Ultrathin Anatase TiO₂ Nanosheets Dominated with {001} Facets: Thickness-Controlled Synthesis, Growth Mechanism, and Water-Splitting Properties†

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Ultrathin anatase TiO₂ nanosheets with dominant {001} facets (~82%) and controllable thickness (1.6–2.7 nm) were firstly synthesized by using a modified one-pot hydrothermal route. As a morphology controlling agent, the concentration of hydrofluoric acid has significant impact on the thickness of the as-synthesized TiO₂ nanosheets. In addition, according to the XRD patterns and TEM images of the products on different reaction stages, the growth process of TiO₂ nanosheets was clarified for the first time. We further measured the efficiency for H₂ evolution of the ultrathin anatase TiO₂ nanosheets loaded with 1 wt % Pt from photochemical reduction of water in the presence of methanol as a scavenger. The TiO₂ nanosheets exhibited a H₂ evolution rate as high as 7381 $\mu mol \cdot h^{-1} \cdot g^{-1}$ under UV-visible light irradiation, attributing to their exposed reactive {001} facets and high crystallinity.

1. Introduction

Owing to their importance for technological applications and fundamental research, tailored synthesis of anatase TiO₂ nanocrystals has been widely investigated during the past decades.[1-6] Unfortunately, due to the minimization of surface energy during the process of crystal growth, most available anatase TiO₂ nanocrystals were dominated by the thermodynamically stable {101} facets other than the more reactive {001} facets (0.90 J/m^2 for {001} > 0.53 J/m^2 for {100} > 0.44 J/m^2 for {101}).[7-11] Recently, by using hydrofluoric acid (HF) as a capping agent, Yang et al. successfully synthesized anatase TiO₂ single crystals with a large percentage of reactive {001} facets.[12] After that, various reaction systems and capping agents have been exploited to achieve TiO₂ with exposed {001} facets.[13-18] For instance, by hydrothermal reaction of tetrabutyl titanate and hydrofluoric acid, Han et al. synthesized nano-sized sheet-like anatase TiO₂ with up to 89% of {001} facets, which showed superior photocatalytic performance.[14a] Nevertheless, most research involved pure anatase TiO₂ dominated with {001} facets mainly focused on the synthetic chemistry of the products and

their application in photocatalytic degradation. Very few research was carried out to intensively investigate the optical spectroscopy characteristics as well as their applications in hydrogen evolution driven by water-splitting.[15-18]

Recently, one breakthrough has been made to prepare angstrom-sized one dimensional (1D) anatase atomic wires, which motivated us to fabricate ultrathin two dimensional (2D) anatase TiO₂ nanosheets with large percentage of highly reactive {001} facets due to their exciting photoactivity and potential industrial applications.[19] However, how to obtain an ultrathin, 2D sheet-like anatase TiO₂ single crystal is quite challenging because of the exposed unstable {001} facets. To the best of our knowledge, the thickness of available anatase TiO₂ single crystals with dominant {001} facets are all larger than 5 nm, which is quite different from the Bohr radius (~2.0 nm) of anatase TiO₂.

Herein, we prepared ultrathin anatase TiO₂ nanosheets with dominant highly reactive {001} crystal facets *via* a modified one-step hydrothermal route. By simply adjusting the reaction parameters such as HF concentration and reaction temperature, the thickness of TiO₂ nanosheets can be subtly tailored in the range of 1.6–2.7 nm. Furthermore, attributed to the intrinsic high percentage of reactive {001} facets and small size, such TiO₂ nanosheets exhibited high efficiency for splitting water into hydrogen under UV-visible light irradiation. Growth mechanism of the ultrathin anatase TiO₂ nanosheets was also investigated through analyzing the early stage products.

2. Experimental section

2.1 Materials preparation

The synthesis of ultrathin anatase TiO₂ nanosheets was carried out by a modified hydrothermal method.[14] Tetrabutyl titanate (Ti(OBu)₄, 98%, Aldrich) and hydrofluoric acid (HF, 48%, Sigma-Aldrich) were all used as received without

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† Electronic Supplementary Information (ESI) available: TEM images and XRD patterns of the samples on different reaction stages; UV-visible absorption spectra of the synthesized anatase TiO₂ nanosheets with various thickness; XPS spectra of TiO₂ nanosheets before and after NaOH treatment. See DOI: 10.1039/b000000x/

further purification. ***Caution: Hydrofluoric acid (HF) is extremely corrosive and toxic and it should be handled with extreme care! Hydrofluoric acid solution should be stored in plastic containers and used in fume hood.*** In a typical experiment, 5 mL of Ti(OBu)$_4$ was injected into a dried Teflon-lined stainless steel autoclave with a capacity of 50 mL. Then 0.4–0.6 mL of HF solution was dropped into the above liquid slowly. After sealed in fume hood, the autoclave was heated to 160–180 ℃ and kept for 24 h in an electric oven. After reaction, the white precipitate was separated by using a centrifugation method. Then the products were washed thoroughly with absolute ethanol, 0.1 M NaOH aqueous solution and deionized water for at least 3 times to remove the residual contamination and fluorine species absorbed. After dried at 80 ℃ in vacuum overnight, TiO$_2$ nanosheets with clean surface were harvested. Generally, the average yield of anatase TiO$_2$ nanosheets can reach approximately 80% (mole ratio of the obtained TiO$_2$ to the injected Ti(OBu)$_4$).

For comparison, TiO$_2$ nanosheets with a thickness of 5 nm were synthesized as reported previously.[14] Moreover, to investigate the growth mechanism of TiO$_2$ nanosheets with dominant {001} facets, products on different reaction stages were prepared by heating the mixtures containing 5 mL of Ti(OBu)$_4$ and 0.4 mL of HF at 160 ℃ for different time.

2.2 Materials characterization

X-ray diffraction (XRD) patterns of the samples were obtained by using a Bruker D8 advanced X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). Morphology and crystal structure were determined by transmission electron microscopy (TEM) (JEOL, JEM2100) with an acceleration voltage of 200 kV. Chemical compositions of anatase TiO$_2$ nanosheets were analyzed with X-ray photoelectron spectroscopy (XPS). All binding energies were referenced to the C1s peak (285 eV) arising from adventitious carbon. Raman spectra were recorded on a Renishaw InVia Reflex Raman system equipped with a 785-nm diode laser as excitation source. UV-visible absorption spectra were obtained on Cary 500 UV-visible recording spectrophotometer (Varian) with an integrating sphere. For TEM analysis, samples were dispersed in ethanol and dropped on a carbon-coated copper grid. For XRD, XPS, UV-visible absorption and Raman analysis, all of the samples were prepared by drying the resulting precipitates in vacuum overnight at 80 ℃.

2.3 Measurements of hydrogen evolution

In this work, the rate of hydrogen generation from water splitting was measured to evaluate the photocatalytic activity of the TiO$_2$ nanosheets loaded with 1 wt % Pt. Pt loading was conducted by impregnating the as-synthesized TiO$_2$ nanosheets in an aqueous H$_2$PtCl$_6$•6H$_2$O solution, which was prepared by dissolving 1 g of H$_2$PtCl$_6$•6H$_2$O to 1 L of water. Typically, 50 mg of as-synthesized TiO$_2$ powder and 1.32 mL of aqueous H$_2$PtCl$_6$•6H$_2$O solution were added into an evaporating dish and dispersed in ultrasonic bath for 30 min. Then, the suspension was evaporated at 60 ℃ in vacuum for

10 h. After that, the resulting dried light yellow powder was collected and heated in air at 200 ℃ for 1 h. Finally, Pt/TiO$_2$ photocatalyst was obtained and kept for activity measurement.

Water splitting reactions were performed on a top-irradiation vessel connected to a closed gas circulation system with a flow of cooling water during the reaction. Generally, 15 mg of Pt/TiO$_2$ powder was dispersed in 100 mL of aqueous solution containing 10% of methanol in volume. The reaction was carried out at room temperature. The employed light source was a 300W Xe lamp (PLS-SXE300, Beijing Trusttech Co. Ltd) with the wavelength of 220–770 nm. The amount of H$_2$ evolved was determined with an on-line gas chromatograph.

2.4 Computational details

To investigate the effect of thickness on the electronic structures, the density of states (DOS) of ultrathin anatase TiO$_2$ sheets with various thicknesses have been calculated. Spin-polarized DFT calculations were performed within the generalized-gradient approximation (GGA).[20] TiO$_2$ sheets were modeled by the 1×l unit cell. Crystal parameters were fixed to experimental values. All calculations were carried out using the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE),[21] based on the numerical double-numerical polarization (DNP) basis set, which has been implemented in the Dmol3 modules.[22] During the calculations, the energy tolerance for self-consistent field iterations was set as 1.0×10^{-6} Ha. Testing indicated that k-space sampling with a 11×11×l Monkhorst-Pack grid was adequate for the present purpose and feasible to give the size of our systems. Thermal smearing (0.005 Ha) was also employed to speed up the convergence of the SCF procedure by allowing orbitals to relax more rapidly.

3. Results and discussion

Fig. 1 XRD patterns of the as-synthesized TiO$_2$ nanosheets derived from hydrothermal reaction of the mixtures: (a) 0.6 mL of HF and 5 mL of Ti(OBu)$_4$, and (b) 0.4 mL of HF and 5 mL of Ti(OBu)$_4$, respectively. The reaction temperature for both samples is 160 ℃. JCPDS No. 21-1272 is used as a reference of bulk anatase TiO$_2$.

Anatase TiO$_2$ nanosheets with a thickness ranging from 1.6-2.7 nm were obtained by adjusting the concentration of HF in the reaction media. The crystallographic structure of the resulting products was examined by XRD. As shown in Fig.

1a and 1b, four main diffraction peaks at 2θ of 25.8°, 37.7°, 47.8° and 55.0°, are corresponding to the (101), (004), (200) and (211) crystal face of anatase TiO_2 (space group $I4_1/amd$). Meanwhile, there is no observable diffraction peaks at 27° or 31°, indicating that all of the samples were free of rutile and brookite impurities. Compared to the standard pattern of anatase TiO_2 (JCPDS No. 21-1272), it can be concluded that the samples synthesized under different conditions are all in pure anatase phase. It should be noted that the XRD pattern of TiO_2 synthesized by using 0.6 mL of HF (Fig. 1a) shows a similar diffraction intensity to the calculated values of bulk anatase TiO_2. However, by decreasing the amount of HF used from 0.6 mL to 0.4 mL while keeping all the other synthetic parameters unchanged, a notable broadening and intensity decreasing of the diffraction peaks appeares in the XRD pattern of the synthesized TiO_2 (Fig. 1b). The diffraction peak of (001) nearly disappears. These differences in XRD patterns discussed above imply the possibility of the structural changes such as reduction in the size on [001] crystallographic direction as well as the crystallinity of the as-prepared TiO_2 samples.

Transmission electron microscopy (TEM) images (Fig. 2) show morphology and crystal structure of the as-synthesized anatase TiO_2 nanosheets. As shown in Fig. 2a, anatase TiO_2 nanosheets have a well-defined rectangular shape with a sidelength of 25 nm and thickness of 2.7 nm averagely. High-resolution transmission electron microscopy (HRTEM) image (Fig. 2b) of a free standing nanosheet shows that the lattice spacing is ca. 0.189 nm, corresponding to (200) or (020) planes of anatase TiO_2. Meanwhile, the HRTEM image in Fig. 2c demonstrates the lattice spacing of 0.235 nm, corresponding to (001) planes of anatase TiO_2. Based on these structural analyses, it can be concluded that the prepared anatase TiO_2 nanosheets shown in Fig. 2 are dominated by {001} facets and their percentage is estimated to be 82% statistically. As indicated by the white arrow heads in Fig. 2c, the perfect oriented attachment between highly reactive {001} facets can be found.

Fig. 3 TEM (a), HRTEM (b-c) images and corresponding structure model (d) of TiO_2 nanosheets synthesized by using 0.4 mL of HF and 5 mL of Ti(OBu)$_4$ at 160 ℃.

Anatase TiO_2 nanosheets with a smaller thickness can also be prepared by adjusting the concentration of HF in the

Fig. 2 TEM (a) and corresponding HRTEM (b-c) images of TiO_2 nanosheets prepared by using 0.6 mL of HF and 5 mL of Ti(OBu)$_4$ at 160 ℃.

reaction medium. Figs. 3a-c illustrate the typical TEM/HRTEM images of the anatase TiO_2 nanosheets obtained by hydrothermal reaction of 0.4 mL of HF and 5 mL of $Ti(OBu)_4$ at 160 ℃. Similar to the anatase TiO_2 nanosheets shown in Fig. 2, the resulting TiO_2 also consists of sheet-shaped nanostructures (Fig. 3a). In the HRTEM images (Figs. 3b-c), each distinguishable TiO_2 nanosheet was dotted with white dash lines and has a sidelength of 11 nm and thickness of only 1.6 nm. Therefore the percentage of {001} is estimated to be 77%. Nevertheless, if observed along the [001] direction, the shape of the resulting nanosheets is irregular. This phenomenon is quite reasonable because the thickness of the anatase TiO_2 nanosheets is only 1.6 nm (Fig. 3c) and the {101} facets were not fully developed in this case. Corresponding ball-and-stick model for the structure of anatase TiO_2 nanosheets is also given in Fig. 3d, which clearly demonstrates that the nanosheet only contains two layers of anatase crystal units along the [001] crystallographic direction.

Thus ultrathin TiO_2 nanosheets dominated with reactive {001} facets were achieved by a modified hydrothermal method. Correlating the XRD patterns and TEM images with the synthetic parameters of the ultrathin TiO_2 nanosheets, it can be found that the concentration of HF has significant effects on their thickness and crystallinity. Reduction of the concentration of HF helps to decrease the crystal size and crystallinity of the product, which is also consistent with the changes of diffraction peaks of the XRD patterns shown in Fig. 1.

Fig. 4 Schematic diagram of growth mechanism of TiO_2 nanosheets dominated by {001} facets.

To study the growth mechanism of the ultrathin TiO_2 nanosheets dominated with highly reactive {001} facets, samples with different reaction time (t_R) were prepared. TEM images (Fig. S1) and corresponding XRD results (Fig. S2) illustrate the morphologies and crystal phase of the samples synthesized with t_R = 0.5, 2.3 and 6 h, respectively. As depicted in the TEM image (Fig. S1a), only fluffy TiO_2 species can be observed at the early stage of the reaction (t_R = 0.5 h). With a longer reaction time (t_R = 2.3 h), abundant small particles and some ultrathin fibrous nanostructures were produced (Fig. S1b). When the reaction time was further extended to 6 h, the amount of the fibrous nanostructures increased dramatically and some nanosheets appeared. Finally, when the reaction time reached 24 h, the products composed of sheet-shaped materials were achieved (Fig. 3). Furthermore, the corresponding XRD patterns (see Fig. S2) indicate that all of the products can be attributed to pure anatase TiO_2. Therefore, on the basis of the gradual changes in the morphology, crystal growth of the TiO_2 nanosheets was supposed to be a Ostwald ripening process. Moreover, based on the morphology changes illustrated in Fig. 2, Fig. 3, and Fig. S1, it can be concluded that the early products of 2D ultrathin anatase TiO_2 nanosheets are quite irregular and the sizes are also not uniform (as schemed in Fig. 4a). Then these anatase TiO_2 nanosheets gradually develop into quosi-square morphology through the inter- or intra-particle Ostwald ripening process (Fig. 4b). At the end, when the reaction time reach 24 h, uniform well-faceted TiO_2 nanosheets with dominant {001} facets can be achieved (Fig. 4c). It should be noted that at the early stage of the crystal growth, nuclei formed through the hydrolysis of $Ti(OBu)_4$ in the presence of hydrofluoric acid and the subsequent condensation polymerization of linked Ti-O-Ti. Due to the high concentration of F ions in the reaction system, the surfaces of these crystal nuclei were totally surrounded by F atoms and thus the percentage of {001} facets can be as high as 100%, which was explored theoretically in our previous work.[12]

Fig. 5 Calculated DOS for anatase TiO_2 naosheets with different thickness. The numbers are the thickness in unit of nm.

For semiconducting materials, when the size on one specific crystallographic direction decreases to Bohr radius (around 2.0 nm for anatase TiO_2), quantum effects and surface properties become critical and new properties emerge. In this work, UV-visible absorption spectra and Raman spectra were examined to illustrate more structural and spectral characteristics of the ultrathin TiO_2 nanosheets. UV-visible absorption spectra of the synthesized anatase TiO_2 nanosheets (Fig. S3) with different thickness indicate that even though there is no notable difference for light absorption edge which locate around 380 nm, absorption intensity within ultraviolet region ranging from 200 nm to 380 nm are decreasing with the thickness, indicating the high transparency for anatase TiO_2 nanosheets with a thickness of 1.6 nm. Derived from the cutoff wavelength of the light absorbed, the band gap of the obtained anatase TiO_2 nanosheets was estimated to be 3.23 eV, which is nearly identical to that of pure bulk anatase TiO_2. This means that the intrinsic band gap of the TiO_2 sheets have not changed significantly even though the thickness of the TiO_2 nanosheets decreased to as low as 1.6 nm, which can be explained by the insignificant quantum effects of 2D semiconducting materials. These experimental findings are also highly consistent with the theoretical predictions well,

which are shown in Fig. 5. Based on the calculations, it can be derived easily that for the 2D ultrathin anatase TiO_2 nanosheets, the size effect is not so obvious for the electronic structures and bandwidth shows no change even though the nanosheets are as thin as around 1.0 nm. That is, the quantum effects which can change the band gap of anatase TiO_2 materials should rarely occur.[23]

Fig. 6 Raman spectra of TiO_2 nanosheets with thickness of (a) 1.6 nm, (b) 2.7 and (c) 5.0 nm, respectively.

Raman spectroscopy was also applied to examine the crystal phase of anatase TiO_2 nanosheets. Bulk anatase TiO_2 has a tetragonal structure (space group *I41/amd*) containing twelve atoms per unit cell with lattice parameters $a = 3.784$ Å and $c = 9.514$ Å. According to factor group analysis, anatase has six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$). As reported by Ohsaka,[24] Raman spectrum of anatase single crystal has six modes appearing at 144 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}), and 639 cm^{-1} (E_g). Fig. 6 shows the Raman spectra of three types of TiO_2 nanosheets with various thicknesses ranging from 1.6–5.0 nm. Raman peaks at around 142, 394, 512 and 634 cm^{-1} in Fig. 6 can be assigned to those of bulk anatase TiO_2. This conclusion is also consistent with XRD results shown in Fig. 1. However, it can be clearly seen that the peak broadening and Raman shift occur as the thickness of the anatase TiO_2 changes to 2.7 or 1.6 nm. Compared to the Raman spectrum of 5 nm-thick TiO_2 (Fig. 6c), no significant shift for all of the Raman modes can be observed in 2.7 nm-thick TiO_2 nanosheets while the band broadening occurs (Fig. 6b). This difference in Raman spectra can be attributed to the effect of smaller particle size along the [001] crystallographic direction. As to the ultrathin TiO_2 nanosheets with a thickness of only 1.6 nm, E_g vibrational mode (142 cm^{-1}) shifts into a higher wavenumber and the Raman peaks at 197 cm^{-1} disappear (Fig. 6a). Meanwhile, both of the A_{1g} mode and E_g mode (634 cm^{-1}) shift into lower wavenumbers. All of these differences in Raman spectra can also be attributed to the effect of smaller particle size and the resulting variation of the force constant.[25]

To evaluate the photoactivity of the as-synthesized ultrathin anatase TiO_2 nanosheets dominated by {001} facets, we measured the efficiency of hydrogen evolution for the resulting products loaded with 1 wt % of Pt. Prior to Pt-loading, TiO_2 nanosheets was washed thoroughly by 0.1M NaOH aqueous solution and deionized water to remove the F atoms absorbed on the surface. From the XPS spectra (See Fig. S4), it can be confirmed that most of the F ions was removed after NaOH treatment. Fig. 7 shows the hydrogen evolution rates of 4335, 7381 and 6958 μmol·h^{-1}·g^{-1}, corresponding to TiO_2 nanosheets with a thickness of 5.0, 2.7 and 1.6 nm. According to the morphology derived from TEM images shown in Fig. 2 or Fig. 3, the percentages of {001} facets of TiO_2 nanosheets with a thickness of 5.0, 2.7 and 1.6 nm are 69%, 82% and 77%, respectively. Thus the highest rate of H_2 generation for TiO_2 nanosheets with a thickness of 2.7 nm might be attributed to their well-faceted morphology and high percentage of reactive surface. Moreover, for TiO_2 nanosheets with a thickness of only 1.6 nm, H_2 production is a little bit lower than that of TiO_2 nanosheets with a thickness of 2.7 nm.

Fig. 7 H_2 evolution properties of the obtained TiO_2 nanosheets under UV-visible light irradation. The percentages of {001} facets of anatase TiO_2 nanosheets are 69% (a), 80% (b) and 77% (c), respectively. The percentage of {001} facets of each sample is also illustrated on the top of bars.

This result might be due to the lower percentage of high reactive {001} facets, the relative low crystallinity and more defects existing.[8,26]

Conclusions

In summary, we have demonstrated controllable synthesis of ultrathin TiO_2 nanosheets with a thickness of only 1.6–2.7 nm. The concentration of HF used as capping agent significantly affected the thickness and sidelength of the resulting TiO_2 nanosheets. Moreover, the TiO_2 nanosheets were formed through Ostwald ripening process. Due to the high percentage of reactive {001} facets, the synthesized products showed a H_2 evolution rate of 7381 μmol h^{-1} g^{-1}, which was driven by UV-visible light. Importantly, the ultrathin TiO_2 nanosheets with dominant {001} facets are estimated to have more applications such as photocatalysts, smart coating and solar cells, etc.

Acknowledgments

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