Grey facet-controlled anatase nanosheets for photocatalytic H₂ evolution without co-catalyst

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Abstract

Recently, black and grey titania in various morphologies have been intensively investigated for their high performance in photocatalytic H₂ generation. Here we use titania nanosheets (NSs) with a large percentage of (001) facets and hydrogenate them to activate suitable Ti³⁺-O vacancy defects for co-catalyst free H₂ generation. Key to a highly active NS-catalyst is the prevention of serious deformation and sintering during the thermal hydrogenation. In this work, we present a systematic investigation of different thermally treated NSs characterized by scanning electron microscope, high resolution-transmission electron microscopy, TEM-energy-dispersive x-ray, x-ray diffraction, electron paramagnetic response, x-ray photoelectron spectroscopy, and photocatalytic H₂ evolution performance. We describe how to achieve robust grey NSs with an intact two-dimensional shape that can endure hydrogenation at the required high temperatures. Due to a defined faceting, these optimized ‘grey’ NSs can produce photocatalytic H₂ at a higher rate than previously reported best performing grey nanoparticles—this in spite of having a lower Brunauer–Emmett–Teller than the reduced nanoparticles.

1. Introduction

Honda and Fujishima introduced an approach of photocatalytic water splitting in 1972, using titanium dioxide (TiO₂) as a photon absorbing semiconductor [1]. The work laid the basis for photocatalytic generation of the fuel of the future, dihydrogen (H₂), from solar light and water. In principle, photocatalytic H₂ generation provides thus a most promising method for low-cost and environmentally friendly production of energy. In spite of hundreds of photocatalysts explored [2–4], TiO₂ is still a most widely studied photocatalyst for hydrogen generation, due to suitable energetics and even more due to an outstanding resistance to photo-corrosion [5–7]. A main drawback of pristine TiO₂ for photocatalytic H₂ production is its low H₂ generation kinetics, due to the large over-potential for hydrogen generation from aqueous environments [5–7].

In order to overcome this limitation, commonly additional catalysts are deposited on titania—these are typically noble metal nanoparticles such as Pt, Rh, Au and Pd—that can strongly facilitate the H₂ generation reaction [8–10]. These co-catalysts act as electron mediator, facilitating efficient electron-transfer across the interface and in many cases as a recombination center for the reaction 2 H⁰ → H₂. However, because of the limited resources and high cost of noble metals, alternative approaches for an efficient catalysis of the H₂ production reaction are widely investigated.

One of these alternatives is hydrogenated titania (black and grey anatase) in which Ti³⁺ can act as a co-catalytic center that significantly can increase the activity for photocatalytic hydrogen production [11–15]. Originally anatase TiO₂, reduced to black titania, has been intensely investigated since it was
reported by Chen and Mao in 2011 [11–16] to reach a high photocatalytic activity when decorated with Pt. A main point of this black modification is that a disordered surface layer is produced on TiO$_2$ during the hydrogenation process, leading to a greatly narrowed band gap of titania and thus to a visible light response [11]. In contrast, so-called grey titania can be active in a co-catalyst free form (i.e. without any Pt decoration). This ‘grey’ titania shows—in a co-catalyst free state—a remarkably higher photocatalytic H$_2$ production than ‘black’ titania [17–19]. This grey form of TiO$_2$ is obtained by a milder thermal reduction of anatase in H$_2$ atmosphere. More recently, our group reported several works related hydrogenation of different morphologies of titania catalysts, such as nanoparticles [12, 17], nanotubes [20], and multiwalled titanate nanotubes [19]. The different titania catalysts showed a photocatalytic hydrogen production performance not only depending on the level of greyness but also on the morphology.

A most intriguing form of a nanoscale anatase morphology are single crystalline anatase nanosheets (NSs), with a high percentage of (001) facets. This, as the (001) facets have extensively been reported to provide a high photocatalytic activity of titania crystallites. Namely, the fact that (001) facets are considered to be highly beneficial to charge transfer to the aqueous surrounding has made these crystallites to one of the most investigated powder forms in titania photocatalysis [21–23]. Therefore, a systematic investigation of their ‘grey’ form and its performance as a H$_2$ generation photocatalyst is highly desirable.

As such, the synthesis of TiO$_2$ anatase crystallites with a large percentage of (001) facets and with a size in the range of 10 nm to micrometers can be achieved by a facile hydrothermal method [21–23]. However, in the as-formed state of the NSs have two serious drawbacks [21–23]: (a) After the hydrothermal synthesis the flakes are F-terminated which influences the photocatalytic performance [24], (b) the NSs are highly prone to thermal sintering even at comparably low annealing temperatures. The latter, of course, strongly affects attempts to thermally hydrogenate the titania NSs—significant thermal reduction of titania and activation of a noble-metal free reactivity usually requires hydrogenation at temperatures >400 °C.

In this work, we demonstrate a strategy to obtain robust NSs that can endure hydrogenation at high temperatures and with facets where all the F-termination is completely removed. Such grey facet-controlled NSs, compared with grey nanoparticles, show a substantially enhanced photocatalytic hydrogen production.

2. Experimental section

TiO$_2$ NSs were synthesized by a hydrothermal method with commercial reagents, titanium (IV) butoxide (Ti(OBu)$_4$, 97%) and hydrofluoric acid (HF, 48%) from Sigma-Aldrich and Carl Roth, respectively. Both chemicals were used as received with no further purification. Ten milliliters of Ti(OBu)$_4$ was placed in a 250 ml Teflon container and 1.2 ml of HF was added dropwise while stirring at room temperature. The Teflon reactor was sealed in an autoclave after an extra stirring for 40 min. After tight sealing, the autoclave was transferred to a preheated oven at 250 °C. The reaction lasted for 24 h and the autoclave was naturally cooled down in the oven. After the synthesis, the precipitates were collected and rinsed with ethanol and distilled water three times, each by means of a centrifuge, and finally dried in an oven at 70 °C for overnight.

As-synthesized (As-NS) TiO$_2$ anatase NSs were annealed in air at 450 °C, 500 °C and 550 °C for 1 h; these samples are annotated to 450A-NS, 500A-NS and 550A-NS, respectively. After air annealing, the obtained samples were hydrogenated in pure H$_2$ (Linde, 99.99%) flow at 450 °C, 500 °C and 550 °C for 1 h, with a pressure of 20 bar. After a series of thermal treatments, we obtained samples of 450A-500H-NS, 500A-500H-NS, 550A-500H-NS, 500A-450H-NS and 500A-550H-NS. As-synthesized TiO$_2$ anatase NSs were annealed in pure H$_2$ at 500 °C for 1 h to obtain samples of 500H-NS.

For H$_2$ evolution measurements, 10 ml suspension containing 2 mg TiO$_2$ NSs annealed at different conditions and H$_2$O: methanol = 50:50 vol.% solution, was put in a quartz tube reactor sealed with a rubber septum. Before illumination, the suspension was sonicated for 10 min and purged with Ar for 20 min to remove the O$_2$ in the reactor. The quartz tube reactor was put in front of a 365 nm LED (100 mW cm$^{-2}$) for illumination. A gas chromatograph (GC: GCMS-QO2010SE, Shimadzu) with thermal conductivity detector was used to measure the amount of H$_2$ generated. The sample was continuously stirred during irradiation and GC measurements were conducted to evaluate the amount of generated H$_2$. In order to evaluate a visible light response, we used illumination by a 450 nm (1.4 W) green laser or alternatively an AM 1.5 solar simulator with a UV-blocked filter.

A scanning electron microscope (SEM, Hitachi, S-4800) was employed to evaluate the morphology of NSs. The reflectance of the samples was measured between 300 and 800 nm (Avantes, AvaLight-DH-S-BAL, cable IC-DB26-2). X-ray diffraction (XRD) patterns were measured on an X’pert Philips MPD (equipped with a Panalytical X’celerator detector) with a graphite monochromatic CuK$_\alpha$ radiation ($\lambda = 1.54056$ Å). Further information on morphology and crystallization was assessed using high resolution transmission electron microscopy (HR-TEM, CM 30 TEM/STEM, Philips) and selected area electron diffraction (SAED) under a voltage of 300 kV. The elemental composition of the photocatalyst was measured using TEM.
equipped with energy-dispersive x-ray (TEM-EDX). Chemical oxidation states were evaluated by x-ray photoelectron spectroscopy (XPS, PHI 5600). Electron paramagnetic response (EPR) spectra were measured on a JEOL continuous wave spectrometer JES-FA200 (outfitted with an X-band Gunn diode oscillator bridge, a cylindric mode cavity and a N\(_2\) cryostat). Six milligrams of NSs were used for measurements in a quartz EPR tube at 95 K, with a microwave frequency of 8.959 GHz.

3. Results and discussion

Figure 1(a) shows a SEM image of the NS morphology after hydrothermal synthesis, using the parameters given in the experimental section. In line with literature \([22, 23, 25]\), two-dimensional single-crystalline flakes with 20–100 nm side length exposed (001) facets are obtained—the flakes are only a few nanometers thick and electron transparent. In the HR-TEM image (figure 1(b)), lattice fringes with a spacing of 0.352 nm are observed, corresponding to the (101) crystallographic lattice planes of anatase. If the two annealing treatments are compared in SEM, then clearly the two-step annealing (air followed by H\(_2\)) leads to a significantly less agglomerated morphology than the direct H\(_2\) treatment. Without pre-treatment of air annealing, the sample annealed in pure H\(_2\) at 500 °C for 1 h (500 H-NS) shows deformation (sintering) and agglomeration (figure 1(c)). Deformation and agglomeration of the NSs is also evident from Brunauer–Emmett–Teller measurements (see table S1 in supporting information (available online at...
Figure 2. Comparison of the open circuit H$_2$ evolution rates of the anatase NSs treated in different atmospheres at various temperatures. Light source is a 365 nm LED (100 mW cm$^{-2}$). Grey anatase nanoparticles are synthesized according to reported method [17].

stacks.iop.org/JPE/3/034003/mmedia), where a direct hydrogenation leads to a drop from 41.7 m$^2$ g$^{-1}$ to 14.6 m$^2$ g$^{-1}$. This is sharply suppressed by prior air annealing. Moreover, the sample treated in air and subsequently in H$_2$ at 500 °C (500A-500H-NS) shows a flat surface and an intact two-dimensional morphology of the NSs (figure 1(d)).

The As-NS are of a light brown color (figure 1(e)). Upon annealing in air, with higher temperatures, the NSs become increasingly whiter. Subsequent hydrogenation treatments then result in a grey or blue color, which is consistent with a large number of reports on color changes induced by hydrogenation or by other reduction approaches of anatase powders [13, 17]. It is worth noting that an obvious color difference exists between a direct H$_2$ treatment of the as-formed sheets (grey) and sheets that were first air-annealed and then H$_2$ treated (blue).

Absorbance spectra (figure 1(f)) are well in line with the color changes observed in the optical images. Except for UV absorption, corresponding to the bandgap of anatase TiO$_2$ at 3–3.2 eV, the NSs show generally a lower absorbance in the visible range after air annealing and a higher absorption after H$_2$ annealing. After sufficient hydrogenation, a high absorbance in the visible range is detected, which is in line with reports for black TiO$_2$—generally for black TiO$_2$ this change in visible absorption is ascribed to a narrowing of the optical gap due to a partial amorphization of the material [11] (we will discuss this further below).

To assess the ability of different thermally treated or hydrogenated NSs to produce photocatalytic H$_2$, we irradiated the NSs in methanol containing solution (H$_2$O: methanol = 50:50 vol.%) under a 365 nm LED (100 mW cm$^{-2}$). Figure 2 illustrates that the differently heat-treated flakes can become activated for noble-metal-free photocatalytic H$_2$ evolution. Interestingly is that already a heat treatment in air leads to an improved photocatalytic H$_2$ evolution performance. Moreover, compared with as-synthesized or air annealed samples, a significant improvement in the photocatalytic H$_2$ evolution is observed for hydrogenated NSs. A significant difference in the H$_2$ evolution performance is observed for samples that are directly H$_2$ treated and samples that were pre-treated by air-annealing. Clearly, preheating in air leads to an almost three times higher hydrogen production.

In order to benchmark the performance of the grey titania NSs, we compare it to a most efficient grey morphology, that is grey anatase nanoparticles. These nanoparticles are obtained by a treatment of commercial particles (Sigma, diameter 25 nm) at a temperature of 500 °C for 1 h in pure H$_2$. Obviously, the grey NSs obtained by a subsequent air and H$_2$ annealing show a H$_2$ production rate that is around two times higher than the grey nanoparticles [17]. (This although the nanoparticles have an approximately two times higher specific surface area than the NSs (see table S1.) Among the different temperature treatments of the sheets (screening the air annealing and the H$_2$ annealing temperature), a most favorable condition is an air treatment at 500 °C, followed by a treatment in H$_2$ at 500 °C.

To explore differences induced by the thermal treatments and to get insights into mechanistic aspects, we characterized the NSs for structure, composition and defect features. Figure 3(a) shows XRD patterns for key samples, that is As-NS, NSs treated in air at 500 °C (500A-NS), treated in H$_2$ at 500 °C (500H-NS), and treated in air and subsequently in H$_2$ at 500 °C (500A-500H-NS). All samples show a main peak at 2θ = 25.38°, corresponding to the anatase (101) reflection pattern. Among them, the sample of
500A-500H-NS shows the highest crystallinity according to the highest peak intensity. The as-formed NS sample shows an additional peak at $2\theta = 23.61^\circ$ that can be formally ascribed to TiOF$_2$ (JCPDS No. 08–0060), due to the fluoride termination of the sheets. After the thermal treatment at 500 °C for 1 h, in air or in pure H$_2$ atmosphere, this TiOF$_2$ peak cannot be detected any longer.

From HR-TEM (figures 3(b)–(e)), essentially no significant deformation (compared to as-formed NSs) can be observed for differently annealed NSs. This is in contrast to a frequently observed amorphization for...
Table 1. Elemental composition of the As-NSs and the 500A-NS characterized by TEM-EDX.

| Element | As-NS (Atomic %) | 500A-NS (Atomic %) |
|---------|------------------|---------------------|
| C K     | 24               | 2.41                |
| O K     | 35.02            | 34.67               |
| F K     | 3.05             | 0                   |
| Sn L    | 0.03             | 0.01                |
| Ti K    | 34.8             | 58.34               |
| Cu K    | 0.47             | 2.58                |
| Au L    | 2.63             | 1.99                |

black TiO$_2$ [11, 13]. In other words, the optical changes observed upon different annealing treatments cannot be ascribed to amorphization of the structures. For all treatments, HR-TEM shows a typical anatase lattice spacing of 0.352 nm (corresponding to the (101) XRD peak at $2\theta = 25.38^\circ$). The crystal structure was also verified using SAED (see SAED in the insets of figures 3(b)–(e)), which shows in all cases discontinuous features with diffraction patterns corresponding to anatase phase.

TEM equipped with EDX (TEM-EDX) characterization was employed to investigate the elemental composition. Figure 3(f) shows for the as-formed sample a clear F response that is strongly diminished for the annealed sample (figure 3(g)); the elemental composition determined from TEM-EDX is further shown in table 1 for the As-NSs and the sample 500A-NS.

Even more directly, the loss of fluorides (F-termination) is evident from XPS. XPS data of the main elemental peaks are shown in figures 4(a)–(c). For the NSs after different thermal treatments, only the As-NSs show a F1s peak at 683.68 eV. For the samples of 500A-NS, 500H-NS and 500A-500H-NS, there is no F detectable after the thermal treatments. Another observation: all O1s spectra show a similar shoulder at 531.3–531.5 eV. According to some previous reports using powder anatase, hydrogenation results in an increase in OH termination of anatase and thus changes in the shoulder at 531.3–531.5 eV. In our case, we do not observe any significant changes in the O1s peak—indicating that no significant hydroxylation of our samples takes place during the H$_2$ treatment.

To gain information on the electronic nature of the defects introduced by the different treatments, EPR spectroscopy was carried out. EPR spectra were taken for the differently treated samples at 95 K in the dark (figure 4(d)). Noteworthy, the As-NSs shows a broad signal at $g_{avg} \approx 1.86$, which is not observed for other samples. Considering the presence of fluoride termination, the broad signal at $g_{avg} \approx 1.86$ is likely related to defect interaction with F. After annealing in air at 500 °C, a typical signature of Ti$^{3+}$ states in a lattice anatase ($\langle Ti^{3+}_{lattice}\rangle$) [18, 26] can be detected. Upon hydrogenation, an additional defect signature becomes apparent ($\langle Ti^{3+}_{surface}\rangle$ at 330–380 mT with $g_{avg} \approx 1.93$). These states are, as widely reported, beneficial for photocatalytic H$_2$ generation [18, 26]. It is noteworthy that illumination does not change the XPS nor the EPR signature of the NSs (see figures S1 and S2).

As shown in figure 5, the photocatalytic H$_2$ production is very stable. In our case we investigated illumination times up to 144 h and observed a stable photocatalytic H$_2$ evolution for the 500A-500H-NS—in stable as well as in cycling experiments (figure 5(b)). The as-formed NSs in comparison show only a very minor amount of H$_2$ evolution. The inset of figure 5(a) illustrates that an initiation time is observed with a lower H$_2$ production. Over time the hydrogen production rate is accelerated which can be attributed to a light-induced defect re-organization in the initial state of illumination [27].

In order to test, if the states responsible for visible light absorption (see optical absorption spectra in figure 1(f)) can activate a visible light H$_2$ generation, we performed additional experiments using exclusively excitation at 450 nm (450 nm laser, 1.4 W). The results in figure 5(b) clearly show that the grey NSs do not show H$_2$ evolution under visible light illumination. This finding is well in line with previous reports showing that intra band-gap states in grey titania cannot contribute to a visible light activation. This is likely due to a lack of mobility of charge carriers trapped on these states [17].

It has to be pointed out that we do not observe any structurally distorted zone in the titania sheets from HR-TEM, that is our defect states are unlikely related to amorphization but rather, in line with EPR, to discrete Ti$^{3+}$-Ov defects at the surface of the sheets. These are obviously of a distinct nature rather than representing an extended mobile band.

Another aspect to point out is the role of the fluoride termination. Obviously it is detrimental for H$_2$ evolution, as evident from the comparison of the photocatalytic H$_2$ evolution performance of the sheets before and after F removal (figure 2). This may be ascribed to the energetics of the facets, i.e. only after F-removal (restoring the 001 energetics), the real oxide-facet activity of the 001 facet can highly affect the photocatalytic activity.
Figure 4. (a) O1s XPS peak of as-formed NSs and 500A-NS. (b) O1s XPS peak of 500H-NS and 500A-500H-NS. (c) F1s XPS peak of TiO$_2$ NS that were thermally treated at different conditions. (d) X-band EPR envelope recorded at $T = 95$ K of TiO$_2$ NSs that were thermally treated at different conditions.

Figure 5. (a) Open circuit H$_2$ evolution performance of the as-synthesized NSs and the 500A-500H-NSs illuminated by a 365 nm LED (100 mW cm$^{-2}$). Inset shows the H$_2$ evolution performance in the first 4 h. (b) Red curve is cycling experiment of photocatalytic H$_2$ evolution on 500A-500H-NS illuminated by a 365 nm LED (100 mW cm$^{-2}$). The blue curve is the H$_2$ evolution performance of the 500A-500H-NS illuminated by a 450 nm laser (1.4 W). The green curve shows results for a UV-blocked AM 1.5 illumination.

For the present work, more important is, however, that a sequential air annealing followed by a hydrogen annealing prevents sintering of the NSs. This thus allows the fabrication of 'grey' facet controlled titania NSs, with a significantly higher photocatalytic H$_2$ evolution performance than nanoparticles.
4. Conclusions

Overall, the present work shows a pathway to produce anatase NSs that can endure hydrogenation at high temperature and thus allow producing grey single crystalline NSs. The F-termination present in the As-NSs is detrimental to photocatalytic H₂ generation but it can be completely removed by suitable air annealing. Air annealing allows to maintain the morphology of the NSs in a subsequent hydrogenation process (it provides robustness against thermal sintering). Compared with grey nanoparticles, the grey NSs with a well-defined two-dimensional shape show a significantly enhanced photocatalytic hydrogen production. This may be ascribed to the combined effect of faceting that naturally provides an internal energetic gradient that aids charge separation and the enhanced kinetics for H₂ evolution provided by surface induced Ti³⁺ states.

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Conflicts of interest

The authors declare that there is no conflict of interest.

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References

[1] Fujishima A and Honda K 1972 Electrochemical photolysis of water at a semiconductor electrode Nature 238 37–8
[2] Kudo A 2006 Development of photocatalyst materials for water splitting Int. J. Hydrog. Energy 31 197–202
[3] Takanabe K 2017 Photocatalytic water splitting: quantitative approaches toward photocatalyst by design ACS Catal 7 8006–22
[4] Cheng L, Xiang Q, Liao Y and Zhang H 2018 Cds-based photocatalysts Energy Environ. Sci. 11 1362–91
[5] Fujishima A, Zhang X and Tryk D A 2008 TiO₂ photocatalysis and related surface phenomena Surf. Sci. Rep. 63 515–82
[6] Ni M, Leung M K H, Leung D Y C and Sumathy K 2007 A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production Renew. Sustain. Energy Rev. 11 401–25
[7] Linsebigler A L, Lu G and Yates J T 1995 Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results Chem. Rev. 95 735–58
[8] Zou J-J, He H, Cui L and Du H-Y 2007 Highly efficient Pt/TiO₂ photocatalyst for hydrogen generation prepared by a cold plasma method Int. J. Hydrog. Energy 32 1762–70
[9] Yang Y Z, Chang C H and Idriss H 2006 Photo-catalytic production of hydrogen form ethanol over M/TiO₂ catalysts (M=Pd, Pt or Rh) Appl. Catal. B 67 217–22
[10] Rosseler O, Shankar M V, Du M K-L, Schmidlin L, Keller N and Keller V 2010 Solar light photocatalytic hydrogen production from water over Pt and Au/TiO₂ (anatase/rutile) photocatalysts: influence of noble metal and porogen promotion J. Catal. 269 179–90
[11] Chen X, Liu L, Yu P Y and Mao S S 2011 Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals Science 331 746–50
[12] Liu N et al 2014 Hydrogenated anatase: strong photocatalytic dihydrogen evolution without the use of a co-catalyst Angew. Chem., Int. Ed. 53 14201–5
[13] Chen X, Liu L and Huang F 2015 Black titanium dioxide (TiO₂) nanomaterials Chem. Soc. Rev. 44 1861–85
[14] Rajaraman T S, Parikh S P and Gandhi V 2020 Black TiO₂: a review of its properties and conflicting trends Chem. Eng. J. 389 123918
[15] Liu N et al 2020 Long-living holes in grey anatase TiO₂ enable noble-metal-free and sacrificial-agent-free water splitting ChemSusChem 13 1–9
[16] Zhou X, Liu N and Schmuki P 2017 Photocatalysis with TiO₂ nanotubes: ‘colorful’ reactivity and designing site-specific photocatalytic centers into TiO₂ nanotubes ACS Catal 7 3210–35
[17] Liu N et al 2017 Black magic in gray titania: noble-metal-free photocatalytic H₂ evolution from hydrogenated anatase ChemSusChem 10 62–7
[18] Mohajerinia S, Andryskova P, Zoppellaro G, Hejazi S, Kment S, Zboril R, Schmidt J and Schmuki P 2020 Influence of Ti³⁺ defect-type on heterogeneous photocatalytic H2 evolution activity of TiO₂ J. Mater. Chem. A 8 1432–42
[19] Yoo J E et al 2020 Establishing high photocatalytic H₂ evolution from multiwalled titanate nanotubes ChemCatChem 12 2951–61
[20] Liu N, Schneider G, Freitag D, Hartmann M, Venkatesan U, Müller J, Spiecker E and Schmuki P 2014 Black TiO₂ nanotubes: cocatalyst-free open-circuit hydrogen generation Nano Lett. 14 3309–13
[21] Yang H G, Liu G, Qiao S Z, Sun C H, Jin Y G, Smith S C, Zou J, Cheng H M and Lu G Q 2008 Anatase TiO₂ single crystals with a large percentage of reactive facets Nature 453 638–41
[22] Yang H G, Liu G, Qiao S Z, Sun C H, Jin Y G, Smith S C, Zou J, Cheng H M and Lu G Q (Max) 2009 Solvothermal synthesis and photocatalytic activity of anatase TiO₂ nanosheets with dominant [001] facets J. Am. Chem. Soc. 131 4078–83
[23] Ong W-J et al 2014 Highly reactive [001] facets of TiO₂-based composites: synthesis, formation mechanism and characterization Nanoscale 6 1946–2008
[24] Park H and Choi W 2004 Effects of TiO$_2$ surface fluorination on photocatalytic reactions and photoelectrochemical behaviors J. Phys. Chem. B 108 4086–93
[25] Liu S, Yu J and Jaroniec M 2011 Anatase TiO$_2$ with dominant high-energy {001} facets: synthesis, properties, and applications Chem. Mater. 23 4085–93
[26] Naldoni A, Altomare M, Zoppellaro G, Liu N, Kment Š, Zboril R and Schmuki P 2019 Photocatalysis with reduced TiO$_2$: from black TiO$_2$ to cocatalyst-free hydrogen production ACS Catal 9 345–64
[27] Wierzbicka E, Zhou X, Denisov N, Yoo J, Fehn D, Liu N, Meyer K and Schmuki P 2019 Self-enhancing H$_2$ evolution from TiO$_2$ nanostructures under illumination ChemSusChem 12 1900–5