1. Introduction

Hydrogen energy is widely accepted as a promising alternative to traditional fossil fuels. Production of hydrogen using solar light has been intensively investigated due to its distinct advantages, such as highly efficient, environmentally friendly, and cost effective.[1] In particular, photocatalytic hydrogen production from water or sustainable organics under solar irradiation is considered as an ideal solution to the current energy and environmental issues.[2] Many semiconductor materials have been used in solar energy conversion and storage because of their excellent optical and electronic properties.[3] Among them, the application of titanium dioxide ($\text{TiO}_2$) for photocatalytic hydrogen production attracts much attention ever since its first report,[2a] and numerous efforts have been devoted to enhancing the activity of $\text{TiO}_2$ for photocatalytic hydrogen production.[4]

The emergence of nanotechnology has opened up new ways to utilize renewable energy resources by constructing nanostructured materials which possess many unique properties, such as large surface areas, abundant surface states, and diverse morphologies, compared to their corresponding bulk materials.[5] Accordingly, considerable efforts have been made to control the size, shape, and surface structure of $\text{TiO}_2$ to improve the efficiency in heterogeneous photocatalysis. Various nanostructures of $\text{TiO}_2$, such as nanowires,[6] nanorods,[7] nanotubes,[8] and microspheres[9] have been successfully synthesized.

Anatase is the most extensively studied crystal structure of $\text{TiO}_2$ owing to its high photocatalytic activity for hydrogen evolution. Generally, anatase $\text{TiO}_2$ single crystal is dominated by [101] facets, which are thermodynamically stable due to a low surface energy. Although [001] facets with a higher energy are more important and reactive, they usually diminish rapidly during the crystal growth process.[10] Therefore, much attention is focused on controllable exposure of high energy facets of $\text{TiO}_2$ single crystals ever since the first report by Lu group in 2008, where hydrofluoric acid (HF) was found to...
play an irreplaceable role in controllable exposure of [001] facets and formation of the unique truncated-bipyramid morphology.[11] After that, a set of fluoride-mediated experiments were performed to improve the photocatalytic performance of anatase TiO₂ by enhancing the percentage of [001] facets.[12] However, several latest researches demonstrated that the high exposure percentage of [001] facets was not requisite for the high photocatalytic activity. Liu et al. reported that clean [001], [101], and [010] facets followed the photo-reactivity order of [001]<[101]<[010], which was contrary to conventional understanding that the photoreactivity of [001] facets was higher than that of [101] facets.[13] They attributed the high activities of [010] and [101] facets to the more negative conduction bands comparing with [001] facets. Apparently, arguments on the activities of different facets of TiO₂ single crystals have become increasingly complex. Thus, much more experimental investigation and in-depth analysis on this important issue are urgent from both theoretical and practical viewpoints.

In this work, we try to synthesize a novel TiO₂ nanostructure with controllable exposure of crystal facets for efficient photocatalytic hydrogen production by a simple hydrothermal method using peroxy ticianic acid (PTA) as a precursor and HF as a capping agent. The obtained samples are denoted as TiO₂-t in this paper, where t represents the hydrothermal time. X-ray diffraction (XRD) patterns of the as-prepared TiO₂ samples at different hydrothermal times were recorded in Figure 1a. There are only two tiny peaks corresponding to the (101) and (200) diffraction peaks of anatase TiO₂ in the XRD pattern of TiO₂-10 min, indicating that a small amount of TiO₂ nanocrystallites are present in this sample. As the reaction time exceeds 30 min, all TiO₂ samples show sharp diffraction peaks corresponding to the standard anatase phase of TiO₂ (space group I₄₁/amd, JCPDS No. 21-1272), which means that PTA is gradually transformed to TiO₆ coordination polyhedron and then the amorphous TiO₂ clusters crystallize rapidly under hydrothermal conditions.[14]

Figure 1b shows the change of the average grain size along different crystallographic directions, which are calculated by Scherrer’s equation referencing to the diffraction peaks in Figure 1a. The average grain size of TiO₂ crystals varies significantly with increasing hydrothermal time and is distinct along different directions. Especially, the aspect ratio (r₀₀₄/r₂₀₀) of TiO₂ in Table 1 dramatically decreases, e.g. from 1.35 to 0.70 as the hydrothermal time changes from 2 to 4 h, implying that the morphology of TiO₂ crystals undergoes remarkable change during the hydrothermal process.

In order to verify the above judgment, field emission scanning electron microscopy (FE-SEM) was employed.
Table 1. The calculated average grain size, specific surface area, and photocatalytic H₂-production activity of the TiO₂ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( f_{[101]} )</th>
<th>( f_{[004]} )</th>
<th>( f_{[004]}/f_{[200]} )</th>
<th>Surface Area [m² g⁻¹]</th>
<th>Photocatalytic Activity [mmol h⁻¹ g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-F-0.5h</td>
<td>41.9</td>
<td>53.8</td>
<td>45.8</td>
<td>1.17</td>
<td>108.5</td>
</tr>
<tr>
<td>TiO₂-F-1h</td>
<td>56.6</td>
<td>92.6</td>
<td>68.0</td>
<td>1.36</td>
<td>58.1</td>
</tr>
<tr>
<td>TiO₂-F-2h</td>
<td>42.6</td>
<td>58.3</td>
<td>43.0</td>
<td>1.35</td>
<td>53.4</td>
</tr>
<tr>
<td>TiO₂-F-4h</td>
<td>66.7</td>
<td>64.9</td>
<td>92.2</td>
<td>0.70</td>
<td>28.8</td>
</tr>
<tr>
<td>TiO₂-F-8h</td>
<td>50.7</td>
<td>48.0</td>
<td>77.4</td>
<td>0.62</td>
<td>29.2</td>
</tr>
<tr>
<td>TiO₂-F-12h</td>
<td>38.9</td>
<td>39.3</td>
<td>48.5</td>
<td>0.81</td>
<td>41.4</td>
</tr>
</tbody>
</table>

The remarkable morphology change during the hydrothermal process has been demonstrated in Section 2.1. However, the inherent mechanism of this morphology evolution is still unclear. Thus, systematical investigation and in-depth analysis on the morphology change are made in this section for a clear insight on the growth process of the TiO₂ single crystal.

As shown in Figure S1 (Supporting Information), the yellow color and the absorbance between 400 and 500 nm in the UV-vis absorption spectra of the TiO₂ powder, which are caused by the electron transfer from the ligand –O–O– to the metal cation, confirm the presence of –O–O– species.[13] Raman peaks at 282, 522, 676, and 905 cm⁻¹ of TiO₂-10 min and TiO₂-0.5h in Figure S2 (Supporting Information) can also be assigned to the –O–O– groups on the surface of TiO₂.[10] That is, PTA is not completely decomposed at this stage. As the hydrothermal time increases to 1 hour (Figure S1 and S2 in Supporting Information), the color of the as-prepared samples changes from yellow to white and the Raman peaks of –O–O– groups gradually disappear, indicating the complete decomposition of PTA and subsequent formation of anatase TiO₂.[17]

The remarkable morphology change during the hydrothermal process can be assigned to the –O–O– groups on the surface of TiO₂.[16] and TiO₂-0.5h in Figure S2 (Supporting Information) can also be assigned to the –O–O– groups on the surface of TiO₂.[10] That is, PTA is not completely decomposed at this stage. As the hydrothermal time increases to 1 hour (Figure S1 and S2 in Supporting Information), the color of the as-prepared samples changes from yellow to white and the Raman peaks of –O–O– groups gradually disappear, indicating the complete decomposition of PTA and subsequent formation of anatase TiO₂.[17]

The transmission electron microscopy (TEM) images of the as-prepared samples were recorded in Figure 2. The TEM image of TiO₂-10 min shows that there are only some small particles deposited on the thin film with obvious wrinkles which should be the non-decomposed PTA.[18] As the reaction time reaches 1 h, the thin film disappears and the monodisperse rugby-shaped TiO₂ nanoparticles are formed. The selected area electron diffraction (SAED) image of the rugby-shaped particle in Figure S3 confirms that the rugby-shaped nanoparticle is a single crystal. In order to understand the assembly process of the rugby-shaped single crystal, TEM and high-resolution TEM (HR-TEM) images of TiO₂-4h and TiO₂-1h were recorded in Figure 3. A careful view of TiO₂-0.5h in Figure 3a indicates that the rugby-shaped single crystals are surrounded by many small TiO₂ nanosheets. According to the previous reports,[18,19] we suggest that the rugby-shaped single crystal can be possibly formed by self-assembly of the thin nanosheets along the long-axis of the single crystal.
is in accordance with the results in Figure 1b and Table 1. Furthermore, we conclude that the long axis of the rugby-shaped single crystal, and the hollow structure gradually appear after the complete dissolution of the core of the crystal. Especially, the single crystal composed of four bipyramids can be found in the TEM image of TiO$_2$-2h (Figure 2). It is well known that the average surface energies of the different facets of anatase TiO$_2$ are 0.90 J m$^{-2}$ ([001] facets), 0.53 J m$^{-2}$ ([100] facets), and 0.44 J m$^{-2}$ ([101] facets), respectively, which are related to the percentage of the 5-fold-coordinated titanium atoms on the specific facets. Owing to the decomposition of the surface absorbed species, the surface unsaturated titanium species which are quite active will directly expose to the reaction solution. Furthermore, more unsaturated titanium atoms on the top ([001] facets) should be exposed to the reaction solution as deduced from Figure 3d. Thus it is reasonable that dissolution of the rugby-shaped single crystal should start from the tip of the ellipsoid. Numerous reports have demonstrated that HF can induce both interior dissolution of the particle and subsequent mass transfer from the core to the external surface. So the dissolution of the rugby-shaped TiO$_2$ single crystal is probably induced by HF in the reaction solution, and the decrease of the average grain size should be attributed to partial dissolution of the single crystal (Figure 1b and Table 1, TiO$_2$-2h). More importantly, the aspect ratio of \(t_{[100]}/t_{[200]}\) at this stage shows no obvious change (Table 1), indicating rare collapse of the hollow single crystals.

When the hydrothermal time reaches 4 hours, TiO$_2$ single crystal exhibits a quasi-cubic morphology with a penetrated hole (Figure 2), and the particle size shows slight increase compared to that of TiO$_2$-2h. As known, the dissolution phenomenon of the nanoparticle is always related to the Ostwald ripening process, which means that crystallites would redistribute themselves through a dissolution-redeposition process to achieve a more stable state with much lower total energy. The dissolution of the rugby-shaped single crystal is certain to cause the rapid increase of ions or clusters concentration in the reaction solution, following by further growth of the partially dissolved crystal once the reaction solution is supersaturated. Therefore, the significant increase of the particle size of TiO$_2$-4h at this stage should be caused by the redeposition of the dissolved ions or clusters on both the external and the internal surface of the single crystal in the reaction solution, thereby resulting in the formation of the hollow quasi-cubic morphology of TiO$_2$-4h as shown in Figure 2.

Figure 4 shows the TEM and HR-TEM images of sample TiO$_2$-4h. The TEM image in Figure 4a is a typical top view of the TiO$_2$ single crystal with a morphology similar to the four common-edge-bipyramid crystal of TiO$_2$-2h, and the difference between them is that the crystal in Figure 4a exhibits bigger particle size and tighter connection among the four equivalent parts. The clear lattice fringes with the spacing of 0.267 nm corresponding to the (110) plane of anatase TiO$_2$ can be seen from Figure 4b. In view of the anatase structure of TiO$_2$ single crystal, we conclude that the four equivalent facets of the cubic crystal in Figure 4a are [101] facets, thereby confirming the preferential growth along the [200] direction of TiO$_2$-4h, which is in accordance with the results in Figure 1b and Table 1. Furthermore, we conclude that the direction normal to the TEM image is the [001] direction.
based on the crystal orientation of the anatase structure. Thus the growth along [001] direction is probably suppressed by F\(^{-}\) ions, as F\(^{-}\) has been widely reported to be capable of dramatic decrease of the surface energy of [001] facets.\(^{[11]}\)

Afterwards, the penetrated hole gradually disappears, and a crossed valley is visible in the single crystal of TiO\(_2\)-8h, indicating the formation of the four-truncated-bipyramid morphology as shown in Figure 2. Moreover, the TEM image of sample TiO\(_2\)-8h clearly displays a continuing decrease of the TiO\(_2\) particle size, which is consistent with the calculated results in Figure 1b and Table 1. We assume that the morphology change at this stage be also in close relationship with the Ostwald ripening process. As known, the hollow structure is always not stable because of its high surface energy. Thus, in order to decrease the total surface energy, shrinkage or even elimination of the penetrated hole is preferential with further increasing hydrothermal time. Meanwhile, surface reconstruction is also undergoing, and the specific exposure of the stable crystal facets, including [010] and F-terminated [001] facets, is achieved. During this process, the dissolved species originated from surface reconstruction will continuously redeposit on the internal surface of the hollow crystal, resulting in a decrease of the particle size along the [200] direction and missing of the penetrated hole. As a result, a crossed valley can be found in the single crystal while the penetrated hole is eliminated, which seems like that four hillocks appear on the top and the bottom of the crystal respectively, resulting in the formation of the four-truncated-bipyramid morphology. However, as the reaction time further increases, the crossed valley tends to be eliminated under the rigorous hydrothermal conditions because of its high surface energy, and the dissolution-redeposition process is still dominated at this stage.

Therefore, it is reasonable that all single crystals in TiO\(_2\)-12h possess irregular polyhedral shape with significantly decreased particle size as shown in the SEM and TEM images in Figure 1c and 2, which also consists well with the further increase of the surface area of the TiO\(_2\) sample in Table 1.

Accordingly, the morphology change during the hydrothermal process can be divided into several stages as illustrated in Figure 5, including decomposition of PTA, assembly of the rugby-shaped single crystal, dissolution of the rugby-shaped crystal, shaping of the quasi-cubic crystal with a penetrated hole, and formation of the four-truncated-bipyramid single crystal. Obviously, the PTA precursor plays an important role in the formation of the rugby-shaped TiO\(_2\) single crystal, and the oriented attachment mechanism dominates at this stage. And the further morphology change should be attributed to the Ostwald ripening effect, where F\(^{-}\) ions not only induce partial dissolution of the crystals but also direct exposure of the high energy [001] facets.

2.3. Photocatalytic Hydrogen Production

Photocatalytic hydrogen production from biomass derivatives, such as methanol, ethanol, glycerol, and sugars, has been considered as an available candidate for hydrogen production from renewable resources and solar energy.\(^{[23]}\)

It is reasonable as they can be produced renewably from many biomass resources, such as energy plants, agroindustrial wastes, forestry residue materials, and organic fraction of municipal solid waste; moreover, decomposition of these organic compounds can also contribute to a high hydrogen yield, because hydrogen is one of their decomposition products. Among these biomass derivatives, ethanol is mostly studied for photocatalytic hydrogen production using TiO\(_2\) as photocatalyst.\(^{[4a,4b,24]}\) Furthermore, during the photocatalytic reforming of alcohols, water not only promotes oxidation of alcohol into carbon dioxide but also accelerates the reaction rate of dehydration of alcohol.\(^{[23]}\) In order to reveal the relationship between the photocatalytic property and the microscopic morphology of the TiO\(_2\) samples, photocatalytic hydrogen production from an ethanol-water solution were conducted under a 300 W Xe lamp irradiation after loading 1 wt% Pt.

Figure 6 shows the performance of the as-prepared samples for photocatalytic hydrogen production from ethanol-water solution. As displayed in Figure 6a, both TiO\(_2\)-0.5h and TiO\(_2\)-1h need an activation period about 1 hour to achieve a steady hydrogen evolution. This should be attributed to the residue –O–O– species on the surface of the TiO\(_2\) particles. After the residue species are completely decomposed, linear increase of hydrogen amount over irradiation time can be found in all these photocatalysts, indicating their excellent stabilities during the chemical process. The average hydrogen production rates of TiO\(_2\) photocatalysts are also calculated in Figure 6b. It is clear that the hydrogen evolution rates show double peaks with increasing hydrothermal time, and the two peaks locate at TiO\(_2\)-2h and TiO\(_2\)-8h respectively. At the earlier stage of the hydrothermal treatment (<2 h), the enhancement of the hydrogen evolution rate can be attributed to the rapid crystallization of TiO\(_2\) and the decomposition of the surface absorbed species, which...
The photocatalytic activities of TiO₂ samples obtained at different hydrothermal times after loading 1 wt% Pt. (a) Amount of H₂ production under different reaction times; (b) Average H₂ production rate of the samples.

Figure 6

The photocatalytic activity of TiO₂ is closely related to the morphology of TiO₂-8h. Recently, both high-energy {001} facets and low-energy {101} facets in an optimal ratio should be crucial for this high photocatalytic activity. The current findings will provide important scientific references for future investigation on the morphology evolution mechanism of the nanostructures, as well as on the photocatalytic activity of different facets of single crystals.

3. Conclusion

TiO₂ single crystal with a novel four-truncated-bipyramid morphology was synthesized by a simple hydrothermal method using PTA solution as a precursor and HF as a capping agent respectively. Both PTA precursor and HF capping agent are essential for formation of this unique single crystal structure. More importantly, the as-prepared TiO₂ photocatalyst exhibits excellent hydrogen evolution activity from ethanol-water solution. We conclude that the exposure of both high-energy {001} oxidative and low-energy {101} reductive facets in an optimal ratio should be crucial for this high photocatalytic activity. The current findings will provide important scientific references for future investigation on the morphology evolution mechanism of the nanostructures, as well as on the photocatalytic activity of different facets of single crystals.

4. Experimental Section

Synthesis of Peroxo Titanic Acid (PTA) Solution: Peroxo titanic acid (TiO(OH)₄) solution was prepared by a simple method similar to that reported in literature. In a typical procedure: Titanium isopropanoxide (Ti(i-OC₃H₇)₄, 2.91 mL) was added into deionized water (100 mL) drop by drop under vigorous stirring, then the white precipitate was washed with deionized water for several times and filtered to remove organic byproducts. After that, hydrogen peroxide solution (30%, 10 mL) was added into the wet precipitate. As the exothermic reaction led to radical bubbling, the solution was moved into an ice bath so as to make the solution cooling down to room temperature and moved out again to allow reaction continuing at room temperature, which was repeated until no bubbles were released and a clear orange PTA solution was formed.

Synthesis of TiO₂ Photocatalyst: The photocatalyst was synthesized as follows: HF (4.52 M, 1 mL) was added into the fresh-prepared PTA solution, and then the solution was transferred into a
Teflon-lined reactor and sealed. The reactor was kept at 180 °C for different time (0.5 h, 1 h, 2 h, 4 h, 6 h, 8 h, and 12 h), and cooled to room temperature naturally. The final product was filtered and washed with deionized water and ethanol for several times, and finally dried at 80 °C for 24 h in an oven. The obtained powder was denoted as TiO$_2$-t, where t represented the hydrothermal time.

Characterization: X-ray diffraction (XRD) patterns of samples were measured by a D/MAX-2500 diffractometer (Rigaku, Japan) using Cu Kα irradiation ($\lambda = 1.54056 \ \text{Å}$) at a scan rate of $4^\circ \text{min}^{-1}$. The accelerating voltage and the applied current were 50 kV and 300 mA, respectively. Scherrer’s Equation was used to calculate the average grain size of TiO$_2$, as shown in Equation (1),

$$D = \frac{k \lambda}{\beta \cos \theta} \quad (1)$$

where $D$, $k$, $\lambda$, $\beta$, and $\theta$ correspond to the average crystalline size, a constant of 0.89, Cu Kα irradiation wavelength, half maximum peak width, and Bragg’s diffraction angle, respectively. Microscopic morphology of the photocatalysts was observed on an S-4800 field emission scanning electron microscopy (FE-SEM, Hitachi, Japan). The transmission electron microscopy images were collected on a field emission transmission electron microscopy (Tecnai F20 S-TWIN, FEI Co.) operating at 200 kV. UV-vis reflectance spectra of the samples were recorded using a TU-1901 UV-vis spectrophotometer over the wavelength range of 300–800 nm. BaSO$_4$ was used as a reflectance standard. Nitrogen adsorption-desorption isotherms of the samples were conducted using an ASAP 2020 surface area and porosity analyzer (Micromeritics). Before measurement, the samples were degassed in vacuum at 120 °C for more than 12 h. Raman scattering study was performed on a Renishaw inVia plus spectrometer under irradiation from an argon ion 514.5 nm laser.

Evaluation of Photocatalytic Activity: Photocatalytic hydrogen evolution reactions were performed under UV-vis light irradiation (300 W Xe lamp, CEL-HXF 300, AULTT) in a closed circulating vacuum system, where a sealed Pyrex flask (500 mL) with a flat window using a silicone rubber septum for sealing was used as a photocatalytic reactor. Typically, photocatalyst (100 mg) was dispersed in an ethanol-water solution (20 v%, 80 mL). Prior to irradiation, the system was fulfilled with argon, and then evacuated to remove residual oxygen. The amount of hydrogen evolution was measured using online gas chromatography (GC7890II, Techcomp) equipped with a thermal conductivity detector (TCD). Pt (1 wt%) loading was carried out by an in-situ photoreduction method. H$_2$PtCl$_6$ aqueous solution (10 mmol mL$^{-1}$, 267 μL) was injected into the above solution, then the mixture solution was treated under ultrasonic for 1 min to form homogeneous suspension, and irradiated under UV-vis light for 30 min at room temperature. The focused intensity on the reaction solution was ca. 72.2 mW cm$^{-2}$, which was measured over the wavelength in the range of 200–1000 nm.

Supporting Information

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


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TiO$_2$ Single Crystal with Four-Truncated-Bipyramid Morphology as an Efficient Photocatalyst for Hydrogen Production

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Supporting Information

**TiO$_2$ Single Crystal with Novel Four-Truncated-Bipyramid Morphology as an Efficient Photocatalyst for Hydrogen Production**

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**Figure S1.** Photographs and UV-vis absorption spectra of TiO$_2$-t samples at different hydrothermal times of 10 min, 0.5h, 1 h, 2 h, 4 h, 8 h, and 12 h. The orange/yellow color and the absorbance between 400 and 500 nm of TiO$_2$-10min, TiO$_2$-0.5h, and TiO$_2$-1h are induced by the surface absorbed -O-O- groups. When the hydrothermal time exceeds 1h, all the samples possess similar absorption edges, indicating the complete decomposition of -O-O- groups.
**Figure S2.** Raman spectra of TiO$_2$-t samples at different hydrothermal times of 10 min, 0.5h, 1 h, 2 h, 4 h, 8 h, and 12 h. At the earlier stage of hydrothermal treatment, Raman peaks corresponding to -O-O- groups can be found, indicating that many of -O-O- groups are absorbed on the surface of TiO$_2$. With increasing hydrothermal time, Raman peaks of -O-O- groups gradually disappear, and the typical Raman spectra of anatase phase TiO$_2$ are recorded, which is in accordance with the XRD patterns in Figure 1a. Anatase TiO$_2$ has six Raman active modes: A$_{1g}$+2B$_{1g}$+3E$_g$, and peaks at 144 cm$^{-1}$, 399 cm$^{-1}$, 513 cm$^{-1}$, and 639 cm$^{-1}$ can be indexed to the E$_g$, B$_{1g}$, A$_{1g}$, and E$_g$ modes, respectively. The redshift and lineshape change of Raman peak can be attributed to the change in the grain size and the nonstoichiometry of TiO$_2$ sample at the initial stage.[1]
Figure S3. TEM image of a rugby-shaped nanoparticle in TiO$_2$-1h and the corresponding selected area electron diffraction (SAED) pattern of the particle. It is clear that the SAED pattern of the rugby-shaped nanoparticle shows a typical diffraction pattern of single crystal.

Reference