Enhanced Photocatalytic Hydrogen Generation of Nano-sized mesoporous InNbO₄ Crystals Synthesized via a Polyacrylamide Gel Route

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Abstract

As a promising visible-light-driven photocatalyst for hydrogen generation, InNbO₄ of high efficiency dictates the requirements on the high specific surface area and tailored band structure that arouse increasing efforts but remain challenge. Herein, we report fabrication of nanosized InNbO₄ embedded with nano-voids via apolyacrylamide sol-gel route. It exhibits excellent photocatalytic H₂ evolution rates up to ~68.1 μmol·h⁻¹·g⁻¹, much better than as-reported counterparts (~1 μmol·h⁻¹·g⁻¹) obtained via solid-state reaction or doping treatments. The particle sizes, density of nano-voids, as well as the bandgap energy are modulated by using different chelating agents, including tartaric acid (TA), citric acid (CA), acetic acid (AA). Based on high resolution high angle annular dark-field (HAADF) characterizations, it interesting to discover that the photocatalytic performance shows obvious dependence on the voids size. Nano-voids (2~8nm) can maximize the specific surface and thus enhance the photocatalytic performance, while lattice-scale voids (<1.5nm) may become a carrier trapping defects and thus decrease the

photocatalytic performance. This work lays a foundation for further promoting activity of InNbO_4 photocatalysts through balanced optimization of microstructure and band structure.

Key words: InNbO_4 nanoparticles; photocatalytic hydrogen generation; polyacrylamide gel route; chelating agents;

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1. Introduction

Photocatalytic technology is a light-driven chemical process over the surface of a semiconductor-based catalyst. It provides a potential strategy to solve the problem of environmental pollution and energy shortage, and has been continuously attract much attention since Fujishima and Honda found in 1972 that semiconductor TiO_2 can split water under light irradiation [1]. However, in view of practical application, besides the physical and chemical stability and non-toxicity, an excellent and feasible photocatalysts must possess two other essential conditions: (a) the photocatalyst should be based on a narrow bandgap energy (E_g) semiconductor in order to promote the efficiency of solar light utilization; (b) potentials of the conduction band (CB) bottom(E_{CB}) and the valence band (VB) top (E_{VB}) should be higher and lower than the corresponding redox potential of reactants. To date, various semiconductors with relatively small E_g , such as CdS [2-4], Ag_3PO_4 [5], WS_2 [6], $\text{g-C}_3\text{N}_4$ [7-10], have been studied as visible-light-driven photocatalysts. Compared to these semiconductors, InNbO_4 with a narrow E_g (~ 2.5 eV) has many fantastic qualities which makes it being a potential photocatalyst for both hydrogen generation from water splitting and dye degradation. On one hand, InNbO_4 possesses a layered wolframite-type structure with two kinds of octahedra (NbO_6 and InO_6) in a unit cell [11], which is commonly assumed to facilitate the separation of photogenerated electro/hole pairs to improve the photocatalytic activity since that layered structure is preferred to form internal

electric fields between the layers [12,13]. On the other hand, InNbO_4 has a E_{CB} of -0.7 eV vs. normal hydrogen electrode (NHE) (pH=0) [14], which is much higher than that of typical TiO_2 photocatalysts (-0.13 eV vs. NHE, pH=0) as well as the potential of hydrogen generation (0 eV vs. NHE, pH=0), i.e. the InNbO_4 possesses stronger thermodynamic driving force in photocatalytic reduction of hydrogen proton than the typical TiO_2 . Such distinct band structure makes InNbO_4 a promising visible-light-driven photocatalysts for H_2 generation with stronger reduction ability than those TiO_2 -based materials.

Up to now, however, the experimental results reported in the literature shows that the photocatalytic H_2 generation over InNbO_4 is still very inefficient [11,14-18]. The main challenges for the development of InNbO_4 as a promising photocatalysts for H_2 generation are the fabrication of nanostructured InNbO_4 . Since photocatalysis is a typical surface reaction, the photocatalytic performance is significantly affected by the morphology, crystallinity and particle size of photocatalysts except for the intrinsic band alignments. On one hand, good crystallinity and small particle size are preferred to reduce the recombination probability of the photo-induced electron/hole pairs through shortening the distance of the carrier moved [19]. On the other hand, large specific surface area originated from small nanoparticles exhibits higher photocatalytic activity than bulk materials through providing more surface active sites. Therefore, the preparation of nanostructured InNbO_4 photocatalyst of high crystallinity and specific geometry is of great importance for excellent photocatalytic activity. Up to now, representative works have been demonstrated on InNbO_4 photocatalysts fabricated with various approaches besides the most commonly used solid-state reaction [20-25], such as hydrothermal method (producing graphene/ InNbO_4 composites) [26], mechanochemical activation (for N-doping) [17], nonaqueous sol-gel route [27], electrospinning (yielding InNbO_4 nanofibers) [28,29], aerosol assisted atmospheric pressure chemical vapour deposition [30], and low temperature strategy (using niobium citrate complex) [31]. However, most of these recently works were focused on dye

degradation properties of InNbO₄, insights into their photocatalytic water splitting have seldom been put forward.

Herein, we present a polyacrylamide sol-gel route (PSG) route to prepare InNbO₄ nanoparticles as illustrated in Fig. 1. The PSG route takes the advantage of the network structures formed from polyacrylamide and glucose, and this network structures effectively suppresses the migration and agglomeration of source particles in calcination process. As a result, the source particles (*i.e.* In³⁺ and Nb⁵⁺) are dispersed stably and homogeneously in the network structures and are conducive to form small and uniform InNbO₄ nanoparticles. The photocatalytic activity of the as-prepared InNbO₄ nanoparticles is greatly enhanced under both visible light and full arc irradiation compared to samples prepared by solid state reaction (SSR) method. Besides, the chelating agent also plays an important role in the PSG route especially for the ternary metal oxides since the two kinds of metal source ions are connected together by chelating agent. Hence, the influences of different chelating agent on the products were also investigated systematically. We found that the phase purity, particle size, and *E_g* can be tailored by changing the types of chelating agents. The highest average photocatalytic H₂ evolution rates reach up to 68.1 μmol·h⁻¹·g⁻¹ under simulated-sunlight irradiation. Such excellent photocatalytic H₂ evolution rates over single phase InNbO₄ has, to the best of our knowledge, not been reported to date.

2. Experimental

2.1. Preparation of InNbO₄ particles

All raw materials and reagents used in this work are analytical grade without any further purification. Firstly, 3.75 mmol of Nb₂O₅ (99.9%) was added into 40 mL of HF (40%) aqueous solution, and sealed in a 50 mL Teflon-lined stainless steel autoclave, then submitted to hydrothermal treatment in a thermostat drier at 120 °C for 10 h without stirring. After reaction the autoclave were naturally cooled down to room temperature and a niobium colorless transparent solution were obtained. Then the above solution was successively added by excessive amounts of oxalic acid ammonium (≥99.8%) and ammonium hydroxide (25-28%), yielding a white precipitation after centrifugation. Secondly, the above white precipitation was dissolved in 50 mL mixture aqueous solutions of HNO₃ (10 mL, 25-28%), chelating agent (22.5 mmol of tartaric acid

(TA, 98.5%), citric acid (CA, 99.5%), acetic acid (AA, 99.5%), or oxalic acid (OA, 98%)) and H_2O_2 . Then the mixed solution were successively added by 7.5 mmol of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.9%), 20 g of glucose, and 20 of acrylamide monomer (99%). The mixed solution was filled up to 100 mL by adding distilled water. Every aforesaid step was accompanied by a constant magnetic stirring to obtain uniform mixture. The final mixed solution was heated at 80 °C to initiate the polymerization reaction. The formed gel was dried at 120 °C for 24 h in a thermostat drier. The obtained xerogel was ground into powder in an agate mortar, and then subjected to calcination at 600 °C in air for 2 h to produce final samples, samples prepared from TA, AA, CA, and OA were referred as TA-, AA-, CA-, and OA- InNbO_4 , respectively. For comparison, the InNbO_4 crystallites were also prepared by a solid-state reaction method. Stoichiometric amounts of In_2O_3 (99.9%) and Nb_2O_5 (99.9%) were mixed and ground in an agate mortar, and then subjected to calcination at 1000 °C for 10 h and referred as SSR- InNbO_4 .

2.2. Characterization

The structure and phase purity of the as-prepared InNbO_4 samples was investigated by powder X-ray diffraction (XRD) with Cu $K\alpha$ radiation (DX-2700). The particle morphology was investigated using a field-emission scanning electron microscope (SEM, Hitachi S-4800). The atomic structure of InNbO_4 nanoparticles was studied on the scanning transmission electron microscopy (STEM, JEOL 2100F) with a CEOS GmbH probe corrector. Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (ASAP 2020). Fourier transform infrared spectroscopy (FTIR) studies were carried out on a Nicolet 6700 (USA) spectrometer. X-ray photoelectron spectroscopy (XPS) data were recorded on an KRATOS X SAM 800 photoelectron spectrometer (Al $K\alpha$, $h\nu=1486\text{ eV}$). The ultraviolet-visible (UV-vis) diffuse reflectance spectrum was measured using a UV-visible spectrophotometer (TU-1901) with an integrating sphere attachment. Thermogravimetric and differential scanning calorimetry (TG/DSC) analyses were performed in a simultaneous thermal analyzer (STA449F3 Jupiter) at a heating rate of 10 °C/min.

2.3. Photocatalytic activity measurement

Photocatalytic H_2 production experiments were carried out in a top-irradiation vessel connected to a closed gas-circulation system (Fig. S1). In a typical run, 0.05 g of the photocatalysts were dispersed by magnetic stirring in 100 mL methanol solution (10 mL methanol

as sacrificial reagent), 0.5 wt% Pt as a co-catalyst were loaded by *in situ* photo-reduction. After degassing the system for half an hour to remove most of the dissolved oxygen, a 300W xenon lamp was applied to execute the photocatalytic reaction. The photocatalytic H₂ evolution rate was analyzed using an GC-7806 gas chromatograph (GC, TCD detector and Ar carrier). Magnetic stirring was used during the water splitting experiment to ensure homogeneity of the suspension and to eliminate sedimentation.

2.4. Photoelectrochemical analyses

Photoelectrochemical analyses were carried out using an electrochemical workstation (CHI760E, China) with a standard three-electrode cell by respectively using Ag/AgCl as reference electrode and Pt wire as the counter electrode in the Na₂SO₄ solution (1 M). The working electrodes were prepared by depositing the sample slurries onto a clean fluorine-doped tin oxide (FTO) glass surface (1 cm²) as follows: 10 mg of the as-prepared samples were dispersed in 5 mL absolute ethanol by ultrasonically treatment for about 10 min, the suspension was dropped on FTO with a spin coater at 300 r/min, then the working electrodes were dried at 120 °C for 2 h. The I-t curves of the absolute values were recorded under the 300W xenon lamp irradiation with light ON-OFF switches of 20 s at a bias of -0.8 V.

3. Results and discussion

3.1. Crystal structure analysis

Fig. 2 shows the X-ray diffraction (XRD) patterns of samples prepared from PSG and SSR route. All the diffraction peaks of the SSR-, TA-, AA-, and CA-InNbO₄ can be indexed to the monoclinic InNbO₄ phase (PDF card no. 33-0619), and no traces of second phases are found, indicating high phase purity of these InNbO₄ samples. However, the sample prepared by using OA as the chelating agent is dominated by In₂O₃ or Nb₂O₅ phases with almost no InNbO₄ formed,

revealing that choice of chelating agents has a significant influence on the phase purity of final products, and OA seems to be unsuitable for the preparation of InNbO_4 phase in this system. Furthermore, compared to the SSR- InNbO_4 , the spectra of TA-, AA- and CA- InNbO_4 show an broadening diffraction peaks even inducing the overlap of (-111) and (111) planes, indicating the small grain size nature of the products [32].

3.2. FT-IR spectra and XPS analysis

Fourier transform infrared (FT-IR) spectra and X-ray photoelectron spectroscopy (XPS) of the InNbO_4 nanoparticles are shown in Fig. 3. From the FT-IR spectra (Fig. 3A), the weak band at 1639 and 2358 cm^{-1} and broad band at 3445 cm^{-1} observed in all samples can be assigned to the stretching and bending modes of O–H bands [33,34]. The bands at 442 cm^{-1} are In–O feature modes [34-35], and the bands at 535, 602, and 785 cm^{-1} are Nb–O feature modes [35,36]. It is noticeable that there are no bands in the spectra assigned to the organic compounds, revealing that organic additives were completely burned off under the temperature of 600 °C, which was further confirming by TG/DSC analysis as shown in Fig. S2 since no further weight loss is detected above 528, 540 and 591 °C for the TA, AA and CA resulted xerogels in the heating process. The survey XPS spectrum (Fig. 3B) further proves that the three pure InNbO_4 products are composed of In, Nb and O elements and no impurity elements in the samples (the peak of C1s can be attributed to adventitious hydrocarbon from instrument). The content of elements was also given (inserted in Fig. 3B), and one can see that the In/Nb molar ratio of AA- InNbO_4 deviates slightly from the stoichiometry and is greater than 1/1, indicating that more Nb atoms and more defects such as vacancy or interstitial Nb on the surface of AA- InNbO_4 . In addition, oxygen content contributes more signal than the stoichiometric expectation in all samples following order of $\text{CA} < \text{AA} < \text{TA}$, which mainly can be attributed to the surface adsorption of oxygen and inferring that the specific surface area follows order of $\text{CA} < \text{AA} < \text{TA}$ and is consistent with BET results. High-resolution XPS spectra of In 3d are shown in Fig. 3C, two strong peaks at 444.7 and 452.3

eV for $3d_{5/2}$ and $3d_{3/2}$, respectively, with a spin–orbital splitting of 7.6 eV, indicating indium in the as-prepared InNbO_4 exists in In^{3+} [37,38]. As for the Nb 3d spectrum (Fig. 3D), two peaks at 207.3 and 210.0 eV are identified for $3d_{5/2}$ and $3d_{3/2}$, respectively, confirming that the valence state of niobium is Nb^{5+} [39]. Furthermore, a slight shift to lower energy of Nb 3d as well as a clear shoulder peak (the red square in Fig. 3D (b)) at the peak of Nb $3d_{5/2}$ are observed in AA- InNbO_4 , suggesting a trace of Nb_2O_5 and Nb^{4+} [40-42], and further suggesting existence of more defects including vacancy or interstitial Nb on the surface of AA- InNbO_4 . Moreover, the O 1s spectrum could be decomposed into two components at 530.4 and 532.3 eV (Fig. 3E), which can be assigned to lattice oxygen and surface adsorbed oxygen, respectively [43].

3.3. Morphological analysis

The morphology of as-prepared InNbO_4 nanoparticles were studied by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) as shown in Fig. S3 and Fig. 4. The particle sizes and morphologies of InNbO_4 products are highly dependent on the types of chelating agents. Specially, a serious adhesion or welding among particles was observed in CA- InNbO_4 . The average particle sizes of TA, AA and CA resulted InNbO_4 samples from the SEM and STEM are about 12, 20 and 32 nm, respectively, which in anyway are much smaller than of SSR- InNbO_4 samples (0.2–3.5 μm). The high resolution STEM (HR-STEM) images suggest that the three pure InNbO_4 exhibit well-resolved lattice fringes, which evidence the good crystallinity of these nanoparticles. The lattice spacings are measured to be 0.231, 0.209, 0.206, 0.298, 0.367, 0.246, 0.207 and 0.302 nm, which corresponded to (-201), (211), (-112), (111), (011), (0-21), (-112) and (-111) plane of monoclinic structure (PDF card no. 33-0619). Furthermore, black contrast inside the nanoparticles can be clearly observed on the three pure InNbO_4 samples in HR-STEM images, manifesting the presence of nano-void structures. Particularly, the size of nano-void in TA- InNbO_4 mainly ranges from 1.6 to 5 nm (Fig. 4a), while for the AA- InNbO_4 (Fig. 4b), apart from TA- InNbO_4 , there are many nano-void scaled in several

lattice spacings ($<2\text{nm}$), yielding remarkable atomic steps around void surface. However, for the CA-InNbO₄, there are obviously less nano-voids than TA- and AA-InNbO₄, meanwhile the voids are much bigger of about 8 nm (Fig. 4e). To obtain an overall quantitative statistic of nano-voids in the as-prepared InNbO₄ samples, Brunauer-Emmett-Teller (BET) adsorption-desorption isotherms were performed as shown in Fig. 5a. The surface area of the TA-, AA- and CA-InNbO₄ can be calculated to be 43.3, 35.4 and 27.1 m² g⁻¹, which are about 60-100 times higher than that of SSR-InNbO₄ samples (ca. 0.45 m² g⁻¹). Fig. 5b shows the pore size distribution of the three InNbO₄ nanoparticles by Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) method, it demonstrates obviously that the lattice-scale voids ($<1.5\text{ nm}$) density of CA-InNbO₄ is lower than TA- and AA-InNbO₄ (inset of Fig. 5b) suggesting less crystal defects in the CA-InNbO₄, which is consistent with TEM observation. Generally, tiny atomic steps introduced by the lattice-scale voids can be known as most active point defects (such as vacancies) [44,45], which would impede the migration of photo-generated charge carriers and thus reducing the photocatalytic efficiency [46]. While voids in size of several nanometers or larger are far away from lattice scale and does not introduce more carrier trapping defects considering that these large voids are much more smooth on their surfaces (less atomic defects), on the contrary, they can provide more active surface area to promote photocatalytic reaction.

3.4. Optical absorption and VB XPS spectra analysis

The electronic band structure of the InNbO₄ nanoparticles is studied by the optical absorption spectra as shown in Fig. 6A. Compared to the SSR-InNbO₄, the photo-absorption edge of TA-, AA-, and CA-InNbO₄ shows a blue shift from 425 nm to 368, 386, and 410 nm, respectively. This indicates the widening of E_g in these samples and E_g increases with the decrease of particle size, which is commonly observed in nano-sized semiconductors [47]. In addition, TA- and AA-InNbO₄ show an obvious absorption tail extends to the visible light, indicating the existence of the sub band in TA- and AA-InNbO₄ due to the defects introduced by

the lattice-scale voids as observed in HR-STEM images [48]. As clearly seen from the Tauc plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (see in Fig. 6B and 6C), where α is the K–M absorption coefficient and $h\nu$ is the incident photon energy, TA-InNbO₄ have a bandgaps of 2.96 eV with a sub gap of 2.79 eV, and AA-InNbO₄ have a bandgaps of 2.76 eV with a sub gap of 2.48 eV, respectively. In contrast, the larger voids in CA-InNbO₄ (>2nm) do not introduce defects that bring sub levels in the band structure, and therefore the CA-InNbO₄ exhibits single bandgap of 2.51 eV and no sub gap is observed (insert in Fig. 6A). For further understanding the band structure of the InNbO₄ nanoparticles, their band edges were studied by analyzing their VB XPS spectra as shown in Fig. 6D. The VB XPS spectrum of CA-InNbO₄ indicates the position of VB top at 2.00 eV, whereas for the AA- and TA-InNbO₄ the VB top is at 2.18 eV and 2.41 eV, respectively. The shifts of 0.18 and 0.41 eV for VB top of AA- and TA-InNbO₄ implies there forms a tail (or sub band) in these two samples. It is known that InNbO₄ has CB and VB edges at -0.7 and 1.8 eV (vs. NHE, pH=0) respectively [11,14]. Combining the above results, a schematic illustration of the band position in the potential energy diagram (vs. NHE, pH=0) for the as-prepared InNbO₄ nanoparticles is given in Fig. 6E. It's worth pointing out that despite the presence of sub band in TA- and AA-InNbO₄ due to the defects can improving the ability of the absorption of light, but on the other hand, they also lead to the downward shift of the CB bottom and thus lower the thermodynamic driving force in photocatalytic reduction of hydrogen proton, and furthermore, the lattice-scale defects become the recombination center of photo-generated charges and further decrease the photocatalytic performance [46].

3.5. Photocatalytic performance

Photocatalytic H₂ production experiments were carried out over these InNbO₄ samples with Pt as co-catalyst (Fig. S4) and methanol as a hole scavenger under a 300 W xenon lamp irradiation. As shown in Fig. 7A, the photocatalytic activity of SSR-InNbO₄ is almost negligible

under 10 h of the simulated-sunlight irradiation. Whereas for the InNbO₄ samples prepared by PSG, the amount of evolved H₂ production increases almost linearly as the irradiation time extends, implying the superior performance of InNbO₄ samples prepared by PSG. After 10 h of irradiation, 30.2, 24.1, and 34.1 μmol H₂ were produced by the TA-, AA-, and CA-InNbO₄ samples, the average photocatalytic H₂ evolution rates are 60.4, 48.1, and 68.1 μmol·h⁻¹·g⁻¹, respectively. The transient photocurrent response of the InNbO₄ anode under intermittent simulated-sunlight irradiation is illustrated in Fig. 8. It shows a sharp photocurrent response in each switch-on/off event for the InNbO₄ anode under simulated-sunlight irradiation, confirming the photo-induced charge separation and transfer process over InNbO₄. The prompt increase in photocurrent response is commonly ascribed to the quick separation and transportation of photo-generated electrons on the surfaces of the working electrodes. Here, the photocurrent response is in the following order: AA-InNbO₄ < TA-InNbO₄ < CA-InNbO₄, which agrees with photocatalytic performance and further confirms that CA-InNbO₄ can effectively absorb photons and delay the recombination of photo-generated carriers. It is commonly believed that the photocatalytic performance of the catalyst are affected simultaneously by many factors, such as the bandgap energy, particle size and crystallinity. In the present work, the highest photocatalytic activity is observed for CA-InNbO₄ sample, which can be explained by three reasons: (1) relatively narrow bandgap energy of CA-InNbO₄ makes it have a higher efficiency of light utilization; (2) the lower density of lattice-scale nano-voids promotes the effective separation between the electron and hole; (3) a higher CB bottom makes CA-InNbO₄ have a higher thermodynamic driving force in photocatalytic reduction of hydrogen proton. The stability of photocatalyst was investigated by performing recycle experiments with CA-InNbO₄ catalyst as

shown in Fig. 7B, the photocatalytic activity of InNbO₄ nanoparticles does not undergo a significant loss for three consecutive recycles, implying the outstanding stability of photocatalytic activity. Fig. 7C shows the wavelength-dependent hydrogen evolution rate of CA-InNbO₄ together with its UV–vis absorption spectrum. The hydrogen evolution rate decreases as the wavelength increases, and this trend is qualitatively consistent with the optical absorption spectrum, suggesting that the observed hydrogen generation of InNbO₄ comes from a photocatalysis process. Fig. 7D gives a comparison of our present results with previously reported results [11,14–18]. The photocatalytic H₂ evolution rate of present InNbO₄ samples demonstrates remarkable promotion under the solar light irradiation compared to the previously reported works. Such superiority should originate from the nano-crystallization of as prepared InNbO₄ samples.

4. Conclusions

Based on a PSG route, single phase InNbO₄ nanoparticles were prepared separately using TA, AA, and CA as the chelating agents, yielding nanostructures in average sizes of 12, 20 and 32 nm respectively and bandgap energy of 2.51–2.96 eV. The as-prepared InNbO₄ nanoparticles exhibit photocatalytic activity of high efficiency and stability for H₂ generation from water splitting under simulated-sunlight irradiation. The highest average H₂ evolution rate is observed over CA-resulted samples reaching up to 68.1 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ due to smaller E_g and lower density of lattice-scale voids, which is the highest H₂ evolution rate over single phase InNbO₄ reported to date. Overall, these results suggest that the fabrication of nanostructured InNbO₄ by polyacrylamide gel route can greatly enhance the photocatalytic performance.

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Fig. 1 Preparation process of InNbO_4 samples by the PSG route.

Fig. 2 XRD patterns of the as-prepared samples: (a) SSR-InNbO₄; (b) TA-InNbO₄, (c) AA-InNbO₄, (d) CA-InNbO₄, and (e) OA-InNbO₄; (f) standard XRD line pattern for InNbO₄ monoclinic structure (PDF card no. 33-0619).

Fig. 3 (A) FT-IR spectra; (B) Survey XPS spectrum; High-resolution XPS spectra of In 3d (C), Nb 3d (D), and O 1s (E) of the (a)TA-; (b)AA-; and CA-InNbO₄ samples.

Fig. 4 STEM and HRTEM images of the as-prepared pure InNbO_4 samples, (a-b) TA- InNbO_4 , (c-d) AA- InNbO_4 , (e-g) CA- InNbO_4 .

Fig. 5 (a) Brunauer-Emmett-Teller (BET) adsorption-desorption isotherms of the as-prepared InNbO₄ samples; (b) pore size distribution of the three InNbO₄ nanoparticles by BJH and HK method (insert).

Fig. 6 UV-visible diffuse reflectance spectra of pure InNbO₄ samples (A); The plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ using the Tauc relation: TA-InNbO₄ (B), AA-InNbO₄ (C), CA-InNbO₄ (insert in (A)); VB XPS of the samples (D); Band alignments of the InNbO₄ nanoparticles (E).

Fig. 7 (A) Photocatalytic activities of the InNbO₄ photocatalysts under solar light irradiation; (B) Cycling tests of photocatalytic activity of CA-InNbO₄ under solar light irradiation; (C) wavelength dependent hydrogen evolution rate of CA-InNbO₄ together with its UV-vis absorption spectrum; (D) A comparison of present results with previously reported results.

Fig. 8 Transient photocurrent response of the InNbO₄ anodes under solar light irradiation.