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A Photoresponsive Rutile TiO₂ Heterojunction with Enhanced Electron-Hole Separation for High Performance Hydrogen Evolution

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Keywords: rutile TiO₂, facet heterojunction, charge separation, water splitting

Abstract: Rutile TiO₂ is a promising photocatalyst due to its narrower band gap, higher thermodynamic stability and fewer intragrain defects. However, it has not yet to achieve comparable photocatalytic activity to anatase TiO₂ owing to its higher recombination rate of electron-hole pairs. In order to effectively separate the electron-hole pairs in rutile TiO₂, we propose a facet heterojunction (FH) structure to prolong the lifetime of photogenerated electrons. Ultrathin TiO₂ nanosheets with different facets were in-situ coated on TiO₂ nanorod substrates, where facet heterojunctions are built among nanosheets as well as between nanosheets and nanorod substrates. The as-prepared rutile TiO₂ with FH mechanism (FH-TiO₂) served as an effective photocatalyst for water splitting. More than 45 and 18 times higher of photogenerated current density and H₂ production rate were obtained respectively, compared to pure rutile TiO₂ nanorod. Moreover, FH-TiO₂ delivered 0.566 mmol g⁻¹h⁻¹ H₂

production rate even in pure water, which is the highest value for pure rutile TiO_2 photocatalysts to the best of our knowledge. This study offers important insights into rational design of rutile TiO_2 structure for highly efficient photocatalytic reaction.

During the past decades, titanium dioxide (TiO_2) has been extensively investigated for photocatalytic water splitting due to its chemical stability, environmental benignity, and avoidance of photocorrosion.^[1-8] It is well known that TiO_2 has four main polymorphs in nature, including rutile, anatase, brookite, and TiO_2 (B).^[9] So far, anatase TiO_2 , with slow charge recombination rate, has been considered as the most active phase for photocatalytic H_2 production.^[10-15] However, rutile TiO_2 in principle is superior to anatase.^[16] First, rutile is the thermodynamically stable phase while anatase is metastable.^[17,18] Second, rutile TiO_2 is likely to exhibit more efficient charge separation due to fewer intragrain defects, which may serve as the recombination centers for the photogenerated electron-hole pairs.^[19] Most importantly, the smaller band gap of rutile TiO_2 (3.02 eV) than anatase (3.20 eV) could extend the photoresponse range from ultraviolet (UV) light to the visible light region (410 nm)^[20-22] as shown in **Figure 1a**. Therefore, rutile TiO_2 is a more potential photocatalyst theoretically. However in reality, rutile TiO_2 usually exhibits less efficient photocatalytic performance than anatase TiO_2 due to higher recombination rate of electron-hole pairs.^[23-25] Previous works have proved that anatase TiO_2 is an indirect band gap semiconductor, implying that the photoexcited electrons can separate easily with holes, thus increasing the electron lifetime (Figure S1a, Supporting Information).^[26,27] However, rutile TiO_2 is a direct band gap semiconductor, allowing fast recombination of photoexcited electron-hole pairs (Figure S1b, Supporting Information).^[27,28] Therefore, higher separation efficiency for the photoexcited electron-hole pairs becomes imperative for rutile TiO_2 . A lot of efforts have been devoted to achieving higher separation efficiency through nanostructure engineering, doping strategy,

surface treatment, and junction structure modification.^[29-31] For example, crystalline Ti^{3+} core/amorphous Ti^{4+} shell nanostructure was designed to activate the inert rutile TiO_2 for photocatalytic H_2 evolution.^[20] A fluorine and tin co-doped indium oxide conductive glass (FTO)/FTO-nanocrystal/ TiO_2 inverse opal structure was fabricated to provide direct pathways for effective separation of electron-hole pairs in photoelectrochemical water splitting.^[32] Besides, tuning junction structure is also a rational strategy to suppress charge recombination in semiconductors, such as heterojunction, phase junction, and Scotty junction.^[13, 33-38]

Inspired by ‘surface heterojunction’ concept,^[39] we introduce the facet heterojunction (FH) strategy to facilitate the separation of electron-hole pairs in rutile TiO_2 . First of all, first-principles calculations on the electronic band structures of rutile TiO_2 nanosheets were carried out to verify the FH mechanism. The rutile TiO_2 nanosheets considered in this work have the (111) or (101) facets with the thickness of about 18.7 Å and 23.9 Å, respectively, which were built by cutting rutile TiO_2 crystals, as shown in Figures 1b-d. Two-dimensional periodical boundary conditions were applied along the direction parallel to the surfaces of the nanosheets, while a vacuum region of about 20 Å was applied along the direction perpendicular to the surfaces. Both the (111) and (101) facets are terminated by oxygen atoms. Structural optimizations show that reconstruction takes place on the surfaces due to dangling bonds, but the rutile lattice is preserved in the interior of the nanosheets. The electronic band structures of the two TiO_2 nanosheets are plotted in Figure 1b and 1d. The surface states, corresponding to the flat bands, appear within the band gap of the (111) nanosheet, which are well separated from the bulk states (Figure 1b). However, no surface states exist in the bandgap of the (101) nanosheets. The band gap of the (101) nanosheet is very close to that of rutile TiO_2 bulk crystal. The band diagram of (111)/(101) FH can be obtained by aligning the band lines of the (111) and (101) nanosheets according to the vacuum level, as shown in Figure 1c. It is obvious that the conduction band minimum (CBM) of the (111) nanosheet is lower in energy than that of the (101) nanosheet by about 0.36 eV. Therefore, the photo-generated electrons in

the (101) nanosheet will inject to the conduction bands of the (111) nanosheet. The photo-generated holes in the bulk states of the (111) nanosheet, however, will move in the opposite direction, because the valence band maximum (VBM) of the (101) nanosheet is higher in energy than that of the bulk states of (111) nanosheet. In short, the type-II band alignment in the (111)/(101) FH could facilitate the charge separation process. Therefore, we propose that the FH mechanism can accelerate the electron-hole pairs separation in rutile TiO_2 .

Even though FHs can theoretically accelerate electron-hole pair separation, establishing reliable heterojunctions is challenging in reality. We overcome this problem by building three dimensional (3D) hierarchical nanostructures. Taking P25 powder as an example, a mixture of anatase and rutile TiO_2 particles, not every particle can form tight bonding with different polymorphs, making it intrinsically difficult for isolated particles to separate electron-hole pairs by heterojunction (Figure S2, Supporting Information). In this work, a 3D rutile TiO_2 photocatalyst, with ultrathin and highly crystalline TiO_2 nanosheets uniformly coated on the surface of TiO_2 nanorods (NRs), were constructed (**Figure 2a-b**). This 3D rutile TiO_2 contains countless FHs, formed by the interfacing nanosheets in different facets as well as the coated nanosheets with their NRs substrate. This novel FH mechanism was proposed and utilized to guide the design of high performance TiO_2 photocatalyst for water splitting by accelerating the spatial charge transportation and separation. The energy band gap for NRs- TiO_2 is 3.02 eV. The ultrathin nanosheets uniformly coated on the surface of NRs- TiO_2 , and the different facets of ultrathin nanosheets vary the energy band gap of FH- TiO_2 with different internal electric field. As verified by the first-principles calculations shown in Figure 1, the band gap discontinuity could accelerate the transportation of spatial charge carrier from (101) ultrathin nanosheets to (111) ultrathin nanosheets simultaneously (Figure 2c). From the Scanning Electron Microscopy (SEM) image, it is clearly seen that vertically-aligned rutile NRs- TiO_2 arrays anchor uniformly on the transparent FTO (Figure 2d), serving as the photoelectrode substrate. The average size of the NRs- TiO_2 is about 50-100 nm in diameter and 4 μm in

length. Following the growth of NRs, rutile TiO_2 nanosheets ($\sim 2\text{-}5$ nm in thickness) are uniformly coated on the surface of NRs- TiO_2 (Figure 2e), and the corresponding cross-sectional SEM image is shown in Figure 2f. The tight bonding among the ultrathin TiO_2 nanosheets and between the ultrathin nanosheets and NR- TiO_2 ensures the internal 3D transportation of excited electrons. The preparation processes of FH- TiO_2 are detailed in the Supporting Information. The effects of reaction time, initial titanium precursor concentration, and temperature to the morphology of FH- TiO_2 are shown in Figure S3-S5.

We then looked further in details at the morphology and the crystal structure of FH- TiO_2 . **Figure 3a** shows a typical Transmission Electron Microscopy (TEM) image of single crystal FH- TiO_2 ; where the size of the nanorod matches very well with the SEM result shown in Figure 2f. The Selected Area Electron Diffraction (SAED) pattern (top left in Figure 3a) further confirms the rutile single crystal structure. The crystallography of the NRs- TiO_2 was investigated from the indicated region with high-resolution TEM imaging (HRTEM), and a clear single-crystal structure in $[110]$ and $[001]$ axis direction for NRs- TiO_2 is shown in the lower right of Figure 3a. Lattice fringes of 0.32 and 0.30 nm correspond to $d_{[110]}$ and $d_{[001]}$ of rutile NRs- TiO_2 , respectively.^[41] In Figure 3b, the HRTEM image taken near the edge of the FH- TiO_2 as marked in Figure 3a confirms there are two coexistent crystal facets, and the exact lattice plane of the dominant nanosheets are (101) and (111). Lattice fringes of 0.25 and 0.22 nm correspond to the orientation of $d_{[101]}$ and $d_{[111]}$, respectively. The phase structure was further studied by X-Ray Diffraction (XRD) (Figure 3c). The exposed facet of the top portion of NRs- TiO_2 is (101) facet (from XRD) and the body part are (110) facets (from HRTEM). Phase evaluation of NRs- TiO_2 and FH- TiO_2 were further conducted by room temperature Raman Spectroscopy (Figure S6). The broad bands near 110, 232, 446, and 608 cm^{-1} are the characteristic Raman bands of rutile phase. Besides, the peak height to half-width ratio also lowers with decreased grain size. The particle size (or thickness) of ultrathin rutile TiO_2

nanosheets is about 2-5 nm in average, so the intensity of Raman peaks decreased from NRs-TiO₂ to FH-TiO₂ with decreased grain size.

To prove FH-TiO₂ is indeed capable of facilitating charge carrier separation, a series of photoluminescence (PL) measurements were done. Firstly, PL emission from the recombination of free carriers was monitored to reveal the efficiency of charge carrier trapping, immigration, transfer and separation. The significant decrease of emission intensity from NRs-TiO₂ to FH-TiO₂ indicates that FH can effectively reduce the radiative recombination rate of photo-generated electron-hole pairs (Figure 3d). Furthermore, the lifetimes of electron-hole pairs in FH-TiO₂, NRs-TiO₂, and P25 were investigated by time-resolved photoluminescence (TRPL) measurements with the emission wavelength at 425 nm. As shown in Figure 3e, the corresponding PL lifetimes are obtained by fitting the data with biexponential decay function,^[42] and the fitted parameters are listed in Table S1 (Supporting Information). The average lifetimes (τ_{ave}) for NRs-TiO₂, P25, and FH-TiO₂ samples are about 2.09 ns, 2.72 ns, and 8.67 ns, respectively. The τ_{ave} of the charge carriers in FH-TiO₂ is more than 3 times larger than those in NRs-TiO₂ and P25, implying that the FH mechanism could enhance the charge separation efficiency and prolong the lifetime of the excited electrons. In addition, the porous structure and the enhanced surface areas (by Brunauer–Emmett–Teller analysis) of FH-TiO₂ is expected to help the transportation of dissociating water molecules and produced H₂ gas (Figure S7, Supporting Information).

In a proof-of-concept experiment, photocurrent responses, using FH-TiO₂, rutile NRs-TiO₂, NRs-anatase-TiO₂, and P25 as photoanodes, were monitored in the presence of 10 vol % methanol and intermittent UV irradiation. Photocurrent-time (I-t) curves, in a chopping mode with several typical on-off cycles for the above four samples, are shown in **Figure 4a**. The photocurrents of these four samples rapidly increase to the net saturated values and then decrease to zero along with the light irradiation being turned on and off, respectively. Photocurrents from all samples can reach the previous value when the light is turned on again,

indicating great reproducibility. FH-TiO₂ exhibits the highest photocurrent values of 2.24 mA cm⁻², followed by 1.02, 0.41, and 0.05 mA cm⁻² for NRs-anatase-TiO₂, P25, and rutile NRs-TiO₂, respectively. Almost 45 times of increment in generated photocurrent was obtained from FH-TiO₂ as compared to rutile NRs-TiO₂, suggesting the enhanced separation efficiency by FH mechanism for photo-induced electron-hole pairs. The long-term photocurrent measurements show that TiO₂ in all tested phases have fairly stable photoresponse (Figure 4b). A significant increase of photocurrent densities from FH-TiO₂ under UV light irradiation with the increase of bias potential ranging from -1.0 V to 1.0 V (vs. Ag/AgCl as reference electrode) is seen in Figure S8. The photocurrent increases to a plateau at around 2.7 mA cm⁻² with increasing anodic bias from 0 V to 1 V, indicating the UV irradiation presumably to be more crucial than voltage bias for photocurrent response. Furthermore, H₂ production measurements were carried out to evaluate the water splitting activity of FH-TiO₂, NRs-TiO₂, NRs-anatase-TiO₂, and P25 photocatalysts (50 mg with 1 wt % Pt as the cocatalyst). First, the typical H₂ evolution kinetics increases almost linearly with irradiation time as shown in Figure 4c, using 10% v/v methanol as sacrificial reagent. The low H₂ production rate for NRs-TiO₂ in rutile than in anatase (0.078 vs. 0.835 mmol g⁻¹h⁻¹) is mainly caused by the high recombination rate of electron-hole pairs. The significant increase of H₂ production rate for P25 indicates the efficacy of heterojunction formed between the tightly bonded rutile and anatase TiO₂ particles. With the assistance of FH mechanism, FH-TiO₂ exhibits the highest H₂ production rate (1.441 mmol g⁻¹h⁻¹). FH-TiO₂ demonstrates more than 18 and 1.7 times higher H₂ production rates than rutile NRs-TiO₂ and NRs-anatase-TiO₂, respectively, confirming that the numerous FHs present in FH-TiO₂ show synergistic effect to make rutile TiO₂ a highly active H₂ photocatalyst. In addition, FH-TiO₂ also demonstrates 0.566 mmol g⁻¹h⁻¹ H₂ production rate in pure water (Figure 4c), about 4.6 and 13.5 times higher than NRs-anatase-TiO₂ and P25 (no apparent H₂ production from NRs-TiO₂, Table S2), which is the highest value achieved to date for pure rutile TiO₂ photocatalysts in our knowledge.^[43-46] As

discussed before, we believe that the synergistic effect is driven by the band gap discontinuity. Recycling test of H₂ production, with intermittent evacuation every 2 h under UV irradiation, was performed to demonstrate the long-term stability. No apparent activity decrease was observed for FH-TiO₂ after 20 h of continual testing, indicating that rutile TiO₂ with FH mechanism is very stable for H₂ production.

In summary, rutile TiO₂ was demonstrated as high performance photocatalyst for H₂ production with a FH mechanism to accelerate the spatial charge separation. The FHs were formed at the interfaces of ultrathin rutile TiO₂ nanosheets and the surface of NR-TiO₂, prolonging the lifetime of photoexcited electrons by band gap discontinuity. FH-TiO₂ generated a photocurrent of 2.24 mA cm⁻² and H₂ production rates of 1.441 mmol g⁻¹h⁻¹ in 10% v/v methanol and 0.566 mmol g⁻¹h⁻¹ in pure water, respectively. These results demonstrate the potential of rutile TiO₂ as efficient photocatalyst, and may stimulate the research on new design schemes for robust, cheap and commercially available photocatalytic materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 2. a) and b) Schematic diagrams for NRs-TiO₂ and FH-TiO₂ arrays, respectively. c) Scheme showing exposed facets on NRs-TiO₂ and ultrathin nanosheets as well as mechanism of H₂ generation on the surface of FH-TiO₂ photocatalyst. d) SEM image of NRs-TiO₂. e) and f) SEM images for the corresponding top and cross-section of FH-TiO₂.

Figure 3. a) TEM image and the corresponding SAED image (top left inset) of the FH-TiO₂ and the HRTEM image with (110) and (001) direction of the NRs-TiO₂ (bottom right inset). b) HRTEM image of the ultrathin nanosheets as marked in a). c) XRD patterns of FH-TiO₂, NRs-TiO₂ anchored on FTO substrate, and pristine FTO substrate. d) and e) Photoluminescence and time-resolved photoluminescence spectrums of NRs-TiO₂ and FH-TiO₂.

Figure 4. Evaluation of photocatalytic activity with FH-TiO₂, NRs-TiO₂, NRs-anatase-TiO₂, and P25 as photoanode. a) Typical saturated anodic photocurrent curves measured under the UV irradiation, 6 mol L⁻¹ KOH and 10% v/v methanol as electrolyte solution, Ag/AgCl and Pt as reference and counter electrode, respectively. b) Long-term photocurrent-time curves measured vs Ag/AgCl as reference electrode. c) 23 h long-term cyclic plots of H₂-production. Pure N₂ was used to bubble the reaction system for 30 min every 2 h to remove the obtained H₂ from reaction solution. 1 wt% Pt was loaded as co-catalyst.

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Rutile TiO_2 photocatalyst with facet heterojunction structure was designed for high performance hydrogen evolution. Benefited from the enhanced electron-hole separation, the heterojunction structure sample delivered more than 45 and 18 times higher of photocurrent density and H_2 productive rate, respectively, compared to pure rutile TiO_2 nanorods.

Keywords: rutile TiO_2 , facet heterojunction, charge separation, water splitting

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A Photoresponsive Rutile TiO_2 Heterojunction with Enhanced Electron-Hole Separation for High Performance Hydrogen Evolution

TOC Figure

Supporting Information

**A Photoresponsive Rutile TiO₂ Heterojunction with Enhanced Electron-Hole Separation
for High Performance Hydrogen Evolution**

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Experimental Section

Rutile FH-TiO₂ Sample Preparation: Three-dimensional (3D) FH-TiO₂ samples with rutile phase were synthesized via a two sequential hydrothermal synthesis. The procedure for NRs-TiO₂ preparation on FTO substrates is given using previously reported hydrothermal method.^[1] First, FTO glass substrate was degreased by sonicating in acetone, ethanol and ultrapure water, respectively. Second, mix ultrapure water (10 mL) with concentrated HCl (12 M, 10 mL) by stirring for 10 min, and then add tetrabutyl titanate (0.4 mL) into this solution with stirring for 30 min. The clear transparent solution was then transferred into a Teflon-lined stainless steel autoclave (25 mL), and a piece of FTO glass (1*5 cm) was immersed in this solution with the conducting side facing down. The autoclave was sealed and placed in an oven at 150 °C for 4 h, which was then allowed to cool to room temperature naturally. Finally, the product was rinsed thoroughly with ultrapure water and dried in ambient air at 60 °C (named as NRs-TiO₂).

The FH-TiO₂ samples were grown over the FTO glass with NRs-TiO₂ as substrate by the hydrothermal method. Briefly, 20 mL ultrapure water mixed with 0.25 mL of 12 M HCl, followed by adding of 0.25 mL TiCl₃ to this solution dropwise to prepare a forming solution. The FTO glass with NRs-TiO₂ was placed in a beaker against the wall at an angle. The breaker was kept in an oven at a temperature of 80 °C for varying durations (30 to 120 min). Finally, on FTO glass, the obtained FH-TiO₂ samples with rutile phase were rinsed with ethanol and dried at 60 °C. All of the samples (NRs-TiO₂ and FH-TiO₂) were subsequently annealed at 450 °C for 60 min in air prior to further studies.

Anatase NRs-TiO₂ sample preparation: The anatase NRs-TiO₂ are obtained with the same procedures of rutile NRs-TiO₂ other than the HCl was change to the mixture of HCl and H₂SO₄ (14:1 molar ratio).

Photocatalytic Reactions: TiO_2 as a high performance photocatalyst, there is a large overpotential when the evolution of H_2 prepared from water splitting on TiO_2 samples surface. In practice, TiO_2 alone will become inactive if no co-catalyst. Usually, noble metals such as Pt, Pd, or Rh were used on TiO_2 surface as co-catalyst. Here nano Pt particles were used as co-catalyst coated on the surface of sample FH- TiO_2 , NRs- TiO_2 and commercial P25 for evaluation of H_2 production. 50 mg of testing samples were dispersed in 100 mL of 10 v/v% methanol aqueous solutions, and then Pt particles from aqueous H_2PtCl_6 solution were loaded onto the TiO_2 particle surfaces by an in situ photo deposition method. 300 W high-pressure Hg lamp equipped with a 365 nm filter was used as light source with illumination intensity at 350 nm.

Hydrogen production from water splitting was conducted in a Pyrex top-irradiation vessel connected to a glass closed gas circulation system. The testing samples were first scraped from FTO glass and dispersed by ultrasonic vibration in ultrapure water. In a typical process, the well dispersed suspension (the upper part of the dispersed solution) was chosen as photocatalyst powder (50 mg sample of 1% Pt-loaded rutile TiO_2 powder) by centrifugation. After being evacuated under vacuum several times to completely remove any residual air under magnetic stirring, the photocatalysts were irradiated by UV light (350 nm) from 100 W Hg lamp in 100 mL pure water (for overall water splitting) solutions containing 10 v/v% methanol as sacrificial agent (for H_2 evolution half reaction). The irradiation wavelength was controlled by a cold mirror and water filter ($\lambda > 350$ nm). The reactant solution was maintained at room temperature by a water bath during the reaction. The amounts of H_2 or O_2 gas were determined by online gas chromatograph.

First-principles calculations: Our first-principles calculations were performed within density functional theory (DFT) implemented in the plane wave basis Vienna ab initio simulation package (VASP) code.^[2-4] The electron-ion interactions were described by the projector augmented wave (PAW) method.^[5] The electron-electron interaction was treated within a

generalized gradient approximation (GGA) in the form proposed by Perdew, Burke and Ernzerhof (PBE) for the exchange-correlation functional.^[6] Because of deficiency for GGA in describing the strong Coulomb interaction between the partially filled 3d-shells of the transition metals, the GGA+U method was adopted in our calculations.^[7] The values of correlation energy (U) and exchange energy (J) were set to 7.9 eV and 0.9 eV, respectively, as used in previous works.^[8, 9] The energy cutoff employed for plane-wave expansion of electron wave functions and convergence criteria for energy and force were set to be 400 eV, 1×10^{-5} eV and 0.01 eV/Å respectively. The Brillouin zone integrations were carried out by the Monkhorst-Pack k-points meshes^[10] of $4 \times 4 \times 1$. The convergence of this strategy has been verified. All the atom positions and the lattice constants were fully optimized using a conjugate gradient (CG) algorithm.

Figure S1. The schematic model of the band gap of anatase a) and rutile b) TiO_2 . The indirect band gap in anatase TiO_2 makes direct transitions of excited electrons from the bottom of the conduction band (CB) to the top of the valence band (VB) impossible.

Figure S2. Combined Schematic for P25 samples with and without heterojunction structure. a) Diagram of possible charge transfer pathways from anatase to rutile TiO₂ by heterojunction structure. b) and c) Diagram of possible charge transfer pathways for bonded anatase and rutile TiO₂. d) Diagram of possible charge transfer pathways for separated anatase or rutile TiO₂ particles.

Figure S3. SEM images of the obtained FH-TiO₂ prepared at a temperature of 80 °C with different reaction times: a) 30 min. b) 60 min. c) 90 min. d) 110 min. e) 120 min. f) 130 min.

In order to investigate the growth mechanism of FH-TiO₂ samples, time-dependent procedures were carried out with NRs-TiO₂ on FTO glass as substrate. The representatives of time-resolved SEM images obtained at different growing stages are shown in Figure S3a to f. As shown in Figure S3a, smooth NRs-TiO₂ samples with lots of space between each other are anchored vertically on FTO substrate. With the initial nucleation and growth sites on the surface of NRs-TiO₂, only a few tiny buds formed on the NRs-TiO₂ surface at the initial reaction stage (30, 60 min in Figure S3a and b). As seen, there was an obvious growth of the branch structures on the surface of the backbone. When the reaction time was prolonged to 90 min, a branched nanostructures became conspicuous and appeared uniformly on the whole surface of NRs-TiO₂ backbone, Figure S3c. Specifically, the branch structures became larger with reaction time to 110 min, which indicated the evolution from 1D to 3D treelike architecture of TiO₂ (Figure S3d). Intriguingly, at a reaction times of 120 min, plentiful of short and thin nanorods as coating layer were produced on the surface of NRs-TiO₂ backbones owing to the affluence of precursor concentration, Figure S3e. The coating layer as revealed from Figure 2 in main paper showed obvious porous structure and the thickness of the coating layer was from 100 to 150 nm in average. And the average particle sizes of the porous and ultrathin nanosheets are varies from 2 to 5 nm in thickness. However, when

further extended the reaction time to 150 min, the products tend to merge as shown in Figure S3f.

Figure S4. SEM images of samples with the variation of TiCl_3 concentrations at a) 10 mM. b) 20 mM. c) 30 mM. d) 40 mM. e) 50 mM. f) 60 mM.

In our experiment, the morphologies of the resulting products are tailored by changing the TiCl_3 concentrations during the second-step hydrothermal process. Figure S4a-f exhibit the representative SEM images of obtained products by using 20 mL of H_2O and 0.25 mL HCl as constant and increasing the concentration of TiCl_3 . Obviously, the length of branch structures and the thickness of the whole coating layer increased directly with the increasing of TiCl_3 concentration from 10 to 60 mM. And the morphology of obtained products was admired when the concentration of TiCl_3 was 40 mM.

Figure S5. SEM images of resulting samples with the variation of reaction temperature at a) 30 °C. b) 50 °C. c) 60 °C. d) 70 °C. e) 80 °C. f) 90 °C.

As reaction temperature is an important factor for hydrothermal process. Here the relationship between reaction temperature and morphology was studied in the second-step hydrothermal reaction process. As shown in Figure S5a, NRs-TiO₂ remained the smooth surface when the reaction temperature was 30 °C. When reaction temperature increased to 50 °C, some tiny buds were observed. Furtherly from 60 °C to 90 °C, the nanosize buds grew to porous branch structure as coating layer on NRs-TiO₂ surface. Visibly, with the reaction temperature at 80 °C, the resulting products were the wanted.

Figure S6. Raman spectrums of NRs-TiO₂ and FH-TiO₂.

Figure S7. Nitrogen adsorption-desorption isotherm and the corresponding BJH pore size distribution of NRs-TiO₂ (black curve) and FH-TiO₂ (red curve).

The porous structures of NRs-TiO₂ and FH-TiO₂ samples are investigated by nitrogen sorption. Figure S7 presents the nitrogen adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution curves (inset) of the two samples. The two samples exhibit IV shapes according to the IUPAC classification,^[11] which is characteristic of mesoporous materials. As exhibited in Figure S7 and inset, the BET surface area and pore size of NRs-TiO₂ were 20.4032 m² g⁻¹ and 2.8 nm. The surface area of FH-TiO₂ is larger (37.4326 m² g⁻¹) than NRs-TiO₂. Except the 2.8 nm pore size, an additional 1.8 nm pore size is observed, resulting in an increase of mesoporous surface area and mesoporous volume for FH-TiO₂. In addition, the 1.8 to 2.8 nm pore size is favorable for H₂O molecules getting into inner of the NRs substrate from molecular regime (MR) structure layer and for the generated H₂ gas come out easily. So the water splitting reaction will not only occur at ultrathin rutile TiO₂ nanosheets but also can extend to inner of NRs substrate, which may be one of explains for the high-active catalyst for water splitting.

Figure S8. Typical saturated anodic photocurrent curves measured under the irradiation of a 300 W Hg lamp, 6 mol L⁻¹ KOH and 10% v/v methanol as electrolyte solution, Ag/AgCl and Pt as reference and counter electrode. Chopped LSV testing (from -1 to 1 V) of CHI-TiO₂ with irradiated on/off cycles.

Table S1 Decay parameters and average lifetime according to a biexponential fitting model of the PL decay curves obtained for the samples.

Samples	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{ave} (ns)
FH-TiO ₂	0.44	12.95	0.64	0.04	8.67
P25	0.96	5.23	0.86	0.11	2.72
NRs-TiO ₂	0.69	2.95	0.58	0.22	2.09

Table S2 Comparison of H₂ production rate (mmol g⁻¹h⁻¹) for FH-TiO₂, NRs-TiO₂, NRs-anatase-TiO₂, and P25 (with 1 wt % Pt as the cocatalyst) photocatalysts in 10% v/v methanol or pure water solution.

Solution	FH-TiO ₂	P25	NRs-TiO ₂	NRs-anatase-TiO ₂
10% v/v methanol	1.441	0.263	0.078	0.835
Pure water	0.566	0.042	/	0.124

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