratio of C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ is 0.06, all of the diffraction peaks observed are exactly consistent with those of the orthorhombic phase KNb$_3$O$_8$ (JCPDS No. 75–2182, Amam (63), Z = 4, a = 8.903 Å, b = 21.16 Å, c = 3.799 Å, α = β = γ = 90°), where the strong diffraction peaks of the (020), (120), and (240) facets appear at 8.3°, 12.9°, and 26.1°, respectively. In addition, there are also weak diffraction peaks corresponding to (040), (140), and (011) facets, etc. The obtained sample is a pure orthorhombic phase KNb$_3$O$_8$. Figure 2 shows the FE-SEM images of the above samples. When the molar ratio of C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ is 0, the sample shows irregular granules as shown in Figure 2A. When the molar ratio is 0.03, some sheet-like morphology in the sample can be observed as shown Figure 2B. When the molar ratio is 0.06, the sample displays regular belt-like morphology with a size of 4−8 µm in length, about 400 nm in width and about 20 nm in thickness (Figure 2C). When the molar ratio of the two is 0.12, the length of the particles is about 10 µm, the width is about 600 nm, and the thickness is about 45 nm (Figure 2D). The size of the sample particles has obviously grown, which indicates that the addition of sodium oleate is conducive to the formation of KNb$_3$O$_8$ crystals. But when the molar ratio is 0.24, the FE-SEM images of the sample (Figure 2E) show not only the belt-like morphology of KNb$_3$O$_8$ particles, but also the floculent morphology, which is found to be residual organic sodium oleate by EDX analysis. We found that the KNb$_3$O$_8$ nanoparticles gradually become longer, wider and thicker as the amount of sodium oleate increases and its morphology has also changed from the original short irregular rectangular nanosheets to slightly longer and regular nanobelts, finally to the longer strip-like nanobelts (see Figure 2B-2D). The above results indicate that the addition of an appropriate amount of sodium oleate is beneficial to the formation of the precursor KNb$_3$O$_8$. However, excessive addition of sodium oleate not only made it difficult to clean, but also made the prepared KNb$_3$O$_8$ nanoparticles larger, thus affecting the photocatalytic performance of the prepared oxide. In summary, C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ molar ratio of 0.06 is the best choice for the preparation of pure orthorhombic phase KNb$_3$O$_8$ nanobelts with particle size meeting the requirements of the precursor. The synthesis time of the precursor KNb$_3$O$_8$ nanobelts has been greatly reduced by compared with the hydrothermal synthesis method of KNb$_3$O$_8$ reported.

2.2 Characterization of protonated niobate H$_3$ONb$_3$O$_8$ sample

Proton niobate was obtained by the ion exchange reaction between the precursor KNb$_3$O$_8$ nanobelts and HNO$_3$ solution (1.2 mol·L$^{-1}$). The XRD patterns of niobate before and after acid exchange are shown in Figure 3. The peak position of the XRD pattern is exactly the same as that of the orthorhombic phase H$_3$ONb$_3$O$_8$ (JCPDS No. 44–0672, Pnnm (58), Z = 4, a = 9.183 Å, b = 22.47 Å, c = 3.775 Å, α = β = γ = 90°). The peak shape is high and sharp, indicating good crystallinity of the sample obtained after the acid exchanges. Compared with the XRD pattern of the KNb$_3$O$_8$ sample before acid exchange at the bottom, the diffraction peak of (020) facet shift to low angle, indicating that the interlayer spacing of the sample H$_3$ONb$_3$O$_8$ increased from 1.06 to 1.12 nm. The EDX analysis result of chemical composition of the sample H$_3$ONb$_3$O$_8$ shows that there is almost no K element, which indicates that the K$^+$ ions in the sample KNb$_3$O$_8$ have been exchanged completely (Figure S1).

The FE-SEM, HRTEM images and SAED patterns of the precursor KNb$_3$O$_8$ nanobelts and the H$_3$ONb$_3$O$_8$ sample are shown in Figure 4. It can be observed that both the precursor KNb$_3$O$_8$ and H$_3$ONb$_3$O$_8$ sample show the...
FIGURE 2 FE-SEM images of the samples obtained by hydrothermal treatment at 200°C for 24 hours at different C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ molar ratio.

FIGURE 3 XRD patterns of the precursor KNb$_3$O$_8$ obtained by hydrothermal treatment at 200°C for 24 hours under C$_{17}$H$_{33}$CO$_2$Na/Nb$_2$O$_5$ molar ratio as 0.06 and the obtained H$_3$ONb$_3$O$_8$ sample.

nanobelt-like morphology (Figure 4A and 4B). The H$_3$ONb$_3$O$_8$ nanobelts (Figure 4B) have the size similar to the precursor KNb$_3$O$_8$. The clear lattice fringes of the precursor KNb$_3$O$_8$ sample can be observed in Figure 4C. The lattice spacings with $d$-values of 0.89 and 0.37 nm be assigned to the (100) and (001) facets of the orthorhombic phase KNb$_3$O$_8$ crystals, respectively. It is found from the inset SAED pattern of the KNb$_3$O$_8$ sample that the diffraction spots with $d = 0.89$, 0.37 and 0.35 nm correspond to the (100), (001), and (101) facets of the orthorhombic phase KNb$_3$O$_8$, respectively. These results show that the long axis direction of the orthorhombic KNb$_3$O$_8$ nanobelts corresponds to the [001] direction, and the short axis corresponds to the [100] direction, and the dominant exposed surface is the (010) facet. This indicates that added surfactant sodium oleate mainly adsorbed on the [010] surface of KNb$_3$O$_8$ particles, which reduced the surface energy and promoted the growth of the ions constructing the crystal on [001] and [100] facets, accelerating the formation of KNb$_3$O$_8$ banded crystal.$^{[44,45]}$ Figure 4D and 4E correspond to the HRTEM image and SAED pattern of the orthorhombic phase H$_3$ONb$_3$O$_8$, respectively. The lattice fringe spacings of $d = 0.91$ and 0.37 nm correspond to the (100) and (001) facets of the orthorhombic phase H$_3$ONb$_3$O$_8$ crystal, respectively (Figure 4D). According to Figure 4E, it is found that the diffraction spots with $d = 0.91$, 0.37 and 0.35 nm correspond to the (100), (001), and (101) facets of the orthorhombic phase H$_3$ONb$_3$O$_8$, respectively. The above results show that the long axis direction and dominant exposed surface of the H$_3$ONb$_3$O$_8$ crystal obtained by H$^+$ exchange are consistent with those of the precursor KNb$_3$O$_8$ crystal.

To determine the chemical composition of the samples, the XPS spectra of precursor KNb$_3$O$_8$ sample and H$_3$ONb$_3$O$_8$ sample are showed in Figure S2. The C 1s peak from the adventitious carbon with band energy of 284.8 eV, was used as an internal standard. In the XPS spectrum of the KNb$_3$O$_8$ nanobelts measured, the peaks from K, Nb, C, and O elements are detected and shown in Figure S2a. The high resolution XPS spectrum of Nb 3d in Figure S2b can be assigned to a binding energy of
206.84 eV for Nb 3d_{5/2} and 209.58 eV for Nb 3d_{3/2}, which are identified as the binding energies of Nb^{5+}.

The two binding energy peaks of 292.56 and 295.28 eV shown in Figure S2c, corresponding to K 2p_{3/2} and K 2p_{1/2}, respectively, can be identified as the binding energies of K^{+} within the K Nb_{3}O_{8} nanobelts. Figure S2d shows the XPS measurement spectrum of the protonated niobate H_{3}O Nb_{3}O_{8} sample. It is found that the two binding energy peaks of K 2p_{3/2} and K 2p_{1/2} disappeared, again proving that the component K was completely replaced. The high resolution XPS spectrum of Nb 3d of the H_{3}O Nb_{3}O_{8} sample is shown in Figure S2e. The binding energies of Nb 3d_{5/2} and Nb 3d_{3/2} is 207.77 and 210.53 eV respectively, which is determined as the binding energy of Nb^{5+}. The valence band position of the H_{3}O Nb_{3}O_{8} sample has moved up by 0.95 eV compared with the precursor K Nb_{3}O_{8} sample.

The Raman spectra of the obtained samples K Nb_{3}O_{8} and H_{3}O Nb_{3}O_{8} are shown in Figure S3. In the Raman spectrum of the K Nb_{3}O_{8} nanobelts (Figure S3a), the peaks observed at 950.9, 920.6, and 894.1 cm^{-1} are attributed to stretching modes of the short Nb–O bonds. The peaks between 656–571 cm^{-1} can be assigned to stretching vibration of the longer Nb–O bonds. The peak at 451.2 cm^{-1} is assigned to Nb–O–Nb bending modes, and the bands at 321.5 and 351.7 cm^{-1} can be assigned to the E mode corresponding to deformation in the NbO_{6} framework. This indicates that the orthorhombic phase K Nb_{3}O_{8} has two different types of octahedral. The first one has shorter Nb–O bonds causing a sharp deformation of such NbO_{6} units. The other has longer Nb–O bonds and is slightly distorted. Compared with that of the layered K Nb_{3}O_{8}, the Raman spectrum of the H_{3}O Nb_{3}O_{8} indicates that the Nb–O terminal bond was affected by the H^{+}-exchanged reaction, resulting in the Raman energy band at 950.9 cm^{-1} becoming weaker and broader and a new weak band at 965.7 cm^{-1} arising at the same time (Figure S3b). The hydrogen bonds, which were formed by the H^{+}-exchange reaction, in the layered H_{3}O Nb_{3}O_{8} crystal structure, associated with the interlayer terminal oxygen atoms of NbO_{6} to form Nb–O–H bonds. This is similar to the phenomenon appearing in the previous studies.

2.3 Characterization of the obtained T-Nb_{2}O_{5} nanobelts

The transformation temperature from H_{3}O Nb_{3}O_{8} into T-Nb_{2}O_{5} is related to the pH value of the reaction solution. The XRD patterns of the samples obtained by treating hydrothermally H_{3}O Nb_{3}O_{8} nanobelts suspension with different pH value are shown in Figure S4. According to the XRD analysis results of the samples obtained under different pH conditions, the temperature and pH dependences of the samples are summarized in Figure 5. The dashed line delineates boundary between T-Nb_{2}O_{5} phase and the mixed phase with H_{3}O Nb_{3}O_{8} and T-Nb_{2}O_{5}, meaning that the T-Nb_{2}O_{5} phase is transformed in the area above the dashed line. The full line delineates boundary between H_{3}O Nb_{3}O_{8} phase and the mixed phase with H_{3}O Nb_{3}O_{8} and T-Nb_{2}O_{5}, implying that the H_{3}O Nb_{3}O_{8} phase is retained in the area under the full line. And the mixed phase with H_{3}O Nb_{3}O_{8} and T-Nb_{2}O_{5} can be formed.
between the full and the dashed line. It can be seen that the T-Nb$_2$O$_5$ sample can be topologically transformed from H$_3$ONb$_3$O$_8$ nanobelts under the conditions of 230°C and pH value of 1.5 and 220°C and pH value of 0.5. A possible trend can be observed that the transformed temperatures into T-Nb$_2$O$_5$ from H$_3$ONb$_3$O$_8$ increase with the growth of the pH value of the reaction system. It is speculated that the stability of the H$_3$ONb$_3$O$_8$ nanobelt increases due to the increase of pH value, so that the energy required for the topology conversion reaction also increases. It provides a reference for subsequent hydrothermal synthesis of niobium pentoxide with expose specific crystal facet.

Figure 6 shows the XRD pattern, FE-SEM image, HRTEM image and SAED image of the sample obtained at 230°C under the pH value of 1.5. The positions of all the diffraction peaks of the sample are exactly the same as those of the tetragonal Nb$_2$O$_5$ phase [53] (JCPDS No. 32-0711, I4/mmm (139), Z = 16, a = b = 20.20 Å, c = 3.857 Å, α = β = γ = 90°) (Figure 6A). The characteristic diffraction peaks located at 23.70°, 24.92°, 43.91°, and 47.56° correspond to the (101), (211), (1000), and (761) facets of T-Nb$_2$O$_5$, respectively. It can be seen from Figure 6B that the sample obtained by the topological transformation still presents a uniform belt-like particle morphology of 3–5 μm in length, 300 nm in width and 20 nm in thickness. The HRTEM image and SAED pattern of the T-Nb$_2$O$_5$ nanobelts are shown in Figure 6C and 6D, respectively. The clear lattice fringes with lattice spacing as 0.38 and 1.01 nm in HRTEM image correspond to the (001) and (200) facets of T-Nb$_2$O$_5$ crystal, respectively (Figure 6C). The diffraction spots with d-value of 1.01, 0.38, 0.192, and 0.189 nm in the SAED pattern correspond to the (200), (101), (002), and (202) facets of T-Nb$_2$O$_5$, respectively (Figure 6D). The results indicate that the exposed facet of T-Nb$_2$O$_5$ nanobelts dominantly is the (010) facet and the [001] direction is the long axis direction of the particles, which is the same as the precursor KNb$_3$O$_8$ nanobelts.

The XPS measurement spectrum of the T-Nb$_2$O$_5$ sample is shown in Figure S2f. The centers of the two double peaks in the high resolution XPS spectrum of Nb 3d are 207.4 eV (3d5/2) and 210.14 eV (3d3/2) (Figure S2g). Both peaks are derived from the Nb$^{5+}$ state within T-Nb$_2$O$_5$ nanobelt crystals. [54–56] The binding energy was reduced by 0.37 and 0.39 eV compared to the H$_3$ONb$_3$O$_8$ sample, respectively, which means that the Nb$^{5+}$ state in the sample become slightly weaker after the in-situ hydrothermal topological reaction.

For comparison, the O-Nb$_2$O$_5$ nanosheet crystals with a regular rectangular morphology (Figure S5) were used as a contrast in this study. The Raman spectra of T-Nb$_2$O$_5$ sample and the contrast O-Nb$_2$O$_5$ nanosheets are shown in Figure S6. It can be observed from Figure S6a that the four weak Raman bands of T-Nb$_2$O$_5$ nanobelts appear in 124.86, 261.12, 626.43, and 993.62 cm$^{-1}$, respectively. The Raman shifts at 993.62 and 626.43 cm$^{-1}$ can be attributed to the vibration modes of A$_1$g (n$_1$) and E$_g$ (n$_2$) of NbO$_6$ octahedra in Nb$_2$O$_5$. [57] The Raman band at 261.12 cm$^{-1}$ probably arises from the T$_2$u mode associated with the noncubic structures of the edge-shared octahedral. [48] Compared with the T-Nb$_2$O$_5$ nanobelts, the Raman bands of the O-Nb$_2$O$_5$ nanosheets became stronger, and the weak Raman band at 993.62 cm$^{-1}$ disappear, and the Raman band at 626.43 cm$^{-1}$ is shifted to 681.35 cm$^{-1}$, while the two bands in the low-wave-number region moved towards each other. These changes are due to their different crystal structures. [52]

2.4 | Transformation mechanism of morphology and crystal structure

The evolution mechanism of the crystal structure and morphology in the process of T-Nb$_2$O$_5$ formed by acid exchange and dehydration reactions with KNb$_3$O$_8$ as the precursor is shown in Figure 7. There are three Nb-O octahedrons in the structural unit existing in the KNb$_3$O$_8$ crystal structure. In which, two Nb1-O octahedrons formed by Nb1 are connected by sharing an edge, and are connected sharing angle through the two vertexes on the same side with the two angles on one side of another Nb2-O octahedron formed by Nb2 to form a stacked 3Nb structural unit. The Nb2-O octahedron in each structural unit is connected respectively by sharing angle with the Nb1-O octahedron in the other two structural units, forming a long
**FIGURE 6** XRD pattern (A), FE-SEM image (B), HRTEM image (C) and SAED pattern (D) of the sample T-Nb$_2$O$_5$ obtained by hydrothermally treating an H$_3$ONb$_3$O$_8$ nanobelt suspension with pH value as 1.5 at 230$^\circ$C for 24 hours.

**FIGURE 7** Crystal structure evolution from a KNb$_3$O$_8$ nanobelt crystal into a T-Nb$_2$O$_5$ nanobelt crystal.
chain along the a-axis direction. Each chain is superposed and connected by sharing angle to form a two-dimensional layered skeleton structure along the c-axis. The layers are stacked in a mirror image and staggered along the b-axis direction, and the layer space is filled by K+ to form a three-dimensional structure.

In the H3ONb3O8 crystal structure formed by acid exchange, the skeleton structure of the layer is still retained, but the layer spacing is increased slightly from 2.11 to 2.25 nm due to exchanging K+ into the H3O+ between the layers. Therefore, the morphology of H3ONb3O8 crystals is still a strip particle with a main exposed surface of the (010) and a long axis direction of the [001].

In the process of hydrothermal treating the H3ONb3O8 nanobelts, the T-Nb2O5 is formed by a topological dehydration reaction between two adjacent columns in the same layer along the b-axis direction and the interlayer H3O+ in the crystal structure of the H3ONb3O8. In the T-Nb2O5 crystal structure, every 16 Nb-O octahedrons are connected by common angles to form a square parallel to the (001) facet and perpendicular to the (110) facet. The four corners of these squares are connected by sharing edges together to form the two-dimensional network structure, and the nets are interlaced and superposed along the [001] direction to form the three-dimensional structure of the T-Nb2O5. In the small square structure unit formed by 16 Nb-O octahedrons, Nb has three different connection ways. One is that an Nb-O octahedron is connected sharing angles with the four Nb-O octahedrons in the same layer; the second is that an Nb-O octahedron is connected sharing angles with the three Nb-O octahedrons in the same layer; and the third is that an Nb-O octahedron is connected by the common edge with another Nb-O octahedron in the same layer. It can be found that Nb-O octahedron in the H3ONb3O8 is mainly connected in the form sharing edges, while Nb-O octahedron in the T-Nb2O5 formed after the dehydration reaction is mainly connected in the form of common angles. However, these changes mainly occurred in the plane (010), while the octahedron’s connection mode in c-axis direction did not change. Therefore, its morphology still maintains the shape of belt-like particles with the long axis direction of the [001] and exposing mainly the (010) plane.

2.5 Photoelectric performance of the obtained T-Nb2O5 nanobelts and Ag/T-Nb2O5 nanobelts

The visible light catalytic activity of the material can be remarkably improved by increasing the absorption of the material on the visible light. In order to increase the absorption of the T-Nb2O5 nanobelts in the visible light range and improve its utilization of solar energy, Ag ions are in situ photo-reduced and deposited on the surface of the sample in AgNO3 solution. Its formation mechanism is similar to that of Ag deposited on TiO2 under irradiation of UV light in AgNO3 solution.[58] The XPS and EDX of the Ag/T-Nb2O5 sample are shown in Figure S7. Figure S7a shows the XPS measurement spectrum of the Ag/T-Nb2O5 sample. The two double peaks in the Nb 3d high resolution XPS spectrum of the Ag/T-Nb2O5 nanobelts are 207.33 eV (3d5/2) and 210.08 eV (3d3/2) respectively (Figure S7b). Compared with the T-Nb2O5 nanobelt, it has a negative shift of 0.06 eV but it still derived from the two peaks of Nb5+ state. Two peaks located at 374.14 and 368.14 eV can be assigned to 3d5/2 and 3d3/2 of metallic Ag in the high resolution XPS spectrum of Ag 3d, respectively (Figure S7c). But there is a negative shift of 0.16 eV relative to bulk Ag (368.3 eV for 3d5/2 and 374.3 eV for 3d3/2), suggesting interactions between the T-Nb2O5 nanobelts and Ag nanoparticles. The Ag content in the Ag/T-Nb2O5 nanobelts determined by XPS is 5.1%, which is basically consistent with the result (5.2%) of EDX analysis (Figure S7d).

The contrast O-Nb2O5 nanosheets with a regular rectangular shape was used for comparison. The visible light photoelectrochemical performance of the obtained T-Nb2O5 and Ag/T-Nb2O5 nanobelts as photocatalysts was evaluated by decomposing water to H2 under simulated sunlight and measuring the accompanying photocurrent. The preliminary electrocatalytic activity of catalysts T-Nb2O5 nanobelts, Ag/T-Nb2O5 nanobelts and O-Nb2O5 nanosheets was studied toward hydrogen evolution reaction by linear sweep voltammetry (LSV).[59] technique under the dark and the simulated sunlight (LED, 30 W, 380~780 nm) illumination. In LSV measurement process, 0.5 mol·L−1 Na2SO4 aqueous solution, Ag/AgCl reference electrode and 10 mV·s−1 scanning rate were used for hydrogen evolution. It can be seen from Figure 8A that the current density is almost zero under dark conditions and within the bias range given by the experiment when the T-Nb2O5, Ag/T-Nb2O5, and O-Nb2O5 electrodes are linearly scanned. It shows that the hydrogen evolution effect of the electrode can be ignored under dark conditions. Under simulated sunlight, it is found that T-Nb2O5 electrode, Ag/T-Nb2O5 electrode, and O-Nb2O5 electrode have obvious catalytic hydrogen evolution effects. However, to achieve 200 µA·cm−2 of the current density, the Ag/T-Nb2O5, T-Nb2O5, and O-Nb2O5 electrodes require −90, −150, and −280 mV potential, respectively. It indicates that Ag/T-Nb2O5 nanobelts show better catalytic activity than T-Nb2O5 nanobelts and O-Nb2O5 nanosheets under simulated sunlight irradiation. Under chopping illumination, the current and potential diagrams of samples Ag/T-Nb2O5, T-Nb2O5,
FIGURE 8  A, Linear sweep voltammograms collected in the dark and under the simulated sunlight (LED, 30 W, 380–780 nm) illumination using a three electrodes setup in 0.5 mol·L−1 Na2SO4 electrolyte. B, Current potential diagram of samples Ag/T-Nb2O5, T-Nb2O5, and O-Nb2O5 under chopping illumination (sodium sulfate solution: pH = 7; scan rate 10 mV·s−1). C, Current-time curves of the obtained samples Ag/T-Nb2O5, T-Nb2O5, and O-Nb2O5 in the dark and under irradiation with the simulated sunlight at the bias of zero voltage and O-Nb2O5 are shown in Figure 8B. Figure 8C shows the typical current–time curves obtained by irradiating intermittently the electrodes T-Nb2O5, Ag/T-Nb2O5, and contrast O-Nb2O5 using the LED light at zero applied voltage, respectively. The amount of H2 evolved by the photocatalyst (µmol·h−1·g−1) is calculated by equation:

$$\text{Amounts of } H_2 = \frac{It}{nmF}$$  \hspace{1cm} (1)

where I is the current (µA), t is the time duration (h), m is the mass of the photocatalyst (g), n is the transfer electron number, F is the Faraday constant as 96,487 C·mol−1. The results show that the photocurrent densities of the samples Ag/T-Nb2O5, T-Nb2O5, and O-Nb2O5 are 48.1, 20.5 and 13.1 µA·cm−2, respectively. It is found that the photocurrent density generated by the Ag/T-Nb2O5 sample is 2.3 times that of the T-Nb2O5 sample, and the photocurrent density generated by the T-Nb2O5 sample is 1.5 times that of the O-Nb2O5 contrast. And the specific surface area of the samples T-Nb2O5 and O-Nb2O5 are 67 and 12 m²·g−1, respectively. After calculation, the hydrogen production of Ag/T-Nb2O5, T-Nb2O5, and O-Nb2O5 samples are 718, 306, and 195 µmol·h−1·g−1, respectively. After the measurement splitting water to H2, the XRD pattern, FE-SEM image and EDX pattern of the samples as a photocatalyst are shown in Figure S8. It can be observed that there is no appreciable change in the crystal phase, morphology and composition content, which means that the stability of the samples T-Nb2O5 and Ag/T-Nb2O5 can meet the requirement of being a photocatalyst.

In order to explain the difference of the photoelectric conversion efficiency of the samples, the surface electronic band structure of the Ag/T-Nb2O5 and T-Nb2O5 samples were investigated. Their UV-vis DRSs are shown in Figure 9. The absorption edge of the Ag/T-Nb2O5 nanobelts and T-Nb2O5 nanobelts are estimated to be 466 and 434 nm from the spectrum, respectively. The absorption edge of the contrast O-Nb2O5 is 413 nm.\[38\] The Kubelka-Munk function $A = B(h\nu - E_g)^2/(h\nu)$ represents the relation between absorption coefficient (A) and incident photon energy (h\nu), where B and $E_g$ are the absorption constant and bandgap energy respectively.\[60\] The $E_g$ is estimated from the transformed Kubelka-Munk function versus the energy of light (inset in Figure 9). The band gap of the Ag/T-Nb2O5 nanobelts, T-Nb2O5 nanobelts and O-Nb2O5 nanosheets was determined to be 2.66, 2.85, and 3.0 eV, respectively, based on the value of the absorption edge. The reduced band gap of the sample is favorable for absorbing
visible light, which means Ag/T-Nb_2O_5 nanobelts can absorb visible light more easily than T-Nb_2O_5 nanobelts and O-Nb_2O_5 nanosheets. This is one of the reasons that the photoelectric conversion efficiency of the T-Nb_2O_5 is better than that of the O-Nb_2O_5. From the perspective of the crystal structure of the samples, the atomic filling rate on the surface of the orthorhombic phase Nb_2O_5 is larger than that of the tetragonal phase Nb_2O_5, which is also one of the reasons why the band gap value of the T-Nb_2O_5 nanobelts is smaller than that of the O-Nb_2O_5 nanosheets. The Mott Schottky curves of the samples T-Nb_2O_5 and O-Nb_2O_5 are shown in Figure 10. From the curves, the flat band potentials (V_f) of the samples T-Nb_2O_5 and O-Nb_2O_5 are −0.61 and −0.74 V, respectively. According to the obtained band gap value, the valence band potentials of the two are calculated to be 2.24 and 2.26 V respectively, which means that the h^+ oxidation ability of the T-Nb_2O_5 and the O-Nb_2O_5 is not much different. The above results indicate that the photocatalytic activity of the T-Nb_2O_5 is higher than that of the O-Nb_2O_5 because the forbidden band width of the T-Nb_2O_5 is narrower and has a larger specific surface area, which is beneficial to its absorption and utilization of sunlight. And compared with the Nb_2O_5 samples reported in the literatures [18,27,38,61] (Table S1), the prepared T-Nb_2O_5 sample is obviously advantage as a photocatalyst.

When Ag nanoparticles are deposited onto the surface of the Nb_2O_5 nanobelt, a Schottky barrier forms between the Nb_2O_5 and Ag particles because the Fermi level of Ag is lower than that of Nb_2O_5, which drives the e^- from the CB of the Nb_2O_5 into the Ag nanoparticles. This electron transfer process can not only promote the separation of photogenerated e^-–h^+ pairs, but also inhibit the recombination. [62,63] Therefore, the deposition of Ag improves the visible photoelectric conversion efficiency of the T-Nb_2O_5 sample.

### CONCLUSIONS

The orthorhombic phase KNb_3O_8 nanobelts with better morphology and uniform particle size can be obtained by hydrothermal reaction between Nb_2O_5 and KOH at 200°C for 24 hours under C_{17}H_{33}CO_2Na/Nb_2O_5 molar ratio as 0.06. The KNb_3O_8 nanobelts were acid exchanged to obtain the orthorhombic phase protonated niobate H_3ONb_3O_8 nanobelts, and then the T-Nb_2O_5 nanobelt crystals main exposed [010] facets were prepared for the first time by treating hydrothermally H_3ONb_3O_8 nanobelts suspension. The crystal structure and morphology transition mechanism from layered KNb_3O_8 nanobelt to T-Nb_2O_5 nanobelt are introduced in detail. Furthermore, the visible photoelectrochemical performance of the obtained Ag/T-Nb_2O_5 nanobelts and T-Nb_2O_5 nanobelts is evaluated by splitting water under simulated sunlight illumination. The generated photocurrent density and the amounts of H_2 evolved by the obtained Ag/T-Nb_2O_5 nanobelts as the photocatalyst is 48.1 μA·cm^-2 and 718 μmol·h^-1·g^-1, respectively, which is 2.3 and 3.7 times that of the T-Nb_2O_5 sample and the O-Nb_2O_5 contrast, respectively. The results indicate that the Ag/T-Nb_2O_5 nanobelts have high visible photoelectrochemical performance and excellent visible photovoltaic performance. Therefore, the Ag/T-Nb_2O_5 nanobelt crystals have potential application value in photocatalysts and photovoltaic nanodevices.

### EXPERIMENTAL SECTION

#### 4.1 Preparation of nanobelts KNb_3O_8 and protonated niobate H_3ONb_3O_8

The preparation of KNb_3O_8 sample using the hydrothermal method has two steps. First, 0.6 g of Nb_2O_5 (99.9%, Aladdin America) and 20 mL of 3 mol·L^-1 KOH (95%, Aladdin America) aqueous solution were placed in a Teflon-lined, sealed stainless-steel vessel with an inner volume of 100 mL, and then hydrothermally treated at 200°C for 4 hours under stirring condition. In the second step, the solid sodium oleate was added to the resulting solution, and the pH of the solution was adjusted between 5 and 6 using a 3 mol·L^-1 HCl solution under stirring condition. The obtained solution was added to the same autoclave with above, and hydrothermally treated at 200°C for 4 hours under stirring condition to obtain the KNb_3O_8 sample. The sample was centrifuged and washed with deionized water and ethanol, and dried at the room temperature.

0.6 g of KNb_3O_8 sample was stirred in 100 mL 1.2 mol·L^-1 of HNO_3 solution for 2 days to exchange K^+ in the layered structure with H_3O^+, and then the sample was washed.
with ethanol and deionized water. After the acid treatment was done twice, an H\(^+\)-form layered protonated niobate H\(_3\)ONb\(_3\)O\(_8\) sample was obtained.

4.2 Preparation of tetragonal crystal T-Nb\(_2\)O\(_5\) nanobelts

15 mL of 2 mg\(\cdot\)mL\(^{-1}\) H\(_3\)ONb\(_3\)O\(_8\) suspension was placed in a Teflon-lined, sealed stainless-steel vessel with an inner volume of 50 mL. The pH value of the H\(_3\)ONb\(_3\)O\(_8\) suspension was adjusted to 0.5–5.0 with a 3 mol\(\cdot\)L\(^{-1}\) of HCl aqueous solution, and then hydrothermally treated at a desired temperature under stirring condition. After the hydrothermal treatment, the product was centrifuged and washed with deionized water and ethanol, finally dried at the room temperature.

4.3 Preparation of the Ag/T-Nb\(_2\)O\(_5\) nanobelts

The crystalline Ag/T-Nb\(_2\)O\(_5\) nanobelts are prepared by a photo-reduction process. 20 mg of the obtained T-Nb\(_2\)O\(_5\) nanobelt sample was dispersed to a 4 mL 0.01 mol L\(^{-1}\) AgNO\(_3\) solution, and stirred for 10 minutes under light emitting diode light illumination (China, 30 W, 6000 K). Then, the product was washed with deionized water, centrifuged, and dried at room temperature.

4.4 Physical analysis

Powder X-ray diffraction (XRD) analysis of the samples was carried out on a Rigaku D/max-2200 PC X-ray diffractometer with Cu K\(\alpha\) (\(\lambda = 0.15418\) nm) radiation. A field-emission scanning electron microscope (FE-SEM, HitachiSU8010) with an accelerating voltage of 5 kV were used to characterize the size and morphology of the sample particles. Raman-scattering data were collected by using Raman microscope (Invia, Renishaw), from a laser operating at 532 nm, 50 times objectives. The laser power at the sample was estimated to be 1% and the nominal laser spot size was 0.5 \(\mu\)m. A transmission electron microscope (TEM, FEI Tecnai G2 F20) and selected-area electron diffraction (SAED) were performed by using a system at 200 kV. The solid-state UV–vis diffuse reflectance spectra (DRS) of the samples were measured on a UV-vis spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere attachment and a standard BaSO\(_4\) plate is used as 100% reflectance standard. The chemical composition of the sample is analyzed by using in situ energy dispersive X-ray spectroscopy (EDX) equipped in the FE-SEM system and in situ energy dispersive X-ray photoelectron spectroscopy (XPS), which uses a Nexsa multifunctional X-ray photoelectron spectroscopy system and Al-K\(\alpha\) radiation as the excitation source. The C 1 second peak from the adventitious carbon, with band energy of 284.8 eV, was used as an internal standard. The Mott-Schottky plots were collected at 5 KHz a Zahner XPOT electrochemical analyser. The Brunauer-Emmet-Teller (BET) specific surface area was measured by N\(_2\) adsorption and desorption on a ASAP-2460 specific surface area tester instrument (Mike, USA). The pretreatments of the obtained catalysts were degassed under vacuum at 120\(^\circ\)C.

4.5 Measurement of the photocatalytic performance of the samples for splitting water

Photoelectrochemical measurements of the samples were carried out on a Zahner XPOT electrochemical analyser by using a three-electrode system consisting of a fluorine-doped tin oxide (FTO) glass covered with the sample as working electrode, the platinum sheet as the counter electrode, and an Ag/AgCl electrode (KCl saturated) as reference. The three electrodes were immersed in 0.5 mol\(\cdot\)L\(^{-1}\) of Na\(_2\)SO\(_4\) electrolyte solution. The 5 mg sample was dispersed in 1 mL of deionized water to form a suspension, and then 0.25 mL suspension was dropped on clean FTO glass and dried at room temperature to form a working electrode with an area of about 1 cm\(^2\). The distance between the working electrode and the light source was kept at 10 cm. And the working electrode was irradiated with a light emitting diode flat downlight (LED, Wolike, China, 30 W, 380–780 nm) during the measurement. A contrast orthogonal phase Nb\(_2\)O\(_5\) (O-Nb\(_2\)O\(_5\)) nanosheets was prepared according to the method in Reference.[38] The preparation method of the contrast O-Nb\(_2\)O\(_5\) electrode was the same as that of the sample electrode.

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DECLARATION OF INTEREST STATEMENT

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

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in figshare at https://doi.org/10.6084/m9.figshare.14481960, reference number [14481960].
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\section*{SUPPORTING INFORMATION}
Additional supporting information may be found online in the Supporting Information section at the end of the article.

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