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Ti_{0.89}Si_{0.11}O₂ single crystals bound by high-index {201} facets showing enhanced visible-light photocatalytic hydrogen evolution[†]

Long Wu,^a Hai Bo Jiang,^a Feng Tian,^b Zhigang Chen,^c Chenghua Sun^{*d} and Hua Gui Yang^{*a}

Silicon (Si) doped anatase titanium dioxide ($Ti_{0.89}Si_{0.11}O_2$) single crystals bound by high-index {201} facets and high-energy {001} facets were synthesized by a facile method. It was found that the Si-doping can widely extend the optical absorption edge into the visible-light region and highly reactive facets can enhance their photocatalytic activity, as revealed by the combination of experimental and computational studies.

In the field of solar energy utilization, photocatalysis to produce clean hydrogen (H₂) energy has been viewed as a potential solution to solve the energy crisis and environmental issues, due to its simplicity, environmental friendliness and technical feasibility. Generally, developing suitable semiconductors is one of the most important ways to enhance the efficiency of photocatalysis. Since the first report of photoelectrochemical splitting of water on a titanium dioxide (TiO₂) electrode in 1972,¹ TiO₂ has been intensively studied and regarded as one of the most promising materials owing to its high chemical stability, low toxicity and resistance to photocorrosion.²

Photocatalysis generally involves three main steps: (i) the photo-induced excitation, (ii) bulk migration of hot carriers and (iii) surface chemical reactions. In the first step (i), most photocatalysts, such as pure TiO_2 , can only be excited under ultraviolet (UV) irradiation as determined by its wide bandgap of 3.2 eV, and thus the photons in the visible light region cannot be utilized, which underlines the significance of band

engineering to increase the limited optical absorption of TiO₂ under visible light irradiation. A basic approach is to introduce impurity atoms into the TiO₂ lattice, namely doping, to modify the electronic structures.³ Previously, Si-doping has been employed to enhance the photocatalytic activity and it is believed that Si dopants can reduce the band gap.⁴ While such Si-doped TiO₂ crystals are often dominated by the majority surface (101), and thus the surface reaction needs to be improved further. In the second step (ii), the dopants, such as Si in the TiO₂ matrix, are suitable for separating the photogenerated electrons and holes and thus inhibiting the recombination,^{4,5} which results in an improved quantum yield of the catalysts. In the third step (iii), the photocatalytic reactions occur on the surfaces of TiO2 crystals and the atomic arrangement and coordination on the surface intrinsically determine the adsorption of reactant molecules, the charge transfer between TiO₂ and reactant molecules, and the desorption of generated molecules.⁶ Thus, the external crystal facets play an important role in the overall photocatalytic efficiency. Recently, Yang et al. successfully synthesized uniform anatase TiO₂ single crystals with a large percentage of highly reactive {001} facets for the first time.⁷ Moreover, high-index facets that contain a high density of atomic steps, ledges and kinks were found to exhibit higher catalytic activities.⁸ High-index facets have high surface energy and thus grow much faster than the other facets; consequently, they diminish rapidly and even disappear during crystal growth. Therefore, it is a big challenge to synthesize tailored photocatalysts bound by high-index facets.

To sum up, the photocatalytic activity of the photocatalysts is heavily governed by their band structure and the exposed crystal facets. To date, however, as-prepared TiO_2 samples have been limited to the single crystals with wide bandgap or polycrystals dominated by less-active facets. Although a highly reactive minority surface (001) has been successfully obtained, the surface reconstruction is still a big problem. Herein, we report a facile route to prepare $Ti_{0.89}Si_{0.11}O_2$ single crystals with both preferential high-index {201} facets exposed and a controllable bandgap for the first time. As shown below, the visible-light

^a Key Laboratory for Ultrafine Materials of Ministry of Education,

School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

E-mail: hgyang@ecust.edu.cn; Fax: +86 21 64252127; Tel: +86 21 64252127 ^b School of Materials Science and Engineering,

University of Shanghai for Science and Technology, 200093, Shanghai, China

^c Centre for Microscopy and Microanalysis and School of Engineering,

The University of Queensland, Queensland 4072, Australia

^d Australian Institute for Bioengineering and Nanotechnology, The University of Oueensland, Oueensland 4072, Australia.

E-mail: c.sun1@uq.edu.au; Fax: +61 7 33463992; Tel: +61 7 3346397

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Fig. 1 (a) A digital camera image of $Ti_{0.89}Si_{0.11}O_2$ (denoted ST-201) single crystals and pure white TiO_2 products (denoted T-101). (b and c) SEM images of $Ti_{0.89}Si_{0.11}O_2$ single crystals bound by {001} and {201} facets. The inset shows images of the same individual ST-201 crystal. (d and e) A typical TEM image, the SAED pattern (inset of Fig. 1d) and a high-resolution TEM image of the representative $Ti_{0.89}Si_{0.11}O_2$ crystals.

induced photocatalytic H₂ production can be achieved by Si-doping, and the $\{201\}$ facets, which combine the (101) and (001)features, offer similar high reactivity to perfect (001) but are more stable. The results demonstrate the advantages of combining band engineering and crystal shaping at the same time. In a typical synthesis, the Si-doped TiO₂ single crystals bound by {201} facets (ST-201) were obtained through a hydrothermal route at 150 °C for 48 h, by using titanium disilicide (TiSi₂) and hydrofluoric acid as a Ti source and a crystallographic controlling agent, respectively (see the experimental details for ST-201, ST-101, and T-101 in the ESI⁺). A photo of the obtained green black ST-201 crystals, as compared to the reported pure TiO₂ (T-101),⁷ is shown in Fig. 1a. Powder X-ray diffraction analysis (Fig. S1, ESI⁺) shows that the as-produced samples have anatase structure (space group I41/amd, JCPDS No. 21-1272). The scanning electron microscopy (SEM) image in Fig. 1b shows a typical morphology of the obtained anatase TiO₂ crystals which display sharp-truncated bipyramids with smooth surfaces. The interfacial angle indicated in Fig. 1c is 78.5°, which is consistent with that of $\{001\}$ and $\{201\}$ facets. Fig. S2 (ESI^{\dagger}) presents a schematic model of an ideal anatase TiO2 truncated-bipyramidal crystal bound by {001} and {201} facets. According to the symmetries of anatase TiO₂ crystals, the two flat and square surfaces should be {001} facets and the eight hexagonal surfaces must be high-index {201} facets. By contrast, pure and Si-doped anatase TiO₂ crystals bound by low-index facets (T-101 and ST-101) were also synthesized (Fig. S3-S5, ESI⁺). More detailed structural information of the ST-201 crystals was obtained using transmission electron microscopy (TEM) and the corresponding selected-area electron diffraction (SAED) pattern (Fig. 1d). The SAED pattern (inset in Fig. 1d) can be



Fig. 2 (a) UV-vis absorption spectra of the prepared anatase samples. The inset is the plot of the transformed Kubelka–Munk function vs. the energy of light of the prepared anatase products. (b) Hydrogen evolution per hour and unit surface area with different samples under visible light (420–770 nm). The inset is the time course of evolved hydrogen from 1% Pt-deposited samples under visible light irradiation in water containing a 10 vol% methanol scavenger.

indexed to the [001] zone axis diffraction which implies that the as-prepared sharp-truncated bipyramidal TiO₂ particles are single crystals. The high-resolution TEM image in Fig. 1e shows that the continuous lattice fringes with a lattice spacing of 0.19 nm correspond to the (200) and (020) atomic planes, respectively. On the basis of the above characterizations, we can conclude that the Ti_{0.89}Si_{0.11}O₂ single crystals are bound by {001} and {201} facets.

The UV-visible absorption spectroscopy (Fig. 2a) reveals that ST-201 exhibits highly intense visible light absorption in contrast to the pure sample, which is consistent with the green black color of the samples (Fig. 1a). From the plot of the transformed Kubelka-Munk function versus the energy of the light absorbed (inset of Fig. 2a), the bandgap of the obtained ST-201 and ST-101 is found to be 2.29 and 2.19 eV, respectively. In other words, the samples demonstrate a widely extended optical absorption edge in the visible-light region. The control experiment shows that it is the Si element dopant that effectively changes the band structure of anatase TiO2. Raman spectroscopy is a widely used tool to characterize the fine surface structure.⁹ As shown in Fig. S6 (ESI⁺), the Si-doped TiO₂ single crystals show remarkably different Raman-active modes compared to that of the pure TiO_2 . The shifted E_g mode from the original 144 cm^{-1} to 148 cm^{-1} (ST-201) and 151 cm^{-1} (ST-101) can be recovered, which arises most likely from the additional incorporation of silicon.^{9a}

To further examine the chemical states of silicon in the surface of the ST-201 crystals, X-ray photoelectron spectroscopy (XPS) was used to measure the Si 2p binding energy. Fig. S7 (ESI⁺) shows the silicon with its Si 2p level binding energy in Ti-Si of 100.1 eV and Si-O of 103.0 eV, which is 0.8 eV smaller than that of pure silica. The shift in the binding energy could be ascribed to the interaction of Ti and Si ions in the Ti-O-Si linkage.¹⁰ Because the electronegativity of Si (1.8) is larger than that of Ti (1.5), the positive charge on the Ti species will increase due to the decrease of the electron density around Ti species resulting from the greater electronegativity of Si via O acting on Ti.¹¹ The chemical composition of Si in the Si-doped powder sample was found to be 6.73% (w/w). The molar ratio of Si to Ti is 0.11 : 0.89. However, the intensity of the obtained XPS peak is very low, which may be due to a strong corrosive effect on the silicon by hydrofluoric acid on the crystal surface.

From the above experimental evidence, we can speculate that silicon is mainly doped into the bulk anatase TiO₂ crystals.

The photocatalytic activity of the samples was evaluated by detecting the formation of active hydroxyl radicals (•OH), which are considered as the most important oxidative species in photo-oxidation reactions.¹² As shown in Fig. S8a-c (ESI[†]), significant fluorescence spectra associated with TAOH were observed upon visible-light irradiation of the as-prepared samples. The nearly linear relationship between fluorescence intensity and irradiation time (Fig. S8d, ESI⁺) verifies the stability of silicon doped anatase TiO₂ single crystals. The ST-201 shows three times higher efficiency than the ST-101. We further studied the photocatalytic H₂ evolution rates of the Si-doped anatase TiO₂ (ST-201 and ST-101) and compared them to those of the T-101. As shown in Fig. 2b, on the basis of the surface area of the samples ST-201 and ST-101 (0.40 and $0.34 \text{ m}^2 \text{ g}^{-1}$, respectively), the amount of hydrogen evolved in 2.5 hours for ST-201 was 2.3 times higher than that for ST-101 under visible light and was also 7.8 times higher than that for the reported nitrogen-doped TiO2.2f Although the pure anatase TiO₂ single crystals exhibit high activity under UV light, there is no hydrogen evolution under visible light for comparison (inset in Fig. 2b). The capability of water splitting was still maintained without a noticeable decrease in H₂ production after 20 cycles (Fig. S9, ESI⁺). The enhanced photocatalytic activity of Ti_{0.89}Si_{0.11}O₂ single crystals bound by {201} facets can be explained by the higher active atomic arrangement on the surface and in situ incorporation of the Si element to extend the photoresponse of TiO₂ from the UV to the visible light region.

It is well known that (001) can easily be reconstructed. In this work, the (201) surface is targeted because it combines the features of (101) and (001), as shown in Fig. S10 (ESI[†]). As a result, the (101) part can stabilize the whole surface and prevent the reconstruction. Moreover, to improve the absorption of visible light, Si-doping has been employed. To illustrate its role in band gap narrowing, density functional theory plus Hubbard model (DFT + *U*) calculation¹³ has been carried out, with U = 4.0 eV. More computational details are listed in the ESI.[†] Fig. S11a and b (ESI[†]) show the calculated band structures for undoped and Si-doped anatase TiO₂; it is found that the indirect band gap ($E_{\rm g} = 2.60$ eV) has been reduced and changed to the direct gap (2.34 eV). This calculated data can explain the improvement in the sunlight absorption observed in the experiment.

To understand the role of (201), water molecules have been introduced on the (201) surface randomly and further optimized. Interestingly, one water molecule being close to the (001)-featured part dissociates spontaneously, as shown in Fig. S11c and d (ESI[†]). Such spontaneous dissociation has been observed on perfect (001) before, but different from (001), surface Ti–O bonds are intact on (201), perhaps due to the stabilization of the (101)-featured part. In addition, Si-doping does not affect such water dissociation. Overall, we can see that (201) can offer high reactivity for water dissociation, but has relatively higher stability than (001).

In conclusion, for the first time, we have successfully synthesized $Ti_{0.89}Si_{0.11}O_2$ single crystals with high-index {201}

facets by a facile and one-step solution method. This photocatalyst exhibits excellent stability and a high hydrogen evolution rate under visible light. The results clearly demonstrate that it is the unique stepped atomic configuration on the highindex {201} facets and incorporation of silicon in the bulk of TiO₂ that enhance their photocatalytic activity, which is also proved by theoretical calculations. We expect that this finding will inspire us to design other new and highly reactive photocatalysts for hydrogen evolution.

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