Porous single-crystalline titanium dioxide at 2 cm scale delivering enhanced photoelectrochemical performance

Fangyuan Cheng1, Guoming Lin1, Xiuli Hu1, Shaobo Xi1 & Kui Xie1

Porous single-crystalline (P-SC) titanium dioxide in large size would significantly enhance their photoelectrochemical functionalities owing to the structural coherence and large surface area. Here we show the growth of P-SC anatase titanium dioxide on an 2 cm scale through a conceptually different lattice reconstruction strategy by direct removal of K/P from KTiOPO4 lattice leaving the open Ti-O skeleton simultaneously recrystallizing into titanium dioxide. The (101) facet dominates the growth of titanium dioxide while the relative titanium densities on different parent crystal facets control the microstructures. Crystal growth in reducing atmospheres produces P-SC Ti_{n}O_{2n-1} (n = 7-38) in magneli phases with enhanced visible-infrared light absorption and conductivity. The P-SC Ti_{n}O_{2n-1} shows enhanced exciton lifetime and charge mobility. The P-SC Ti_{9}O_{17} boosts photoelectrochemical oxidation of benzene to phenol with P-SC Ti_{9}O_{17} showing 60.1% benzene conversion and 99.6% phenol selectivity at room temperature which is the highest so far to the best of our knowledge.
Titanium dioxide has been receiving widespread attentions in solar energy conversion1−7. The effectiveness of energy conversion is dedicated to a great extent by the capability of semiconductor itself including effective suppression of rapid electron/hole recombination and efficient light absorption in visible−infrared region8,9. The suppression of charge recombination requires instantaneous charge separation, transport and collection as well as large surface area to host surface reactions. Porous single-crystalline (P-SC) TiO2 would significantly enhance these functionalities owing to the unique advantage by the combination of structural coherence and large surface area10−12. The resolved long-range ordering features would significantly reduce the recombination center and the electron/hole scattering in these grainboundary-free TiO2 skeletons.

Crystal growth is normally along fixed directions while the inside pores are typically considered as inclusion defects in bulk crystals, which makes it extremely difficult to directly grow porous single crystals using traditional approaches13,14. P-SC TiO2 nanoparticles at ~1 μm scale have been prepared using template approaches15,16; however, electrode assembly would require proper loading of nanoparticles that produces contact interfaces15. P-SC TiO2 at centimeter-scale would reduce the grain boundaries and contact interfaces in electrode assembly at the largest extent. The photoelectrochemical performance would be significantly enhanced by the combination of highly accessible surface areas and the long-range electronic connectivity. P-SC TiO2 at centimeter-scale would therefore demonstrate huge potential both in fundamental research and practical applications.

The wide band gap of TiO2 (~3.2 eV) considerably limits the optical absorption under sunlight. Visible−infrared light absorption has been achieved through tailoring the chemical composition by doping either metal or nonmetal in lattice which produces localized defect structures that generate donor or acceptor states in the band gap17,18. Self-doping with Ti3+ in TiO2 different from impurity incorporation, is another effective approach to improve visible-light absorption19,20. These doping strategies with point defect impose improved light-absorption to some extent either by lowering the conduction band or by upgrading the valence band. Black TiO2 through hydrogenation has also been demonstrated for the core-shell nanoparticles in which the crystalline TiO2 quantum structures are covered with disordered phases21,22. Here we show a different approach of band gap engineering to achieve visible-infrared light absorption through tailoring the electronic structures by the incorporation of disordered Ti3+ interstitials in magnei phases.

In a photoelectrochemical cell, the photogenerated holes on TiO2 photoanode surface would readily oxidize water in electrolyte solution to evolve oxygen while the electrons transport to counter electrode and reduce proton into hydrogen under light irradiation and external bias23−25. The generation of *OH radical from H2O is an important step in this photo-oxidation process, which provides a unique opportunity of direct utilization of the highly active *OH radical to facilitate heterogeneous oxidation catalysis before the *OH radicals themselves transform into oxygen. Direct catalytic conversion of benzene to phenol is one of the most active topics in fundamental and applied research26,27. The highly-stable C−H bond of benzene requires a reaction temperature of 50−140 °C using efficient catalysts28−30. Highly active *OH radical would to facilitate the C−H bond activation and accordingly convert benzene to phenol at room temperature. Here we demonstrate highly-efficient conversion of benzene to phenol using P-SC TiO2 photoanode in photoelectrochemical cells.

In this work, we demonstrate the growth of P-SC Ti9O27 crystals grown along the a-axis of KTP parent crystal. The porous single crystals are grown only along the <101> direction, which may be due to that the (101) facet is the low-index facet with the lowest surface free energy33−39 as shown in Supplementary Fig. 2. And the defect formation energy is gradually decreased with smaller n values in Ti9O2n−1 system; however, they are still much lower than zero, which indicates an exothermic process that would favor the formation of magneli phases.

We use a transmission electron microscopy (TEM) coupled with focused ion beam (FIB) to examine the nature of microstructures of the P-SC anatase Ti9O27 crystals. Figure 2 shows the cross-sectional view of porous crystal grown along the a-axis of KTP, which further confirms the distribution of interconnected pores with the diameter of 50−100 nm. The selected area electron diffraction (SAED) at different locations on the porous skeleton shows identical facet orientations and single-crystalline nature. We further show the microstructures and single-crystalline nature of porous crystals grown along with the b-axis and c-axis of KTP as shown in Supplementary Figs. 3 and 4. P-SC crystals not only keep the single-crystalline nature but also maintain the porous microstructures when the crystal growth performs in a stronger reducing atmosphere (Ar/H2 atmospheres, 67−333 mbar at 600−800 °C). We take the P-SC Ti9O27 crystal grown in reducing atmosphere as an example shown in Supplementary Fig. 5. In this case, the further loss of oxygen leads to the presence of more Ti3+ interstitials in bulk that generates magneli phase, which would tailor the electronic structures and band gap structures to better suit light absorption.

Growth mechanism. We use a spherical aberration corrected scanning transmission electron microscope (Cs-corrected STEM) coupled with FIB to investigate the P-SC Ti9O27 and P-SC Ti38O75 crystals. There is no H residual in the porous crystals as confirmed by a solid state Nuclear Magnetic Resonance (NMR) test. Figure 3a shows the high-resolution TEM of the P-SC anatase Ti9O27 grown along the a-axis of KTP parent crystal. The
axis of KTP. The KTP substrates with dimensions of 20 mm × 10 mm × 0.5 mm are used for the growth of P-SC Ti38O75 crystals in Ar at 600 °C.

Fig. 1 XRD and SEM characterization of porous single-crystalline (P-SC) anatase TiO2 crystals. a the XRD of P-SC TiO2 crystals grown along the a-axis, b-axis and c-axis of KTiOPO4 (KTP) substrates. The inset is the crystal structure of anatase TiO2 view along 101 axis. b the SEM of P-SC Ti38O75 crystals grown along the α-axis of KTP. c the SEM of P-SC Ti38O75 crystals grown along the b-axis of KTP. d the SEM of P-SC Ti38O75 crystals grown along the c-axis of KTP. The KTP substrates with dimensions of 20 mm × 10 mm × 0.5 mm are used for the growth of P-SC Ti38O75 crystals in Ar at 600-800 °C. The scale bar is 1 μm in b, c and d.

lattice spacing of 0.237 and 0.352 nm could be assigned to (002) and (011) fringe as further confirmed by the SEAD pattern shown in the inset33. A slight content of random dislocations is present in the anatase Ti38O75 crystal while the single-crystalline features remain unchanged. Crystal growth in a stronger reducing atmosphere (H2/Ar atmosphere, 67–333 mbar at 600–800 °C) produces the P-SC anatase Ti9O17 in magneli phase as shown in Fig. 3b. The oxygen loss produces high concentration of Ti3+ interstitials in bulk while periodical dislocations are present to tolerate these point defects. We use high-sensitive low-energy ion scattering (HS-LEIS) with He+ (3 keV) and Ne++ (5 keV) ions to analyze the atomic surface termination layer. The Ne+ ions scattering could detect surface heavy elements like Ti atom while the He+ ion scattering is more sensitive to O atoms34. Both P-SC Ti38O75 and Ti9O17 crystals terminate with Ti-O skeleton on (101) facets even though there is oxygen loss in reduced crystal as shown in Fig. 3c. The atomic termination layer on (101) facet is well consistent with the stabilized structure shown in Supplementary Fig. 2c. X-ray Photoelectron Spectroscopy (XPS) results in Fig. 3d show that the Ti is mainly +4 in the P-SC Ti38O75 while the contents of Ti3+ are accordingly increased in Ti9O17 (n = 7–38) with the decrease of n values in magneli phases. We finally obtain different P-SC anatase Ti9O2n-1 crystals in magneli phases by gradually varying growth atmospheres and temperatures as shown in Supplementary Fig. 6a. In Supplementary Fig. 6b–f, we observe similar microstructures for the different Ti9O2n-1 crystals in magneli phases though higher oxygen loss leads to more compressed microstructures.

We conduct the measurements of Raman spectroscopy of the porous Ti9O2n−1 single crystals as shown in Supplementary Fig. 7. The peaks at 145, 197, 395, 515, and 636 cm−1 are well consistent with the anatase phase of TiO240,41 through slight Raman shift is observed for different Ti9O2n−1 compositions. We further conduct Brunauer-Emmett-Teller (BET) tests of the porous Ti9O2n−1 single crystals as shown in Supplementary Fig. 8. These porous single crystals demonstrate similar surface areas (~7 m2 g−1) even for the crystals with different chemical compositions. And the mean pore sizes are in the range of 80-100 nm which are well consistent with the SEM results. Figure 4a shows the crystal structure of KTP viewed from the a-axis which demonstrates the vertical and periodical lattice channels of K atoms while the P-O polyhedrons are closely distributed42. The removal of K atoms would proceed accompanied with P-O polyhedron collapsing while the channels would facilitate the atom diffusion leaving the open TiO2 skeleton in Fig. 4b. To maintain a low-energy state, the left TiO2 skeleton finally transforms into porous anatase TiO2 single crystals while the growth is dominated by the low energy (101) facet as shown in Fig. 4c43. The energy barrier of removing K atom through the lattice channel is only 3.58 eV and the removal of O linked to P in polyhedron is as low as 3.52–4.41 eV as shown in Supplementary Fig. 9. The removal of O linked to P may lead to the P-O polyhedron collapsing together with the evaporation of P atom from KTP lattice. The atomic diffusion of K/P/O atoms in lattice would finally lead to the transformation of the KTP crystal into anatase TiO2 crystal in Fig. 4d.
Crystal property. Figure 5a shows the ultraviolet-visible spectroscopy of the P-SC anatase Ti$_n$O$_{2n-1}$ crystals ($n = 7−38$) between 200 and 800 nm. With the increase of Ti$^{3+}$ interstitial concentration, the visible-infrared light absorption gradually becomes stronger and finally demonstrate nearly complete light absorption. P-SC Ti$_n$O$_{2n-1}$ crystals ($n \leq 25$) with significant concentration of Ti$^{3+}$ actually become black and electronic conductors. We also consider the possible influence of the dipole moment of (101) facet in Ti$_n$O$_{2n-1}$ with different ratio between Ti and O atoms. As shown in Supplementary Fig. 10, the dipole moment is approximately −0.2 Debye even though slight fluctuation is observed for Ti$_n$O$_{2n-1}$ with different $n$ values. The dominance to enhance light absorption would be the band gap engineering through control of tailored electronic structures. We calculate the band structures for the pure and reduced TiO$_2$ (101) surface with HSE06 hybrid density functional by VASP software. The calculated total density of states (TDOS) for pure TiO$_2$ (101)−(1 × 4) surface unit cell and reduced TiO$_2$ with Ti interstitials are summarized in Fig. 5b while the projected density of states (PDOS) is shown in Supplementary Fig. 11. For pure TiO$_2$, the Fermi level is located just above its valence band maximum, indicating the typical properties of semiconductor with band gap of 3.29 eV. The conduction band is mainly composed of Ti-3d orbitals while O-2p orbitals dominate the valence band. In contrast, the Fermi level goes through the conduction band for Ti$_6$O$_{17}$ with Ti$^{3+}$ interstitial in magneli phase, which narrows the band gap down to only 1.12 eV while the valence band position remain unchanged. The anatase Ti$_n$O$_{2n-1}$ ($n = 7−38$) in magneli phases would extend the photoabsorption from the visible−infrared range, which is well consistent with our experimental results. The free electrons filled in the bottom of conduction band would make conductivity significantly improved.

We further study the transient absorption spectroscopy of the P-SC Ti$_n$O$_{2n-1}$ ($n = 7−38$) under excitation as shown in Fig. 5c and Supplementary Fig. 12, which confirms the unusual lifetime of exciton (~10 ns) in P-SC Ti$_n$O$_{2n-1}$ ($n = 7−38$) crystals. This lifetime is comparable to that of bulk crystals and ~10 times higher than that of polycrystalline materials, indicating the considerably enhanced suppression of charge recombination with structural coherence. The fluorescence decay in Supplementary Fig. 13 further validates the long lifetime of photoexcited charge in P-SC Ti$_n$O$_{2n-1}$ ($n = 7−38$) crystals. Similar $\tau$ values which indicate the lifetime of free electron−hole recombination in bulk are obtained while similar $\tau$ values which indicate the lifetime of electron−hole recombination on surface are observed, which may be due to the similar structural coherence of Ti$_n$O$_{2n-1}$ single crystals even with different chemical compositions. P-SC Ti$_n$O$_{2n-1}$ crystals with smaller $n$ values give rise to enhanced electron density and mobility that contribute to increased electronic conduction as shown in Fig. 5d and Supplementary Fig. 14. Excessive Ti$^{3+}$ interstitials lead to the decrease of electron mobility though the conductivity is further improved. As shown in Fig. 5d, the growth of titanium dioxide along the $a$-axis of parent KTP crystal in reducing atmosphere gives rise to enhanced electron mobility with the Ti$_6$O$_{17}$ demonstrating the best performance. However, the Ti$_n$O$_3$ shows a decreased mobility which could be due to the increase of point defects in the form of Ti interstitials in lattice. We then have further measured the porous Ti$_n$O$_{2n-1}$ ($n = 7−38$) single crystals grown along the $b$-axis and $c$-axis of the parent KTP crystals to check the possible fluctuations of electron mobility related to microstructures. As shown in Supplementary Fig. 14, for a fixed chemical composition, the fluctuations of electron mobility are negligible for the porous single crystals even though they are grown along the three different axis of the parent KTP crystal.
Photoelectrochemical performance. Figure 6a shows the photocurrent-potential curves of P-SC Ti₉O₁₇ (n = 7−25) in 1 M NaOH solution under 10 times of air mass (AM) 1.5 G irradiation. The dimensions of the free-standing P-SC Ti₉O₁₇ single crystals are 10 mm × 20 mm × 0.5 mm with the cross-sectional view shown in the Supplementary Fig. 15a. With band gap engineering, light absorption dominates photocurrent densities in relation to the n values in the magneli phases. A volcano curve is observed with Ti₉O₁₇ showing the highest photocurrent density, which may be ascribed to the synergy of electronic structures and transport properties. The photocurrent density is as high as 3−9 mA cm⁻² for the P-SC Ti₉O₂₅₋₁ (n = 7−25) photoanodes under irradiation while the dark current densities are generally below 0.5 mA cm⁻² in Supplementary Fig. 15b. Higher potentials facilitates the separation of electron and hole that further leads to enhanced photocurrent densities as shown in Supplementary Fig. 15c. The applied bias photon-to-current efficiencies (ABPEs) of Ti₉O₁₇ at 1.23 V is generally higher than 90% below the incident light of 400 nm, and still contribute in a similar trend with photocurrent densities in Supplementary Fig. 15d. The ABPEs with different P-SC Ti₉O₂₅₋₁ crystals under different applied voltages ranging from 0.4 to 1.23 V are shown in Supplementary Fig. 16. It is observed that higher voltages are favorable for the enhancement of electron−hole separation which therefore leads to improved ABPEs. Although similar transient absorption spectroscopies and transient fluorescence spectroscopies are observed for the porous Ti₉O₂₅₋₁ single crystals, we still clearly observe the gradually enhanced photocurrent densities with smaller n values. The increase of Ti interstitial in lattice engineers and narrows the band gap to enhance the visible−infrared light absorption. In this case, the photocurrent densities would be mainly dominated by the light absorption while the transport properties of the single crystals would also deliver influences, which therefore lead to the optimum composition with the porous Ti₉O₁₇ single crystal showing the best performance.

Figure 6b shows the photocurrent densities versus light intensity using P-SC Ti₉O₁₇, nonporous single crystalline (N-SC) Ti₉O₁₇, and nonporous polycrystalline (N-PC) TiO₂ photoanodes under simulated solar light. The P-SC Ti₉O₁₇ shows a linear enhancement versus light intensity and finally reaches ~50 mA cm⁻² at 1.23 V under illumination intensity of 20 AM 1.5 G, which represents the highest photocurrents using titanium dioxide photoanode. The synergy of porous microstructure, structural coherence and transport property significantly enhances the functionalities of TiO₂ itself and thus contribute to this exceptionally high photoelectrochemical water oxidation performance. The N-SC Ti₉O₁₇ shows a saturated photocurrent densities even under illumination intensity of 20 AM 1.5 G at 1.23 V, demonstrating the limited performance with low surface area. The N-PC TiO₂ film (200 nm in thickness) on FTO shows the saturated photocurrent densities of ~1 mA cm⁻² under illumination intensity up to 50 AM 1.5 G, indicating the limited solar energy conversion with excess grain boundaries and interfaces in electrode. The performance of P-SC Ti₉O₁₇ is ~50 times higher than that of N-PC TiO₂ at high light intensity. Figure 6c shows the
photocurrent density - potential curves of P-SC Ti_nO_{2n−1} (n = 7−25) photoanodes for the photoelectrochemical oxidation of benzene to phenol in 0.5 M Na_2SO_4 electrolyte under illumination intensity of 10 AM1.5 G. Similar photocurrent densities with maximum values at ~9 mA cm^{−2} are observed in contrast to NaOH electrolyte while the onset potentials move forward for ~0.2 V. The dark current densities are still below 0.5 mA cm^{−2} in Supplementary Fig. 17a. We operate the photoelectrochemical oxidation for a duration of 24 h in Supplementary Fig. 17b and then analyze the benzene conversion and phenol yield in Supplementary Fig. 17c and d. The generation of *OH radicals would readily oxidize benzene while the large surface area in porous microstructures would host these surface reactions.

Figure 6d shows the benzene conversion and phenol yield at a constant voltage of 1.0 V using the P-SC anatase Ti_nO_{2n−1} photoanodes. With band gap engineering, we observe a volcano curve for different Ti_nO_{2n−1} in mageli phases with the P-SC Ti_9O_{17} photoanode showing the highest benzene conversion of 60.1% and phenol selectively of 99.6%. The benzene hydroxylation to produce phenol in photochemistry oxidation process is generally believed to proceed via an oxygenation pathway induced by the in situ-formed *OH radical. These active *OH radicals would readily oxidize the benzene to phenol in aqueous phase. We further conduct electron spin resonance (ESR) measurement to detect the irradiated reaction system containing 5,5-dimethyl-1-pyrroline N-oxide (DMPO) which acts as a trapping agent of *OH radical. As shown in Supplementary Fig. 18, the observed ESR signals confirm the formation of *OH radicals during the photoelectrochemical reactions with phenol formed in this process. Negligible phenol is formed after we add ethanol, which acts as scavenger of *OH radicals, into the reaction system. We further to detect the formation of benzene radical cation in this photoinduced process. We detect the ESR signal of benzene radical cation after we cool the aqueous solution using liquid nitrogen after 1 h reaction. We have not observed the corresponding ESR signal of benzene radical cation. Therefore, the reasonable pathway of benzene oxidation is through a *OH radical reaction in this photoelectrochemical process.

**Discussion**

In conclusion, we demonstrate a conceptually different approach of lattice reconstruction strategy to grow porous titanium dioxide single crystals at an unprecedented 2 cm scale. The synergistic control of porous microstructure, structural coherence and band gap engineering considerably enhances the functionalities of the P-SC anatase Ti_nO_{2n−1} (n = 7−38) in mageli phases. The preferential growth of (101) facet dominates the growth of anatase titanium dioxide while the relative Ti densities on parent crystal facet controls the microstructures. The Ti^{3+} interstitials in Ti_nO_{2n−1} account for the Fermi level going through conduction band that narrows band gap down to better suit visible–infrared light absorption. We show the ultrahigh photoelectrochemical performance using P-SC Ti_nO_{2n−1} crystals with Ti_9O_{17} photoanode showing the highest benzene conversion of 60.1% and phenol selectively of 99.6%. The current work would open a new way for low-cost and high-throughput fabrication of porous single crystals in large scale and may be highly-adaptable as well to tailoring single-crystalline materials to enhance their functionalities in many other fields.
Fig. 5 Physical properties of the porous single-crystalline (P-SC) Ti$_n$O$_{2n-1}$ crystals. a Ultraviolet-visible diffuse reflectance spectra of Ti$_n$O$_{2n-1}$ single crystals with different n values. b Density of states for TiO$_2$ and Ti$_n$O$_{2n-1}$ magneli phase with Ti$^{3+}$ interstitials. The Fermi levels are shown as vertical lines. c Decay profiles of transient absorption of the P-SC Ti$_n$O$_{2n-1}$-crystals. d The resistivity, carrier density, Hall coefficient and Hall mobility of Ti$_n$O$_{2n-1}$ single crystals grown along the α-axis of KTP crystal substrates.

Methods

Growth of P-SC Ti$_n$O$_{2n-1}$ crystals. In this work, we firstly grow single-crystalline KTP substrates using Czochralski method and then cut them into substrates with dimensions of 10 mm × 20 mm × 0.5 mm$^3$ [1, 2]. The surfaces are mechanically polished while the crystal facets and roughness are analyzed using XRD on an X-ray diffractometer (Cu-Kα, Miniflex 600) and atomic force microscopy (AFM, Bruker Dimension Edge), respectively. We then grow the P-SC Ti$_n$O$_{2n-1}$ crystals in vacuum system with H$_2$/Ar gas (50–200 sccm, 6 N purity) pressure controlled at 67–333 mbar at 600–800 °C. The P-SC Ti$_n$O$_{2n-1}$ crystals are obtained after maintaining the treatment duration for 30–60 h followed by a natural cooling process in argon gas (6 N purity).

Characterization of microstructure and property. We analyze the surface morphologies of P-SC Ti$_n$O$_{2n-1}$ samples using field-emission scanning electron microscope (FE-SEM) (Zeiss Auriga) at an accelerating voltage of 10 kV. The phase formation is then examined using XRD on an X-ray diffractometer (Cu-Kα, Miniflex 600). We use FIB (ZeissAuriga) to prepare TEM samples and then characterize them on a Cs-TEM (FEI Titan3 G2 60–300) at 300 kV. The valence of Ti in P-SC Ti$_n$O$_{2n-1}$ crystals is determined using XPS on ESCALAB 250Xi. The transport properties are investigated at a physical property measurement system (6 T, 4 K) with 3 keV He$^+$ ions to analyze the electronic structure. We further calculate the band structures both the perfect and reduced TiO$_2$ (101) with the HSE06 hybrid density functional using VASP software [44, 45]. In our DFT calculation, the plane-wave cutoff energy of 500 eV is used to set the electronic states.

Photoelectrochemical measurement. We test the photoelectrochemical water oxidation using P-SC Ti$_n$O$_{2n-1}$ in aqueous 1 M NaOH on an electrochemical workstation (IM6, Zahner) with a Pt counter electrode and a saturated calomel electrode, referenced to the standard hydrogen electrode and reference electrode are P-SC Ti$_n$O$_{2n-1}$-Pt piece and saturated calomel electrode, respectively. The external bias voltage is 1.23, 1.0, 0.8, 0.6, and 0.4 V versus RHE, respectively. All potentials are converted to RHE reference scale using the Nernst equation: $E_{RHE} = E_{SCE} + 0.059 \times \phi + 0.244$.

Theoretical calculation. To understand the energy barrier of atom removal through the lattice channel and the formation of Ti$_n$O$_{2n-1}$ magneli phases, we calculate the defect formation energy ($E_{\text{form}}$) for the K atom, different O and Ti atoms with the following formula: $E_{\text{form}} = E_{\text{total}}(\text{perfect}) - E_{\text{total}}(\text{defect}) - \sum_{i} \Delta n_i u_i$, where $E_{\text{total}}(\text{defect})$ and $E_{\text{total}}(\text{perfect})$ are the total energy of defect and perfect system, respectively. $\Delta n_i$ and $u_i$ are the number of increase or decrease atoms and the chemical potential of the constituent atoms, respectively [46, 47]. The defect configurations of the KTP (100) surface with the defect formation energies ($E_{\text{form}}$) is shown in Supplementary Fig. 9. We further calculate the band structures both the pure and reduced TiO$_2$ (101) with the HSE06 hybrid density functional using VASP software [44, 45]. In our DFT calculation, the plane-wave cutoff energy of 500 eV is used to set the electronic states.
for water oxidation using a three electrode setup (Ti électrolyte (PH repeated measurements.

\[ \text{Ti}^{12}\text{O}_{23}, \text{Ti}^{9}\text{O}_{17} \text{and Ti}^{7}\text{O}_{13} \text{and the dipole moment of them are calculated along } \text{z direction, respectively.} \]

\[ \text{K-point grids } 3 \times 2 \times 1 \text{ are adopted in the irreducible unit cell of anatase TiO}_2 \text{ and obtained the lattice parameters: } \text{a} = 4.523 \text{Å} \text{ and } \text{c} = 9.683 \text{Å (with a } 8 \times 8 \times 3 \text{ k-point grid) which is consistent with earlier reports}. \]

**Data availability**

All reported data are included in the manuscript and supplementary materials. And the Source Data can be downloaded from the Source File: https://yunpan.360.cn/surl_yLXSUrWQP3s (Code: 3f1a)

Received: 21 March 2019 Accepted: 19 July 2019
Published online: 09 August 2019

**References**

1. Hu, S. et al. Amorphous TiO\_2 coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. *Science* **344**, 1005–1009 (2014).

2. Schrauben, J. N. et al. Titanium and zinc oxide nanoparticles are proton-coupled electron transfer agents. *Science* **336**, 1298–1301 (2012).

3. Li, B. et al. Ultrafast interfacial proton-coupled electron transfer. *Science* **311**, 1436–1440 (2006).

4. Onda, K. et al. Wet electrons at the H\_2O/TiO\_2(110). *Surf. Sci* **308**, 1154–1158 (2005).

5. Khan, S. U. M., Al-Shahry, M. & Ingler, W. B. Efficient photochemical water splitting by a chemically modified n-TiO\_2. *Science* **287**, 2243–2245 (2002).

6. Chen, H.-Y. & Ardo, S. Direct observation of sequential oxidations of a titania-bound molecular proxy catalyst generated through illumination of molecular sensitizers. *Nat. Chem.* **17**, 1–13 (2018).

7. Murdoch, M. et al. The effect of gold loading and particle size on photocatalytic hydrogen production from ethanol over Au/TiO\_2 nanoparticles. *Nat. Chem.* **3**, 489–492 (2011).

8. Tong, H. et al. Nano-photocatalytic materials: possibilities and challenges. *Adv. Mater.* **24**, 229–251 (2012).

9. Guo, Q. et al. Elementary photocatalytic chemistry on TiO\_2 surfaces. *Chem. Soc. Rev.* **45**, 3701–3730 (2016).

10. Butburee, T. et al. 2D porous TiO\_2 single-crystalline nanostructure demonstrating high photo-electrochemical water splitting performance. *Adv. Mater.* **30**, 1705666 (2018).

11. Zhang, P., Guan, B. Y., Yu, L. & Lou, X. W. Facile synthesis of multi-shelled ZnP-CuS cages with enhanced photocatalytic performance for solar energy conversion. *Chem. Commun.* **6**, 162–173 (2018).

12. Liu, Y. et al. Radially oriented mesoporous TiO\_2 microspheres with single-crystal-like anatase walls for high-efficiency optoelectronic devices. *Sci. Adv.* **1**, e1500166 (2015).

13. Chen, C., Sun, S., Chou, M. M. C. & Xie, K. In situ inward epitaxial growth of bulk macroporous single crystals. *Nat. Commun.* **8**, 2178 (2017).

14. Lin, G., Xi, S., Pan, C., Lin, W. & Xie, K. Growth of 2 cm metallic porous TiN single crystals. *Mater. Horiz.* **5**, 953–960 (2018).

15. Crossland, E. J. W. et al. Mesoporous TiO\_2 single crystals delivering enhanced mobility and optoelectronic device performance. *Nature* **495**, 215–219 (2013).

16. Wang, X. D., Summers, C. J. & Wang, Z. L. Mesoporous single-crystal ZnO nanowires epitaxially sheathed with ZnS/Se. *Adv. Mater.* **16**, 1215–1218 (2004).

17. Liu, G. et al. Titanium dioxide crystals with tailored facets. *Chem. Rev.* **114**, 9599–9612 (2014).
18. Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. & Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 293, 269–271 (2001).
19. Tao, J., Luttrell, T. & Ratcliff, M. A two-dimensional phase of TiO2 with a reduced bandgap. Nat. Chem. 3, 296–300 (2011).
20. Lira, E. et al. The importance of bulk Ti3+ defects in the oxygen chemistry on titania surfaces. J. Am. Chem. Soc. 133, 6529–6532 (2011).
21. Wang, Z. et al. Visible-light photocatalytic, solar thermal and photoelectrocatalytic properties of aluminium-reduced black titania. Environ. Sci. Energy 6, 3007–3014 (2013).
22. Chen, X., Liu, L., Yu, P. Y. & Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. Science 331, 746–750 (2011).
23. Nosaka, Y. & Nosaka, A. Y. Generation and detection of reactive oxygen species in photocatalysis. Chem. Rev. 117, 11302–11336 (2017).
24. Kou, J. et al. Selectivity enhancement in heterogeneous photocatalytic transformations. Chem. Rev. 117, 1445–1514 (2017).
25. Zhang, B., Wang, L., Zhang, Y., Ding, Y. & Bi, Y. Ultrathin FeOOH nanolayers with abundant oxygen vacancies on BiVO4 photoanodes for efficient water oxidation. Angew. Chem. Int. Ed. 57, 2248–2252 (2018).
26. Deng, D. et al. A single iron site confined in a graphene matrix for the catalytic oxidation of benzene at room temperature. Sci. Adv. 1, 2375–2548 (2015).
27. Wen, G., Wu, S., Li, B., Dai, C. & Su, D. S. Active sites and mechanisms for direct oxidation of benzene to phenol over carbon catalysts. Angew. Chem. Int. Ed. 54, 4105–4109 (2015).
28. Niu, S. et al. One-step conversion of benzene to phenol with a palladium membrane. Science 295, 105–107 (2002).
29. Yang, J.-H. et al. Direct catalytic oxidation of benzene to phenol over metal-free graphene-based catalyst. Energy Environ. Sci. 6, 793–798 (2013).
30. Chen, X., Zhang, J., Fu, X., Antonietti, M. & Wang, X. Fe–g-C3N4-catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light. J. Am. Chem. Soc. 131, 11658–11659 (2009).
31. Zhang, D. Y. et al. Crystal growth and second harmonic generation properties of Nb/KTP crystal. J. Synth. Cryst. 28, 298–302 (1999).
32. Hong, Y. et al. The growth of potassium titanyl phosphate single crystal by flux seeded method. J. Synth. Cryst. 1, 275 (1988).
33. Ciancio, R. et al. Magneli-like phases in epitaxial anatase TiO2 thin films. Phys. Rev. B 86, 104110 (2012).
34. Padiha, A. C. M., Osorio-Guillen, J. M., Rocha, A. R. & Dalpian, G. M. TiO2n−1 Magneli phases studied using density functional theory. Phys. Rev. B 90, 035213 (2014).
35. Yu, J., Low, J., Xiao, W., Zhou, P. & Jaroniec, M. Enhanced photocatalytic CO2-reduction activity of anatase TiO2 by coexposed [001] and [101] facets. J. Am. Chem. Soc. 136, 8839–8842 (2014).
36. Lrazier, M., Vittadini, A. & Seloni, S. Structure and energetics of stoichiometric TiO2 anatase surfaces. Phys. Rev. B 65, 119901 (2002).
37. Yang, H. G. et al. Anatase TiO2 single crystals with a large percentage of reactive facets. Nature 453, 636–641 (2008).
38. Yang, Y., Feng, Q., Wang, W. & Wang, Y. First-principle study on the electronic and optical properties of the anatase TiO2 (101) surface. J. Solid State Chem. 34, 073004 (2013).
39. Pan, J., Liu, G., Lu, G. Q. & Cheng, H.-M. On the true photoreactivity order of [001], [101], and [100] facets of anatase TiO2 crystals. Angew. Chem. Int. Ed. 50, 2133–2137 (2011).
40. Berger, H., Tang, H. & Levy, F. Growth and Raman spectroscopic characterization of TiO2 anatase single crystals. J. Crystal Growth 130, 108–112 (1993).
41. Zhang, J., Li, M., Feng, Z., Chen, J. & Li, C. UV Raman spectroscopic study on TiO2. I. Phase transformation at the surface and in the bulk. J. Phys. Chem. B 110, 927–935 (2006).
42. Tordjman, L., Masse, R. & Guetel, J. C. Structure cristalline du monophosphate KTiPO4. Kristallografiya 139, 103–115 (1974).
43. Kim, C. W., Yeob, S. J., Cheng, H.-M. & Kang, Y. S. A selectively exposed crystal facet-engineered TiO2 thin film photoanode for the high performance of the photoelectrochemical water splitting reaction. Energy Environ. Sci. 8, 3646–3653 (2015).
44. Mao, X. et al. Band-gap states of TiO2(110): major contribution from surface defects. J. Phys. Chem. Lett. 4, 3839–3844 (2013).
45. Wang, Z. et al. Localized excitation of Ti3+ ions in the photoabsorption and photocatalytic activity of reduced rutile TiO2. J. Am. Chem. Soc. 137, 9146–9152 (2015).
46. Yamada, Y. & Kanemitsu, Y. Determination of electron and hole lifetimes of rutile and anatase TiO2 single crystals. Appl. Phys. Lett. 101, 133907 (2012).
47. Katoch, R., Murai, M. & Furube, A. Transient absorption spectra of nanocrystalline TiO2 films at high excitation density. Chem. Phys. Lett. 500, 309–312 (2010).
48. Zhang, P., Yu, L. & Lou, X. W. D. Construction of heterostructured Fe2O3–TiO2 microdumbells for photoelectrochemical water oxidation. Angew. Chem. Int. Ed. 57, 15076–15080 (2018).
49. Rahman, M. A. et al. Defect-rich decorated TiO2 nanowires for super-efficient photoelectrochemical water splitting driven by visible light. Energy Environ. Sci. 8, 3363–3373 (2015).
50. Wang, D., Wang, M. & Li, Z. Fe-Based metal–organic frameworks for highly selective photocatalytic benzene hydroxylation to phenol. ACS Catal. 5, 6852–6857 (2015).
51. Devaraji, P., Sathe, N. K. & Gopinath, C. S. Ambient oxidation of benzene to phenol by photocatalysis on Au/TiO2: role of holes. ACS Catal. 4, 2844–2853 (2014).
52. Liu, G. et al. Promoting active species generation by plasma-induced hot-electron excitation for efficient electrocatalytic oxygen evolution. J. Am. Chem. Soc. 138, 9128–9136 (2016).
53. Yu, Q., Meng, X., Wang, T., Li, P. & Ye, J. Hematite films decorated with nanostructured ferric oxyhydroxide as photoanodes for efficient and stable photoelectrochemical water splitting. Adv. Funct. Mater. 25, 2686–2692 (2015).
54. Xie, J. et al. Highly selective oxidation of methane to methanol at ambient conditions by titanium dioxide-supported iron species. Nat. Catal. 1, 889–896 (2018).
55. Nayak, S. K. et al. Insight into point defects and impurities in titanium from first principles. Npj Comput. Mater. 4, 11 (2018).
56. Chen, F. et al. First-principles study of point defects in rutile TiO2−x. Phys. Rev. B 73, 193202 (2006).

Acknowledgements
We acknowledge the funding support from the Natural Science Foundation of China (91825020, 11775239, 61775072, 61408023, 61378046, 11804129, 61675029, 11404097, 61378026, 11404098, 61374065, 61075030). The authors declare no competing interests.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-019-11623-w.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/.

Peer review information: Nature Communications thanks Jabor Rabeh Boustany, Youn Soon Kang and other anonymous reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.