Hollow Square RodLike Microtubes Composed of Anatase Nanocuboids with Coexposed {100}, {010}, and {001} Facets for Improved Photocatalytic Performance

Yi-en Du,* Xianjun Niu, Jing He, Leng Liu, Yufang Liu, Changdong Chen,* Xiaojing Yang,* and Qi Feng

ABSTRACT: In this study, hollow square rodlike microtubes composed of anatase nanocuboids with coexposed {100}, {010}, and {001} facets were successfully synthesized via a mild hydrothermal treatment method in the presence of NH4F by using layered H2Ti3O7 ribbons as the precursor. The precursor H2Ti3O7 ribbons were prepared from H+/Na+ ion-exchanged Na2Ti3O7. The suspension solution of protonated H2Ti3O7 ribbons was adjusted to desired pH values (0.5−13.0) prior to hydrothermal treatment. The elongated direction of the microtubes is along the b axis, according to the profile of the H2Ti3O7 ribbons. The transformation from staggered [Ti3O7]2− sheets to hollow square rodlike microtubes contained the formation and recombination of the dispersed octahedral [Ti(OH)2(OH2)4]2+ monomers, the formation and growth of the initial anatase nuclei, and the reassembly of the anatase nanocuboids along the b-axis direction during the continuous hydrothermal process. The degradation rate of pH 0.5-TiO2 was the highest at 1.66 × 10−2 min−1, which was 1.3, 1.5, 2.0, 2.3, and 18.4 folds higher than that of pH 3.0-TiO2 (1.27 × 10−2 min−1), pH 7.0-TiO2 (1.11 × 10−2 min−1), pH 5.0-TiO2 (0.83 × 10−2 min−1), P25−TiO2 (0.73 × 10−2 min−1), and the blank sample (0.09 × 10−2 min−1), respectively. Compared with P25−TiO2 and the other anatase TiO2 samples, pH 0.5-TiO2 exhibited the best photocatalytic activity, which was mainly attributed to its larger proportion of {010} (or {100}) facets, smaller crystalline size, higher band gap, and larger specific surface area.

INTRODUCTION

Nowadays, water pollution caused by many water-soluble organic dyes (such as methylene blue, methyl orange, and rhodamine B (RB), etc.) is becoming more serious.1,2 However, the traditional sewage treatment methods, such as biodegradation and activated carbon adsorption, are invalid to solve the problem of water-soluble organic dyestuff wastewater.3 It is found that semiconductor photocatalysis can replace the abovementioned traditional methods. The dyes in dyestuff wastewater can be decomposed into small organic molecules and eventually mineralized into H2O, CO2, and other inorganic ions under the irradiation of visible or ultraviolet light because of its high catalytic performance, nonselective oxidation, nontoxicity, low expenses, and secondary pollution.3−6 Therefore, it is very important to design and synthesize novel photocatalysts with high catalytic activity to solve the problem of highly polluted textile wastewater. In a variety of semiconductor photocatalysts, titanium dioxide (TiO2) is considered to be the most widely used catalyst for the photocatalytic degradation of organic pollutants because of its outstanding chemical and thermal stability, great oxidizing power, excellent photochemical activity, harmlessness, and nontoxicity.7−9 Among the four confirmed polymorphs of TiO2 (anatase, rutile, brookite, and TiO2-B), the anatase phase has been widely regarded to exhibit the most photoactive reactivity in photocatalysis applications, which can be attributed to the lower rate of charge recombination and the stronger interaction between the organic molecules and the anatase surfaces.10,11 However, the rapid recombination rate of photogenerated electrons and holes leads to a reduction in quantum efficiency and limits the photocatalytic ability of anatase.12 Therefore, the design and synthesis of the anatase TiO2 nanocrystal with a high photocatalytic performance is the key to reduce the
recombination of the photogenerated charge carriers. It is well known that the photocatalytic performance of the semiconductor photocatalyst greatly depends on the crystallinity, particle size, specific area, morphology, and crystal facets.\(^\text{12}\) Particularly, the morphology and crystal facets of anatase have a significant effect on the enhancement of the photocatalytic performance.\(^\text{13}\) Hence, the design and synthesis of anatase TiO\(_2\) nanocrystals with tailored-made exposed crystal facets and well-defined morphologies is necessary. The surface energies of anatase TiO\(_2\) are 0.44, 0.53, 0.90, 1.09, and 1.61 J m\(^{-2}\) for the \{101\}, \{010\} (or \{100\}), \{001\}, \{110\}, and \{111\} crystal facets, respectively.\(^\text{14,15}\) However, the crystal facets with higher surface energies usually decrease rapidly to reduce the total surface energy during the crystal growth process, resulting in the formation of slightly truncated \{101\}-faceted tetragonal bipyramid.\(^\text{16}\) Since \{010\}-faceted single anatase TiO\(_2\) nanocrystals with different morphologies were first reported by Wen,\(^\text{17}\) there have been increasing interest to synthesize anatase TiO\(_2\) crystals with exposed high-energy planes or special morphologies. Particularly, using fluorine as a capping agent, truncated tetragonal bipyramid anatase crystals with 47 and 89\% \{001\} facets exposed were prepared by Yang,\(^\text{16,18}\) which was regarded as a groundbreaking discovery. Following these breakthroughs, more and more synthetic strategies were used to synthesize well-defined anatase TiO\(_2\) crystals with high-energy crystal facets. For instance, using HF as a controlling agent, anatase TiO\(_2\) single crystals with a high percentage of \{001\} facets were synthesized.\(^\text{19,20}\) Without using fluorine and organic capping agents, bipyramid-shaped, nanosheet-shaped, and rodlike anatase TiO\(_2\) nanocrystals with about 95\% \{101\}, 91\% \{001\}, and 90\% \{010\} facets exposed were synthesized, respectively.\(^\text{21}\) Anatase nanorods with dominant \{010\} facets and porous anatase TiO\(_2\) microspheres composed of high-energy \{010\}-faceted nanobelts were prepared by using H\(_0.68\)Ti\(_1.83\)O\(_4\) and titanium glycerolate as precursors under hydrothermal conditions, respectively, which was regarded as a groundbreaking discovery. Following these breakthroughs, more and more synthetic strategies were used to synthesize well-defined anatase TiO\(_2\) crystals with high-energy crystal facets. For instance, using HF as a controlling agent, anatase TiO\(_2\) single crystals with a high percentage of \{001\} facets were synthesized.\(^\text{19,20}\) Without using fluorine and organic capping agents, bipyramid-shaped, nanosheet-shaped, and rodlike anatase TiO\(_2\) nanocrystals with about 95\% \{101\}, 91\% \{001\}, and 90\% \{010\} facets exposed were synthesized, respectively.\(^\text{21}\) Anatase nanorods with dominant \{010\} facets and porous anatase TiO\(_2\) microspheres composed of high-energy \{010\}-faceted nanobelts were prepared by using H\(_0.68\)Ti\(_1.83\)O\(_4\) and titanium glycerolate as precursors, \{010\}-faceted and \{111\}-faceted anatase TiO\(_2\) nanocrystals were prepared.\(^\text{24}\) Using layered titanate-delaminated nanosheets or nanoribbons as precursors, \{010\}-faceted and \{111\}-faceted anatase TiO\(_2\) nanocrystals with various morphologies were prepared.\(^\text{24–58}\) Using HAc as the solvent and \[\text{bmmim}\] [BF\(_4\)] as the capping agent, respectively, wholly coexposed \{100\}-faceted and \{001\}-faceted anatase TiO\(_2\) nanocruboids were synthesized through the hydrolysis of titanium tetraisopropoxide.\(^\text{31}\) Hierarchical anatase TiO\(_2\) microspheres consisting of 45\% \{010\}-faceted nanodecahedrons were synthesized through a facile hydrothermal technique, which showed superior photocatalytic activity.\(^\text{32}\) Truncated tetragonal bipyramid anatase TiO\(_2\) nanocrystals with coexposed high-energy \{001\}, \{010\}, and \{111\} facets were also prepared by the hydrothermal treatment of the protonated titanic acid at different pH values.\(^\text{33}\) Recently, nanotubes/nanowires composed of high-energy \{111\}-faceted nanotube nanoflakes were prepared by the solvothermal method, which showed a high CO\(_2\) reduction activity.\(^\text{34}\) \{101\}-Faceted anatase TiO\(_2\) truncated bipyramid and \{001\}-faceted TiO\(_2\) nanosheet were prepared by a hydrothermal procedure using HF as the capping agent, respectively, and the \{001\}-faceted anatase TiO\(_2\) exhibited higher stability.\(^\text{34}\) M\{-001\}TiO\(_2\)/Ti photoelectrodes with different surface exposure ratios of \{001\}/\{101\} facets were assembled, which could improve the photoelectrochemical oxidation performance of DMP wastewater.\(^\text{35}\)

In this work, we report the synthesis of hollow square rodlike microtubes composed of anatase nanocuboids with coexposed \{100\}, \{010\}, and \{001\} facets via a mild hydrothermal treatment method in the presence of NH\(_4\)F by using layered H\(_2\)Ti\(_3\)O\(_7\) ribbons as the precursor. The elongated direction of microtubes is along the \(b\) axis according to the profile of the H\(_2\)Ti\(_3\)O\(_7\) ribbons. The transformation mechanism from the staggered \[\text{Ti}_2\text{O}_7^{2-}\] sheets to the hollow square rodlike microtubes was investigated. Compared to P25–TiO\(_2\) and the other anatase TiO\(_2\) samples, pH 0.5-TiO\(_2\) with a larger proportion of \{010\} (or \{100\}) facets, smaller crystalline size, higher band gap, and larger specific surface area exhibited the best photocatalytic activity.

## RESULTS AND DISCUSSION

### Structure and Morphology

The precursor, monoclinic Na\(_2\)Ti\(_3\)O\(_7\), is confirmed by the powder X-ray diffraction (XRD) pattern (JCPDS no. 14-0085, \(a = 0.8571, b = 0.3804, c = 0.9135\) nm, and \(\beta = 101.9^\circ\)), as shown in Figure 1a. After the

![Figure 1. XRD patterns of (a) Na\(_2\)Ti\(_3\)O\(_7\) and (b) H\(_2\)Ti\(_3\)O\(_7\) specimens.](https://pubs.acs.org/doi/10.1021/acsomega.0c01827)
where $x$ corresponds to the desired pH value of the solution ($x = 0.5−13.0$). For all specimens, only the diffraction peaks of the anatase phase were observed, indicating that the H$_2$Ti$_3$O$_7$-ribbons were completely transformed to the anatase phase at 180 °C, and the structural transformation had nothing to do with the pH value of the solution, as shown in Figure 2.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c01827)

**Figure 2.** XRD patterns of (a) pH 0.5-TiO$_2$, (b) pH 1.0-TiO$_2$, (c) pH 3.0-TiO$_2$, (d) pH 5.0-TiO$_2$, (e) pH 7.0-TiO$_2$, (f) pH 9.0-TiO$_2$, (g) pH 11.0-TiO$_2$, and (h) pH 13.0-TiO$_2$ specimens obtained from the H$_2$Ti$_3$O$_7$ square rod.

Generally speaking, the pH value in the reaction medium has an important effect on the crystal structure of the resulting TiO$_2$. The strong acidic medium is conductive to the formation of rutile TiO$_2$. With the increase of the pH value, rutile TiO$_2$ disappeared and anatase TiO$_2$ increased. However, the crystalline form of TiO$_2$ obtained in the present work is different from those reported with the exfoliated nanosheets as the precursor, usually rutile, or the coexistence of anatase and rutile are obtained at a low pH value. Compared with the standard card of anatase TiO$_2$ (JCPDS no. 21-1272, tetragonal system, $a = b = 0.3785$ nm, $c = 0.9514$ nm), all the diffraction peaks of the obtained anatase products shift slightly to the right as a whole, implying that the crystal plane spacing of the synthesized anatase TiO$_2$ specimens decreases slightly. As the XRD patterns above were measured with almost the same content of TiO$_2$ samples, the intensity of the XRD peaks increased with the increasing pH value of the solution, which was probably caused by the increase of crystallinity and crystal size. The influence of the pH value of the reaction medium on the crystallinity and crystal size of the resulting TiO$_2$ could be attributed to the influence of the H$_2$Ti$_3$O$_7$ precursor. The shrinkage of the interlayer and the reassembly of the H$_2$Ti$_3$O$_7$-precursor, which made it difficult to destroy the structure of H$_2$Ti$_3$O$_7$, resulted in poor crystallinity and smaller crystal size of the resulting TiO$_2$ specimens.

The morphologies of Na$_2$Ti$_3$O$_7$- and H$_2$Ti$_3$O$_7$ are confirmed by the field emission scanning electron microscopy (FESEM) images, as shown in Figure 3a–d. The FESEM images show the square rodlike morphology of Na$_2$Ti$_3$O$_7$ with $\sim 1−4 \mu$m in length, $\sim 0.5−1.5 \mu$m in width, and $\sim 0.15−0.6 \mu$m in thickness (Figure 3a,b). After the ion-exchange reaction, the obtained H$_2$Ti$_3$O$_7$ specimen retains the morphology of the original Na$_2$Ti$_3$O$_7$ precursor, and the H$_2$Ti$_3$O$_7$ extension direction corresponds to the b-axis direction of the crystal (Figure 3c,d). Figure 3e–t shows the anatase crystals obtained in the hydrothermal system with different pH values, whereas the other synthesis parameters remain unchanged. When the pH is 0.5, many rodlike particles about 160 nm in length and 80 nm in width and many entangled amorphous particles were obtained, as shown in Figure 3e,f. In addition, many hollow secondary square rodlike microtubes with about 1−4 μm in length, 0.5−1.7 μm in width, and 0.5−1.0 μm in thickness were formed by the oriented aggregation of the above particles, and the profiles are very similar to those of the H$_2$Ti$_3$O$_7$ precursor, implying that the long-axis direction of the secondary microparticles is along the b axis. When the pH value is 1.0, in addition to many entangled amorphous particles, some well-faceted anatase TiO$_2$ nanocuboids about 170 nm in length were also observed, which formed hollow secondary square rodlike microparticles along the b-axis direction (Figure 3g,h). When the pH value continues to increase to 3 or above, larger well-defined anatase TiO$_2$ nanocuboids were observed, which also aggregated into hollow secondary square rodlike microparticles along the b-axis direction (Figure 3i–t). Based on the above discussion, we can see that the anatase TiO$_2$ nanoparticles are formed by the splitting of the square rodlike H$_2$Ti$_3$O$_7$ crystals, and the increase of the pH value of the solution can improve the crystallinity and crystal size of the nanoparticles (Figure 2) but has little effect on morphology. The effect of pH value on morphology is different from that previously reported. Generally speaking, the pH value in the reaction medium has an important effect on the crystal morphology of the resulting TiO$_2$. The strong acidic medium is in favor of the formation of rodlike rutile TiO$_2$. With the increase of the pH value, it is favorable to form rodlike, cuboid, rhombic, and spindle-shaped anatase TiO$_2$.

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images, and the corresponding fast Fourier transform (FFT) patterns of the specimens are shown in Figure 4. For the specimen prepared at pH 0.5, aggregation of rodlike, nanocuboid, and entangled amorphous anatase TiO$_2$ particles along the b axis were obtained (Figure 4a), as confirmed by the corresponding FESEM investigation of the pH 0.5-TiO$_2$ specimen (Figure 3e,f). Figure 4b exhibits the HRTEM image of a nanocuboid anatase TiO$_2$ crystal; the clear lattice fringes (0.190 nm) can be well assigned to the (200) facets of the anatase TiO$_2$ nanocrystals. The lateral plane of the nanocuboid anatase TiO$_2$ crystal is parallel to the (200) facings, indicating that the exposed crystal facets of the side is (200) facets, that is to say, the lateral plane exposed is {100} facets. This can also be confirmed by the corresponding fast FFT image (inset in Figure 4b); the observed angles of 28.3° and 42° are identical to the theoretical values for the angles between the (200) and (116) facets and those between the (116) and (1−16) facets, respectively. The HRTEM image (Figure 4c) of the nanocrystal clearly shows two types of nonparallel lattice fringes, and the measured lattice spacing of 0.167 and 0.190 nm of anatase TiO$_2$ confirmed the lattice distances of the anatase (211) and (200) planes, respectively. Further, the 28.3° angle between the (211) and (200) facets.

ACS Omega 2020, 5, 14147−14156 https://dx.doi.org/10.1021/acsomega.0c01827
Figure 3. FESEM images of (a,b) Na$_2$Ti$_3$O$_7$, (c,d) H$_2$Ti$_3$O$_7$, and the obtained anatase TiO$_2$ products (e,f) pH 0.5-TiO$_2$, (g,h) pH 1.0-TiO$_2$, (i,j) pH 3.0-TiO$_2$, (k,l) pH 5.0-TiO$_2$, (m,n) pH 7.0-TiO$_2$, (o,p) pH 9.0-TiO$_2$, (q,r) pH 11.0-TiO$_2$, and (s,t) pH 13.0-TiO$_2$.

Figure 4. TEM and HRTEM images of the anatase TiO$_2$ nanocrystals obtained from different pH values under hydrothermal conditions: (a–c) pH 0.5-TiO$_2$, (d–f) pH 3.0-TiO$_2$, (g–i) pH 7.0-TiO$_2$, (j–l) pH 13.0-TiO$_2$. The insets in (b,c,e,f,h,k,l) are the corresponding FFT patterns.
agrees with the calculated results from the lattice constants of anatase (Tetragonal crystal system, JCPDS 21-1272, \(I\bar{4}\_amd\), \(a = b = 0.37582\ nm, c = 0.95139\ nm\)). \(^3\) The FFT image (inset in the Figure 4c) taken from the nanoparticle exhibits a “single-crystal-like” diffraction, further confirming that the nanoparticle is a single nanocrystal. The TEM image shows that the as-obtained pH 3.0-TiO\(_2\) nanocrystals consist of a large amount of anatase TiO\(_2\) nanocuboids, with lengths ranging from 90 to 230 nm and widths ranging from 40 to 150 nm, respectively (Figure 4d). Figure 4e,f shows the corresponding HRTEM images of the marked area with red dotted boxes in Figure 4d. The lateral plane of the nanocuboids and irregular nanocrystals is {010} facets. It can be indexed to the dihedral planes (101) and (004) planes, respectively, and the angular difference between the (200) and (004) planes is 90°, which can stabilize the {001} facets by reducing the surface energy. Thus, anatase TiO\(_2\) nanocuboids with the coexposed {100}, {010}, and {001} facets were prepared in the presence of NH\(_4\)F by using a modified hydrothermal method.

Transformation Reaction Mechanism from Trititanate to Anatase TiO\(_2\) Nanocrystal.

The basic crystal structure units of H\(_2\)Ti\(_3\)O\(_7\) ribbons are \([\text{Ti}_3\text{O}_7\]\(^{2+}\) sheets that consist of three side-by-side aligned TiO\(_2\) octahedra, as shown in Figure 5. Three TiO\(_2\) octahedra are connected to each other by sharing the edges at one level to form a unit. The unit is connected with similar units located at the same level by sharing the corners. The periodic repetition of the above structure forms a single chain of TiO\(_2\) octahedra. Furthermore, the single chains at different levels are connected above and below by sharing additional apical edges, forming zigzag strings extending in the directions of the \(b\) axis, as well as the axis direction of the H\(_2\)Ti\(_3\)O\(_7\) ribbons. The zigzag strings are assembled into staggered sheets by sharing the corners of the TiO\(_2\) octahedra. The staggered sheets are stacked together in the \(c\) direction in the H\(_2\)Ti\(_3\)O\(_7\) ribbons, forming a layered framework. The H\(^+\) ions are located in the interlayers of the layered framework to balance the negative charge of the \([\text{Ti}_3\text{O}_7\]\(^{2-}\) sheets. During the hydrothermal process, the staggered \([\text{Ti}_3\text{O}_7\]\(^{2-}\) sheets are split into dispersed octahedral \([\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+}\) monomers by the dissolution reaction along the corner-shared and edge-shared oxygen. The transformation from the staggered \([\text{Ti}_3\text{O}_7\]\(^{2-}\) sheets to \([\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+}\) monomers can be described as follows:

\[
\begin{align*}
\text{H}_2\text{Ti}_3\text{O}_7 + 6\text{H}^+ + 11\text{H}_2\text{O} & \rightarrow 3[\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + 13\text{H}_2\text{O} \quad (1) \\
\text{H}_2\text{Ti}_3\text{O}_7 + 17\text{H}_2\text{O} & \rightarrow 3[\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + 6\text{OH}^- + 3\text{H}_2\text{O} \quad (2)
\end{align*}
\]

Subsequently, the dispersed octahedral \([\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+}\) monomers are combined together through oxolation or olation under hydrothermal conditions, forming different polymeric units of anatase, such as dimers, trimers, tetramers, and so forth. The different polymeric units nucleate at the reaction temperature to form the initial anatase nuclei. The transformation process can be expressed simply as follows:

\[
\begin{align*}
[\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + \text{TiO}_2 + 2\text{H}^+ + 4\text{H}_2\text{O} & \rightarrow [\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + 4\text{H}_2\text{O} \quad (3) \\
[\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + 2\text{OH}^- & \rightarrow \text{TiO}_2 + 6\text{H}_2\text{O} \quad (4)
\end{align*}
\]

Further, the initial anatase nuclei gradually grow into crystals during the continuous hydrothermal reaction. Many nanocuboids are gathered in a certain direction, leading to the formation of hollow anatase microtubes. The profile of the microtube is very similar to that of the H\(_2\)Ti\(_3\)O\(_7\) ribbons.
implying that the elongated direction of the microtube is along the $b$ axis. It should be noted here that the crystal phase and morphology in the present work are not dependent on the pH value of the solution, which is different from those reported in the literature.37

**Photocatalytic Activity of the Anatase TiO$_2$ Crystals with Dominant (100), (010), and (001) Facets.** The photocatalytic activity of the hollow square rodlike microparticles composed of anatase TiO$_2$ nanocrystals with the dominant [100], [010], and [001] facets synthesized in the present work and the benchmark P25–TiO$_2$ ($\sim$87% anatase and $\sim$13% rutile) was measured via bleaching of $8.35 \times 10^{-6}$ mol/L RB aqueous solution. The RB solution containing TiO$_2$ nanocrystals was performed for 2 days, so as to achieve better adsorption–desorption equilibrium of RB on the surface of TiO$_2$ nanocrystals. The adsorption values [mol(RB)/g(TiO$_2$)] of RB on the surface of TiO$_2$ nanocrystals were $6.5 \times 10^{-7}, 1.3 \times 10^{-6}, 8.5 \times 10^{-6}, 1.1 \times 10^{-5}$, and $7.5 \times 10^{-5}$ mol/g for the P25–TiO$_2$, pH 0.5-TiO$_2$, pH 3.0-TiO$_2$, pH 5.0-TiO$_2$, and pH 7.0-TiO$_2$ samples, respectively. These results indicated that the enhancement order of adsorption binding of RB to TiO$_2$ was P25–TiO$_2$ < pH 0.5-TiO$_2$ < pH 3.0-TiO$_2$ < pH 5.0-TiO$_2$ < pH 7.0-TiO$_2$ and that the strong anchoring of RB onto the surface of pH 0.5-TiO$_2$ could improve the photocatalytic activity.24

Figure 6a shows the UV–vis spectral changes of the centrifuged RB aqueous solution with pH 0.5-TiO$_2$ as the photocatalyst. It can be seen that the absorbance intensity of the visible region (390–780 nm) gradually decreased with the increase of UV irradiation time. Moreover, the adsorption peaks shifted from 554 to 552, 551, 550, 549, 548, and 547 nm at 0, 15, 30, 45, 60, 75, and 90 min, respectively. The movement of the adsorption peak position can be attributed to the de-ethylation of RB.11 Figure 6b shows the photocatalytic degradation activity plot of the as-prepared anatase TiO$_2$ nanocrystals with dominant high-energy facets and the benchmark P25–TiO$_2$ nanocrystals with a tiny proportion of the exposed [111] facets for the photodegradation of RB under UV light irradiation. It can be seen that the tested anatase TiO$_2$ nanocrystals and the commercial P25–TiO$_2$ nanocrystals exhibited a heterogeneous photocatalytic activity for the bleaching of the RB solution. Comparing the curves of the as-prepared anatase TiO$_2$ nanocrystals, the commercial P25–TiO$_2$, and the blank, one can find that the pH 0.5-TiO$_2$ nanocrystals exhibited improved degradation properties toward RB under UV light irradiation. The degradation efficiency of RB was as follows: pH 0.5-TiO$_2$ (76.0%) > pH 3.0-TiO$_2$ (68.0%) > pH 7.0-TiO$_2$ (63.5%) > pH 5.0-TiO$_2$ (51.5%) > P25–TiO$_2$ (48.1%) > the blank sample (8.5%). It needs to mention that the as-synthesized TiO$_2$ and the commercially available P25–TiO$_2$ cannot degrade RB completely, which is not because of the inactivation of the photocatalysts but because of more RB solution (250 mL), less photocatalyst (50 mg), and greater irradiation distance (25 cm). If the RB aqueous solution was given enough irradiation time, it should be able to be degraded completely. The pseudo-first-order kinetics equation and the corresponding photocatalytic rate constants of RB degradation were obtained by taking the experiment data of photocatalysis into $\ln(\frac{c_i}{c_f}) = kt$, as shown in Figure 6c,d. The degradation rate of pH 0.5-TiO$_2$ was the highest at $1.66 \times 10^{-2}$ min$^{-1}$, which was 1.3, 1.5, 2.0, 2.3, and 18.4 folds higher than that of pH 3.0-TiO$_2$ ($1.27 \times 10^{-2}$ min$^{-1}$), pH 7.0-TiO$_2$ ($1.11 \times 10^{-2}$ min$^{-1}$), pH 5.0-TiO$_2$ ($0.83 \times 10^{-2}$ min$^{-1}$), P25–TiO$_2$ ($0.73 \times 10^{-2}$ min$^{-1}$), and the blank sample (0.09 $\times 10^{-2}$ min$^{-1}$), respectively.

The photocatalytic activity of TiO$_2$ nanocrystals is influenced by many factors, for example, crystalline phase, heterogenous structure, exposed facets, crystal morphology, crystalline size, specific surface area, preparation method, and so forth.43,44 Among the four different polymorphs of TiO$_2$ (anatase, rutile, brookite, and TiO$_2$-B), the anatase phase has been considered to exhibit the most photoactive reactivity for the degradation of wastewater contaminated by organic dyes.10,11 Compared with the as-prepared anatase TiO$_2$ the commercially available P25–TiO$_2$ exhibited lower photo-
catalytic activity, although its heterojunction structure could improve the separation efficiency of the photogenerated electrons and photogenerated holes, indicating that the heterojunction structure is not the main reason for the improvement of photocatalytic efficiency in the present study.7 The pH 0.5-TiO2, pH 3.0-TiO2, pH 5.0-TiO2, and pH 7.0-TiO2 nanocrystals with cuboid morphology have a large proportion of coexposed {100}, {010}, and {001} facets on their surfaces according to the FESEM and TEM analyses; however, the commercial P25-TiO2 (~87% anatase and 13% rutile) nanocrystals have only a few exposed high-energy [111] facets. For anatase TiO2, the order of surface energy increase is {101} facets (0.44 J m⁻²) < {010} facets (or {100} facets) (0.53 J m⁻²) < {001} facets (0.90 J m⁻²) < {110} facets (1.09 J m⁻²) < {111} facets (1.61 J m⁻²).14,15 Because of the cooperative mechanism of the surface atomic structure and surface electronic structure, the obtained white Na2Ti3O7 specimens (15.0 g) were converted into an acid-exchanged form, H2Ti3O7.

### EXPERIMENTAL SECTION

**Preparation of Na₃Ti₃O₇ and H₂Ti₃O₇ Square Rods.** Layered sodium trititanate Na₃Ti₃O₇ was prepared by a conventional solid-phase reaction method.48 In a typical synthesis procedure, titanium dioxide (TiO₂, 98.5%, Tianjin Bodi Chemical Co., Ltd.) and sodium carbonate (Na₂CO₃, 99.0%, Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.) were mixed in a stoichiometric ratio according to the reaction Na₂CO₃ + 3TiO₂ → Na₃Ti₃O₇ + CO₂↑ and grinded in an agate mortar until mixed well. Then, the well-mixed powder (18.0 g) was placed in a corundum crucible and calcined in a high-temperature box furnace at 900 °C for 24 h with 5 °C/min heating rate. After cooling to room temperature, the obtained white Na₃Ti₃O₇ specimens (15.0 g) were treated with an aqueous solution of HCl (1.0 mol/L, 1.5 L) with continuous stirring for 72 h at ambient temperatures to be converted into an acid-exchanged form, H₂Ti₃O₇.

**Preparation of Anatase TiO₂ Crystals with Dominant (100), {010}, and {001} Facets.** The protonated trititanate square rods (1.0 g) and deionized water (60 mL) were added to eight Teflon-lined autoclaves (80 mL), respectively, and then the mixtures were stirred by a magnetic stirrer and adjusted to the set pH value (0.5–13.0) with different concentrations of HCl aqueous solution (0.5–3.0 mol/L) and NaOH aqueous solution (0.5–3.0 mol/L). After this, NH₄F (0.5 g) was added to the pH-adjusted H₂Ti₃O₇ suspension solutions and stirred at room temperature for 30 min. Subsequently, the autoclave was sealed and heated to 180 °C for 24 h in a constant-temperature blast drying oven. After the reaction is finished, the autoclaves were naturally cooled to room temperature, and the final products were separated from the solution by filtration, washed by deionized water, and dried at room temperature.

**Specimen Characterization.** The crystal structure of the obtained Na₃Ti₃O₇, H₂Ti₃O₇, and anatase TiO₂ specimens was examined by powder XRD (XRD-6100, Shimadzu, Kyoto, Japan) with monochromated Cu Kα radiation (λ = 0.15406 nm). The data were collected for scattering angles (2θ) from 5 to 80° with a scanning speed of 8°/min. The size and morphology of the specimens were observed using FESEM (FEI, Quanta FEG 250 FEI, America). The crystalline nanostructures were investigated using TEM, HRTEM, and FFT patterns (JEM-2100-F, JEOL, Japan). The specific surface area was determined by the Brunauer–Emmett–Teller method, using an automatic gas adsorption analyzer (Autosorb-IQ3, Quantachrome, America) by nitrogen gas adsorption. The UV–vis spectrophotometer (model TU-
Evaluation of Photocatalytic Activity. The photocatalytic performance of the as-prepared TiO₂ photocatalyst was evaluated by the photodegradation of RB (obtained from Sinopharm Chemical Reagent Co., Ltd.) in a self-assembled photochemical apparatus. A 50 mg of as-synthesized TiO₂ (pH 0.5-TiO₂, pH 1.0-TiO₂, pH 3.0-TiO₂, pH 5.0-TiO₂, and pH 7.0-TiO₂) photocatalyst and the best commercially available Degussa P25 TiO₂ (~87% anatase and ~13% rutile) photocatalyst were suspended in 250 mL of an aqueous solution containing 4 mg/L RB (8.35 × 10⁻⁶ mol/L) in a 300 mL quartz glass beaker. A 175 W low-pressure mercury lamp (with a peak emission at 365 nm, Shanghai Mingyao Glass Hardware Tools) was used as the analogue light source, and the dark adsorption experiment was performed for 2 days in the dark to reach the adsorption–desorption equilibrium before the above lamp was turned on, where the lamp was located 25 cm away from the surface of the RB solution. The irradiation area of the lamp is 56.7 cm² and the depth of the solution is 5.5 cm. Every 15 min, 5 mL of the suspension was removed from the quartz glass beaker and centrifuged at 2500 rpm for 5 min to remove the solid photocatalysts. Finally, the supernatant obtained was taken for the measurement of absorbance at λ = 544 nm using a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) with deionized water as the reference solution.

AUTHOR INFORMATION

Corresponding Authors

Yi-en Du — School of Chemistry & Chemical Engineering, Jinzhou University, Jinzhou 030619, China; Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China; Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, Takamatsu-shi 761-0396, Japan; orcid.org/0000-0002-3718-3052; Phone: +86-351-398-5766; Email: duyfij@gmail.com

Changdong Chen — College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China; Email: chendc1984@gmail.com

Xiaojing Yang — Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China; orcid.org/0000-0003-3620-3507; Phone: +86-10-5880-2075, +86-10-5880-2960; Email: yang.xiaojing@bnu.edu.cn

Authors

Xianjun Niu — School of Chemistry & Chemical Engineering, Jinzhou University, Jinzhou 030619, China
Jing He — School of Chemistry & Chemical Engineering, Jinzhou University, Jinzhou 030619, China
Leng Liu — School of Chemistry & Chemical Engineering, Jinzhou University, Jinzhou 030619, China
Yufang Liu — School of Chemistry & Chemical Engineering, Jinzhou University, Jinzhou 030619, China
Qi Feng — Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, Takamatsu-shi 761-0396, Japan; orcid.org/0000-0002-5197-4644

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01827

Author Contributions

The paper was written through the contributions of all authors. All authors have given approval to the final version of the paper.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Applied Basic Research Project of Shanxi (no. 201901D111303), the Doctor Research Funds of Jinzhou University, the Shanxi “1331 Project” Key Innovation Team (no. PY201817), the Jinzhou University “1331 Project” Key Innovation Team (nos. jxzyxt2017004 and jxzyxt2019005), Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (no. 2019L0881), the Educational Department of Liaoning Province (no. L2019036), the Liaoning Provincial Natural Science Foundation (no. 20170540583), the National Science Foundation of China (nos. 51272030 and 51572031), and the Grants-in-Aid for Scientific Research (B) (no. 26289240) from the Japan Society for the Promotion of Science and Kagawa University.

REFERENCES

(1) Xu, H.-Q.; Hu, J. H.; Wang, D. K.; Li, Z. H.; Zhang, Q.; Luo, Y.; Yu, S.-H.; Jiang, H.-L. Visible-light photocatalytic reduction of CO₂ in a metal-organic framework: boosting electron-hole separation via electron trap states. J. Am. Chem. Soc. 2015, 137, 13440–13443.
(2) Cao, F.; Xiong, J.; Wu, F.; Liu, Q.; Shi, Z.; Yu, Y.; Wang, X.; Li, L. Enhanced photoelectrochemical performance from rationally designed anatase/rutile TiO₂ heterostructures. ACS Appl. Mater. Interfaces 2016, 8, 12239–12245.
(3) Zhang, T.; Oyama, T.; Aoshima, A.; Hida, H.; Zhao, J.; Serpone, N. Photooxidative N-Demethylation of methylene blue in aqueous TiO₂ dispersions under UV irradiation. J. Photochem. Photobiol., A 2001, 140, 163–172.
(4) Yan, Y.; Yang, H.; Yi, Z.; Xian, T.; Li, R.; Wang, X. Construction of Ag₂S@CaTiO₃ heterostructure photocatalysts for enhanced photocatalytic degradation of dyes. Desalin. Water Treat. 2019, 70, 349–360.
(5) Wei, X.-X.; Cui, B.; Wang, X.; Cao, Y.; Gao, L.; Guo, S.; Chen, C.-M. Tuning the physiochemical property of BiOBr via solvent adjustment: Towards an efficient photocatalyst for water treatment. CrystEngComm 2019, 21, 1750–1757.
(6) Yan, Y.; Yang, H.; Yi, Z.; Wang, X.; Li, R.; Xian, T. Evolution of Bi nanowires from BiOBr nanoplates through a NaBH₄ reduction method with enhanced photodegradation performance. Environ. Sci. Eng. 2020, 37, 64–77.
(7) Liao, Y.; Que, W.; Jia, Q.; He, Y.; Zhang, J.; Zhong, P. Controllable synthesis of brookite/anatase/rutile TiO₂ nanocomposites and single-crystalline rutile nanorods array. J. Mater. Chem. 2012, 22, 7937–7944.
(8) Wu, W.; Zhu, J.; Deng, Y. H.; Xiang, Y.; Tan, Y. W.; Tang, H. Q.; Zou, H.; Xu, Y. F.; Zhou, Y. TiO₂ nanocrystals with the [001] and [101] facets co-exposed with MIL-100(Fe): an egg-like composite nanomaterial for efficient visible light-driven photocatalysis. RSC Adv. 2019, 9, 31728–31734.
(9) Liu, J.; Liu, B.; Ren, Y.; Yuan, Y.; Zhao, H.; Yang, H.; Liu, S. Hydrogenated nanotubes/nanowires assembled from TiO₂ nanoflakes with exposed {111} facets: excellent phoyo-catalytic CO₂ reduction activity and charge separation mechanism between (111) and (100) facets. J. Mater. Chem. A 2019, 7, 14761–14775.
(10) Liu, B.; Khare, A.; Aydil, E. S. TiO₂-B/anatase core-shell heterojunction nanowires for photocatalysis. ACS Appl. Mater. Interfaces 2011, 3, 4444–4450.
(11) Liu, X.; Li, Y.; Deng, D.; Chen, N.; Xing, X.; Wang, Y. A one-step nonaqueous sol-gel route to mixed-phase TiO2 with enhanced photocatalytic degradation of Rhodamine B under visible light. *CrystEngComm* 2016, 18, 1964–1975.

(12) Chen, T.; Bao, L.; Zheng, Y.; Yang, X.; Ruan, L.; Liu, Y.; Xu, G.; Han, G. Hydrothermal synthesis of perovskite CaTiO3 tetragonal microrods with vertical V-type holes along the [010] direction. *CrystEngComm* 2019, 21, 4761–4770.

(13) Yang, Z.; Wang, B.; Gu, H.; An, H.; Pan, Y.; Zhai, J. Synthesis of crystal-controlled TiO2 nanorods by a hydrothermal method: rutile and brookite as highly active photocatalysts. *J. Phys. Chem. C* 2015, 119, 16905–16912.

(14) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. Synthesis of titania nanosheets with a high percentage of exposed {001} facets and related photocatalytic properties. *J. Am. Chem. Soc.* 2009, 131, 3122–3135.

(15) Xu, H.; Reusch, P.; Ouyang, S.; Tong, H.; Umezawa, N.; Kako, T.; Ye, J. Anatase TiO2 single crystals exposed with high-reactive {111} facets toward efficient H2 evolution. *Chem. Mater.* 2013, 25, 405–411.

(16) Yang, H. G.; Sun, C. H.; Qiao, S. Z.; Zou, J.; Liu, G.; Smith, S. C.; Zou, J.; Cheng, H. M.; Lu, G. Q. Solvothermal synthesis and photoreactivity of anatase TiO2 nanosheets with dominant {001} facets. *J. Am. Chem. Soc.* 2009, 131, 4078–4083.

(17) Liu, M.; Li, H.; Zeng, Y.; Huang, T. Anatase TiO2 single crystals with dominant {001} facets: Facile fabrication from Ti powders and enhanced photocatalytic activity. *Appl. Surf. Sci.* 2013, 274, 117–123.

(18) Li, B.; Zhao, Z.; Gao, F.; Wang, X.; Qiu, J. Mesoporous microcrystals composed of carbon-coated TiO2 nanocrystals with exposed {001} facets for improved visible light photocatalytic activity. *Appl. Catal. B Environ.* 2014, 147, 958–964.

(19) Ye, L.; Mao, J.; Liu, J.; Yang, Z.; Peng, T. Y.; Zan, L. Synthesis of anatase TiO2 mncrystals with [101], [010] or [001] single facets of 90% level exposure and liquid-phase photocatalytic reduction and oxidation activity orders. *J. Mater. Chem. A* 2013, 1, 10532–10537.

(20) Pan, J.; Wu, X.; Wang, L.; Liu, G.; Lu, G. Q.; Cheng, H.-M. Synthesis of anatase TiO2 rods with dominant reactive [010] facets for the photoreduction of CO2 to CH4 and use in dye-sensitized solar cells. *Chem. Commun.* 2011, 47, 8361–8363.

(21) Zhao, J.; Zou, X.; Su, J.; Wang, P.-P.; Zhou, L.-J.; Li, G.-D. Synthesis and photocatalytic activity of porous anatase TiO2 microcrystals composed of {010}-faceted nanobelts. *Dalton Trans.* 2013, 42, 4365–4368.

(22) Wen, P.; Xue, M.; Ishikawa, Y.; Itoh, H.; Feng, Q. Relationships between cell parameters of dye-sensitized solar cells and dye-adsorption parameters. *ACS Appl. Mater. Interfaces* 2012, 4, 1928–1934.

(23) Du, Y.-E.; Feng, Q.; Chen, C.; Tanaka, Y.; Yang, X. Photocatalytic and dye-sensitized solar cell performances of {010}-faceted and [111]-faceted anatase TiO2 nanocrystals synthesized from tetratitanated nanoribbons. *ACS Appl. Mater. Interfaces* 2014, 6, 16007–16019.

(24) Chen, C.; Xu, L.; Sewandi, G. A.; Kusunose, T.; Tanaka, Y.; Nakanishi, S.; Feng, Q. Microwave-assisted topochemical conversion of layered titania nanosheets to [010]-faceted anatase nanocrystals for high performance photocatalysis and dye-sensitized solar cells. *Cryst. Growth Des.* 2014, 14, 5801–5811.

(25) Du, Y.-E.; Du, D.; Feng, Q.; Yang, X. Delithiation, exfoliation, and transformation of rock-salt-structured Li2TiO3 to highly exposed {010}-faceted anatase. *ACS Appl. Mater. Interfaces* 2015, 7, 7995–8004.

(26) Du, Y.-E.; Bai, Y.; Liu, Y.; Guo, Y.; Cai, X.; Feng, Q. One-pot synthesis of [111]-/[010] facets coexisting anatase nanocrystals with enhanced dye-sensitized solar cell performances. *ChemistrySelect* 2016, 1, 6632–6640.

(27) Du, Y.-E.; Niu, X.; Li, W.; An, J.; Liu, Y.; Chen, Y.; Wang, P.; Yang, X.; Feng, Q. Microwave-assisted synthesis of high-energy facets TiO2 nanocrystals derived from exfoliated porous metal-organic acid nanosheets with improved photocatalytic and photovoltaic performance. *Materials* 2019, 12, 3614.

(28) Du, Y.-E.; Bai, Y.; Liu, Y.; Guo, Y.; Cai, X.; Feng, Q. Synthesis of anatase TiO2 nanocrystals with defined morphologies from exfoliated nanoribbons: photocatalytic performance and application in dye-sensitized solar cell. *ChemistrySelect* 2019, 4, 4443–4457.

(29) Zhao, X.; Jin, W.; Cai, J.; Ye, J.; Li, Z.; Ma, Y.; Xie, J.; Qi, L. Shape- and size-controlled synthesis of uniform anatase TiO2 nanocuboids enclosed by active {100} and {001} facets. *Adv. Funct. Mater.* 2011, 21, 3554–3563.

(30) Zhong, Z.; Huang, B.; Lu, J.; Qin, X.; Zhang, X.; Dai, Y. Hierarchical TiO2 microspheres: synergic effect of {001} and {101} facets for enhanced photocatalytic activity. *Chem.—Eur. J.* 2011, 17, 15032–15038.

(31) Niu, X.; Du, Y.-E.; Liu, Y.; Qi, H.; An, J.; Yang, X.; Feng, Q. Hydrothermal synthesis and formation mechanism of the anatase TiO2 nanocrystals with co-exposed highenergy {001}, {010} and [111]-facets for enhanced photocatalytic performance. *RSC Adv.* 2017, 7, 24616–24627.

(32) Zhang, H.; Wang, W.; Zhao, H.; Zhao, L.; Gan, L.-Y.; Guo, L.-H. Facet-mediated interaction between humic acid and TiO2 nanoparticles: implications for aggregation and stability kinetics in aquatic environments. *Environ. Sci.: Nano* 2019, 6, 1754–1764.

(33) Han, S. N.; Niu, Q. Y.; Qin, N.; Guo, X. T.; Zhang, Y.-N.; Zhao, G. H. In-situ growth of M-[001]TiO2/Ti photodeleterio: synergic dominated {001} facet and ratio-optimally surface junctions for effective oxidation of environment pollutants. *Chem. Commun.* 2020, 56, 1337–1340.

(34) Du, Y.-E.; Bai, Y.; Liu, Y.; Guo, Y.; Cai, X.; Feng, Q. Synthesis of anatase TiO2 nanocrystals with defined morphologies from exfoliated nanoribbons: photocatalytic performance and application in dye-sensitized solar cell. *ChemistrySelect* 2019, 4, 4443–4457.

(35) Howard, C. J.; Sabine, T. M.; Dickson, F. Structural and thermal parameters for rutile and anatase. *Acta Crystallogr. B* 1991, 47, 462–468.

(36) Feng, J.; Yin, M.; Wang, Z.; Yan, S.; Wan, L.; Li, Z.; Zou, Z. Facile synthesis of anatase TiO2 mesocrystal sheets with dominant {001} facets based on topochemical conversion. *CrystEngComm* 2010, 12, 3425–3429.

(37) Ong, W.-J.; Tan, L.-L.; Chai, S.-P.; Yong, S.-T.; Mohamed, A. R. Highly reactive [001] facets of TiO2-based composites: synthesis, formation mechanism and characterization. *Nanoscale* 2014, 6, 1946–2008.

(38) Liu, J.; Olds, D.; Peng, R.; Yu, L.; Foo, G. S.; Qian, S.; Keum, J.; Guitton, B. S.; Wu, Z.; Page, K. Quantitative analysis of the morphology of [010] and [001] faceted anatase TiO2 nanocrystals and its implication on photocatalytic activity. *Chem. Mater.* 2017, 29, 5591–5604.

(39) Li, J.-G.; Ishigaki, T.; Sun, X. Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: phase-selective synthesis and physicochemical properties. *J. Phys. Chem. C* 2007, 111, 4969–4976.
(44) Zhang, H.; Liu, P.; Li, F.; Liu, H.; Wang, Y.; Zhang, S.; Guo, M.; Cheng, H.; Zhao, H. Facile fabrication of anatase TiO₂ microspheres on solid substrates and surface crystal facet transformation from {001} and {100}. Chem. Eur J. 2011, 17, 5949−5957.

(45) Pan, J.; Liu, G.; Lu, G. Q. M.; Cheng, H.-M. On the true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO₂ crystals. Angew. Chem. Int. Ed. 2011, 50, 2133−2137.

(46) Sitthisang, S.; Komarneni, S.; Tantirungrotechai, J.; Dong Noh, Y.; Li, H.; Yin, S.; Sato, T.; Katsuki, H. Microwave-hydrothermal synthesis of extremely high specific surface area anatase for decomposing NOx. Ceram. Int. 2012, 38, 6099−6105.

(47) Hu, D.; Zhang, W.; Tanaka, Y.; Kusunose, N.; Peng, Y.; Feng, Q. Mesocrystalline nanocomposition of TiO₂ polymorphs: Topochemical mesocrystal conversion, characterization, and photocatalytic response. Cryst. Growth Des. 2015, 15, 1214−1225.

(48) Izawa, H.; Kikkawa, S.; Koizumi, M. Ion exchange and dehydration of layered titanate, Na₂Ti₃O₇ and K₂Ti₄O₉. J. Phys. Chem. 1982, 86, 5023−5026.