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Titanium-defected undoped anatase TiO₂ with p-type conductivity, room-temperature ferromagnetism and remarkable photocatalytic performance

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KEYWORDS: anatase TiO₂, metal vacancy, p-type conductivity, ferromagnetism, photocatalysis.

ABSTRACT: Defects are critically important for metal oxides in chemical and physical applications. Compared with the often studied oxygen vacancies, engineering metal vacancies in n-type undoped metal oxides is still a great challenge, and the effect of metal vacancies on the physiochemical properties is seldom reported. Here, using anatase TiO₂, the most important and widely studied semiconductor, we demonstrate that metal vacancies (V_{Ti}) can be introduced in undoped oxides easily, and the presence of V_{Ti} results in many novel physiochemical properties. Anatase Ti_{0.995}O₂ was synthesized using solvothermal treatment of tetrabutyl titanate in ethanol-glycerol mixture and then thermal calcination. Experimental measurements and DFT calculations on cell lattice parameters show the un-stoichiometry is caused by the presence of V_{Ti} rather than oxygen interstitials. The presence of V_{Ti} changes the charge density and valence band edge of TiO₂, and an un-reported strong EPR signal at $g=1.998$ presents under room temperature. Contrary to normal n-type and non-ferromagnetic TiO₂, Ti-defected TiO₂ shows inherent p-type conductivity with high charge mobility, and room-temperature ferromagnetism stronger than Co-doped TiO₂ nanocrystalline. Moreover, Ti-defected TiO₂ shows much better photocatalytic performance than normal TiO₂ in H₂ generation (4.4-fold) and organics degradation (7.0-fold for phenol), owing to the more efficient charge separation and transfer in bulk and at semiconductor/electrolyte interface. Metal-defected undoped oxides represent a unique material; this work demonstrates the possibility to fabricate such material in easy and reliable way and thus provides new opportunities for multifunctional materials in chemical and physical devices.

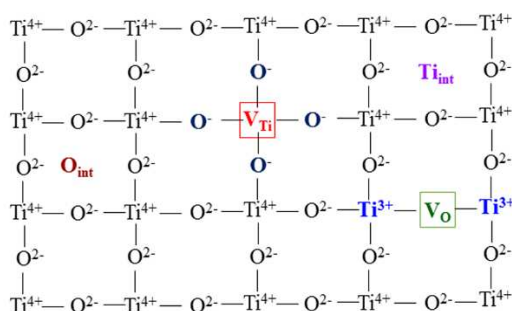
1. INTRODUCTION

The physicochemical properties of metal oxides largely depend on the concentration of intrinsic defects and extrinsic impurities, and it has been demonstrated that pure stoichiometric metal oxides are inactive in catalysis.¹⁻³ Defect engineering is a key factor to tune the functional properties of oxides, such as electronic structure, charge transport, and catalytic performance.⁴⁻⁵ Specifically for semiconductors, density functional theory (DFT) calculations predict that both oxygen vacancies (V_O) and metal interstitials are shallow donors responsible for n-type conductivity, whereas metal vacancies (V_M) are shallow acceptors contributing to p-type conductivity.⁶ In the past decades, V_O related species are thought to be very important and techniques for V_O engineering have been extensively studied,⁷⁻¹¹ but only a few literatures focus on V_M control. Although some theoretical computations have been conducted to study the role of V_M in metal oxides, experimental results are quite rare because it is quite dif-

ficult to engineer and manipulate metal defects in a stable and reliable way.¹²

Since the discovery of photoelectrochemical (PEC) water splitting in 1972,¹³ anatase TiO₂ has attracted intensive attention in photocatalytic hydrogen generation, dye sensitized solar cell, pollutants removal and CO₂ reduction.¹⁴⁻¹⁵ Many approaches have been adopted to improve its photocatalytic performance such as tuning oxygen defects,¹⁶ improving the crystallinity,¹⁷ utilizing slow photon effect,¹⁸⁻¹⁹ exposing active facet,²⁰⁻²¹ and surface fluorination.²²⁻²³ Actually, the photocatalytic performance of TiO₂ greatly depends on the optical and electrical properties that are mostly determined by the crystal structure and defect.²⁴ TiO₂ inherently exhibits n-type conductivity due to the existence of V_O . When the concentration of acceptor dopants increases to a suitable level,^{8,25-26} the Fermi level of TiO₂ will shift towards valence band (VB) edge and its conductivity can be altered from n- to p-type. For example, both Cr- and Fe-doped TiO₂

show p-type conductivity,⁴ and Cr-doped TiO₂ photoelectrodes exhibits photocathodic current.²⁵ However, foreign acceptors may have deteriorating effect on charge separation and transfer.²⁷⁻²⁸ Titanium vacancy (V_{Ti} , Scheme 1) is acceptor type intrinsic defect, so increasing its concentration may lead to n→p transition and thus influence the mobility of charge carriers. Besides, as the only negative ionic defect in undoped TiO₂, V_{Ti} has been predicted as active site for water splitting.^{7,29} However, the study on undoped anatase p-type TiO₂ is quite rare, let alone its performance in photocatalysis. Nowotny *et al* reported that, annealing TiO₂ at 1323 K for 3500 h can lead to Ti-deficient oxide with p-type conductivity,^{27,30} but the obtained TiO₂ is not anatase phase any more. Bhattacharyya and Basu *et al* reported undoped anatase p-type TiO₂ thin films deposited on p-Si substrate but neither checked the structure characteristic nor explained the reason for the p-type conductivity.³¹⁻³³



Scheme 1. Schematic representation of different defects in undoped TiO₂. V_{Ti} : Ti vacancy, V_O : oxygen vacancy, Ti_{int} : Ti interstitial, O_{int} : oxygen interstitial, Ti^{3+} : Ti^{4+} ion accepting one electron, O^- : O^{2-} donating one electron.

Room-temperature ferromagnetic (RT-FM) oxides have attracted great interests from magnetic fluids, biomedicine, magnetic resonance imaging, catalysis, and environmental remediation.³⁴ The discovery of carrier mediated ferromagnetism at high temperature (~170 K) inspires numerous attempts to construct diluted magnetic semiconductors with RT-FM.³⁵ Koinuma *et al* reported cobalt-doped anatase thin film with Curie temperature (T_C) more than 400 K.³⁶ But recently debate arises on whether the ferromagnetism is really caused by the homogeneous $Ti_{1-x}Co_xO_2$ or just by the dopants themselves.³⁷ Meanwhile, the key of high T_C is a large density of states at the Fermi level, which is easier to achieve in p-type semiconductors.³⁵ Also, owing to the electronic structure changed by defects, metal-defected undoped oxides may show intrinsic high- T_C ferromagnetism.³⁸ Therefore, p-type metal oxide with RT-FM are potential candidates of multifunctional materials in both chemical and physical devices.

Recently, we developed a facile method to fabricate ZnO crystals abundant with Zn vacancies, and observed p-type conductivity, RT-FM and excellent photocatalytic activity.³⁹ It demonstrates the possibility of reliable V_M engineering in oxides, and more importantly, suggests the resulted materials may exhibit many interesting properties that have much potential in application. This inspires

us to explore the possibility of introducing V_{Ti} in TiO₂ that is the most important semiconductor oxide in both chemical and physical applications. Herein, we report the successful fabrication of undoped anatase TiO₂ abundant with V_{Ti} using simple solvothermal method, as well its structure characteristics, electrical conductivity, ferromagnetism and photocatalytic performance, based on experiments and density functional theory simulations. The metal-defected TiO₂ represents a new kind of semiconductor and provides new opportunities for TiO₂-based materials.

2. EXPERIMENTAL SECTION

2.1. Materials

Tetrabutyl titanate [$Ti(OC_4H_9)_4$, TBT], ethanol, glycerol, methanol, $H_2PtCl_6 \cdot 6H_2O$, rhodamine B (RhB), and methyl orange (MO) were all purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Phenol was obtained from J&K Chemical. Milli-Q ultra pure water with a resistivity higher than 18.2 M Ω ·cm was used in all experiments. All the reagents were reagent grade and used as received.

2.2. Synthesis of Ti-defected TiO₂

2 g TBT was added into a solution of 20 mL glycerol and 60 mL ethanol under magnetic stirring, then the solution was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 24 h. The obtained powders were collected, washed with absolute ethanol for several times, dried at 60 °C for 12 h, and finally calcined in air at 470 °C for 1 h with a heating rate of 5 °C/min (referred as defected TiO₂). As reference, normal TiO₂ was synthesized with the same procedure but without glycerol in the solvothermal treatment.

2.3. Structure characterizations

XRD patterns were recorded using D/MAX-2500 X-ray diffractometer equipped with Cu K α radiation at 40 kV and 140 mA at a scanning rate of 5 °/min. TEM analysis was carried out using a Tecnai G² F-20 transmission electron microscope with a field-emission gun operating at 200kV. Electron paramagnetic resonance (EPR) measurement was performed with a Bruker EMX-6/1 spectrometer at 9.424 GHz (120 K) or 9.868 GHz (298 K) using a 100 kHz field modulation and a 0.5 G standard modulation width. X-ray photoelectron spectrum (XPS) analysis was conducted with a PHI-1600 X-ray photoelectron spectroscope equipped with Al K α radiation, and the binding energy was calibrated by the C1s peak (284.8 eV) of contamination carbon. Ti/O ratios in bulk and on the surface were analyzed by titration method with deviation <0.5% and XPS analysis, respectively (Details are listed in Supporting Information (SI) and Figure S1). Specific surface area (S_{BET}) was calculated based on N₂ adsorption/desorption isotherms recorded on a Micromeritics TriStar 3000 instrument at 77 K, all samples were outgassed under vacuum at 300°C for 4 h. Steady-state photoluminescence (PL) spectra were measured by a Horiba JobinYvon Fluorolog3-21 with the excitation light at 325 nm. Positron annihilation lifetime was measured with a fast/slow coincidence ORTEC system with a time resolu-

tion of ~ 201 ps full width at half-maximum. A 5×10^{-5} -Bq source of ^{22}Na was sandwiched between two identical samples (10×10 mm, 1 mm thickness).

2.4. Measurements of electrical and magnetic properties

Electrochemical properties were measured using an Autolab potentiostat/galvanostat (Model PGSTAT 302N) in a three-electrode cell with a Pt sheet as the counter electrode and an Ag/AgCl reference electrode. Na_2SO_4 (0.2 M) was used as electrolyte solution. The working electrode was prepared by dip-coating TiO_2 slurry on an F-doped tin oxide (FTO) glass electrode ($1 \text{ cm} \times 1 \text{ cm}$) and heating at 40°C overnight. All investigated working electrodes were of similar thickness. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a sinusoidal ac perturbation of 10 mV applied over the frequency range of 0.01 - 10^5 Hz. Hall-effect measurements were carried out in the van der Pauw configuration (HL5550PC, Accent Optical Technologies Ltd., UK) at room temperature. The contacts were applied on the four corners of $0.5 \times 0.5 \text{ cm}^2$ pressed pellets that were annealed at 300°C for 1 h in air. Magnetic properties were measured using Quantum Design SQUID-VSM at a maximum field of 20 kOe in temperature range of 10-350 K.

2.5. Photocatalytic tests

Photodegradation of organic pollutants was conducted in an opening quartz chamber (150 mL) vertically irradiated by a 300 W high-pressure Xenon lamp (PLS-SXE 300UV, Beijing Trusttech. Co. Ltd.) located on the upper position. The light density was 35.2 mW/cm^2 at 365 nm, and 33.5 mW/cm^2 at 420 nm as measured with a radiometer (Photoelectric Instrument Factory, Beijing Normal University, Model UV-A). The irradiation area was *ca.* 20 cm^2 . Reaction conditions: temperature, $25 \pm 0.2^\circ\text{C}$; $C_0(\text{RhB}) = 20 \mu\text{mol}\cdot\text{L}^{-1}$; $C_0(\text{MO}) = 120 \mu\text{mol}\cdot\text{L}^{-1}$; $C_0(\text{Phenol}) = 400 \mu\text{mol}\cdot\text{L}^{-1}$; TiO_2 : $0.2 \text{ g}\cdot\text{L}^{-1}$; no acid or alkaline reagents were added. For self-sensitized degradation of RhB under visible light, an UV-420 cut was equipped to eliminate UV light. Reaction was conducted by magnetic stirring under atmosphere after stirring for 20 minutes in darkness to achieve adsorption equilibrium. Samples were withdrawn, centrifuged and analyzed using UV-vis spectrometer (U-3010, Hitachi Ltd.).

Photocatalytic hydrogen production was carried out in a Pyrex top-irradiation reaction vessel connected to closed glass gas system. 10 mg catalyst were dispersed in 120 mL aqueous solution containing methanol (30 vol.%). 1.0 wt.% Pt were introduced as co-catalyst by *in-situ* photodeposition. The temperature of reaction solution was maintained at 0°C . The resultant hydrogen was analyzed using an on-line gas chromatography (Bruker 450-GC, thermal conductive detector (TCD), 5 Å molecular sieve column, and N_2 as carrier gas).

2.6. Density functional theory calculations

The calculations were based on density functional theory and the projector augmented wave method implemented in the Vienna Ab initio Simulation Package.⁴⁰⁻⁴⁴ The Perdew-Burke-Ernzerhof spin-polarized

generalized gradient approximation was used for the exchange-correlation potential,⁴³ and the plane-wave cutoff was set to 400 eV together with performing a G-centered $7 \times 7 \times 3$ k mesh Brillouin-zone integration to obtain accurate structure for all systems. The convergence criterion for minimization of the Hellmann-Feynman force was set to less than 0.01 eV/\AA .

A $2 \times 2 \times 1$ anatase supercell was used for the calculation, with one Ti atom removed to construct Ti-defected crystal ($\text{Ti}_{15}\text{O}_{32}$, $\text{Ti}/\text{O} = 0.469$) and one O atom inserted in the interstitial position to construct O-interstitial crystal ($\text{Ti}_{16}\text{O}_{33}$, $\text{Ti}/\text{O} = 0.485$). The lattice parameters were calculated with DFT-GGA method that provides accurate lattice constants but underestimates the band gap. The GGA+*U* method can improve the prediction of band structure,⁴⁴ so it was applied with $U = 7.2 \text{ eV}$ for Ti atom in the static state and density of states calculation.

3. RESULTS AND DISCUSSIONS

3.1. Formation of anatase TiO_2

The intermediated powders formed by solvothermal treatment of tetrabutyl titanate (TBT) in glycerol-ethanol mixture show a sharp peak at $2\theta = \text{ca. } 10^\circ$ and several weak peaks at higher 2θ degree (Figure S2, SI). Although the pattern can not be indexed to any known structure in database, some literatures refer it as titanium glycerolate (TiGly).⁴⁵⁻⁴⁷ The solid state CP/MAS ^{13}C NMR spectrum (Figure S3, SI) shows three well resolved peaks at 73.8, 80.5 and 85.3 ppm, in accordance with the reported NMR data of TiGly.⁴⁶ From TG analysis (Figure 1a), the weight

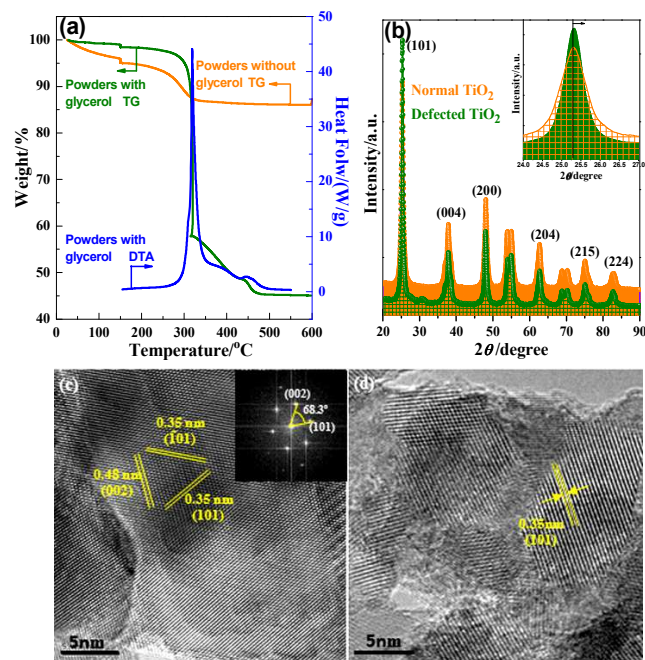


Figure 1. (a) TG and DTA profiles of intermediated powders produced by solvothermal treating TBT with and without glycerol. (b) XRD patterns of defected and normal TiO_2 . Inset: Enlarged XRD patterns of peak (101). (c), (d) TEM images of defected and normal TiO_2 . Inset in (c): Fast-Fourier transform pattern of defected TiO_2 .

loss of the powders in the range of 200–470 °C is 52.9%, which is close to the theoretical weigh loss (52.1%) of TiO₂ to TiO₂.⁴⁵

After calcination at 470 °C for 1 h, the final product (referred as defected TiO₂) can be undoubtedly identified as anatase TiO₂ (JCPDS no. 21-1272) without any other phases or impurities (Figure 1b and Figure S4, SI). The sole Raman-active modes (Figure S5, SI) at around 146, 399, 519 and 641 cm⁻¹ confirm the formation of pure anatase phase.^{48–49} TEM image (Figure 1c) shows the interplanar distances of (002) and (101) planes of anatase TiO₂,⁵⁰ which means the exposed facet is (010) facet. The fast Fourier transform pattern (inset in Figure 1d) also supports this conclusion, with the angle of 68.3° identical to the theoretical value of angle between (101) and (001) facets.^{50–51} In addition, the reference sample synthesized without glycerol (referred as normal TiO₂) is also anatase TiO₂ exposed with (101) facet, see the XRD pattern (Figure 1b) and TEM image (Figure 1d).

3.2. Ti defects in TiO₂

Although the two TiO₂ samples both exhibit anatase phase, element analysis shows they have very different composition. As shown in Table 1, the Ti/O molar ratio in bulk determined by chemical titration is very close to the surface ratio detected by XPS, indicating that the as-prepared TiO₂ samples have homogenous composition from surface to inner bulk. Normal TiO₂ produced without glycerol shows nearly stoichiometric composition, but the Ti/O ratio in defected TiO₂ produced with glycerol is only 0.452, much lower than the stoichiometric ratio. Basically, there are two possibilities responsible for the unstoichiometry of defected TiO₂ (Scheme 1): Ti vacancies and/or oxygen interstitials (O_{int}).

To get more information about the defected TiO₂, EPR spectra were recorded. Under low temperature, many defect-related species and vacancies in TiO₂ can be detected. The EPR signal of Ti³⁺ defects, O₂⁻ and oxygen vacancies (V_O) locate at $g=1.960\sim 1.990$, 2.020 and 2.003,^{10,48,52} respectively. As shown in the inset of Figure 2a, normal TiO₂ has very weak signal at $g=1.990$ at 120 K, which can be assigned to the existence of trace Ti³⁺-oxygen vacancy associates. Generally, the EPR signals of TiO₂ are visible only at sufficiently low temperature.^{14,49,52–53} Surprisingly, defected TiO₂ has a remarkably strong EPR signal at $g=1.998$ under both room temperature (298 K) and 120 K (Figure 2a, b). This signal can not be indexed to any species reported in literatures, such as Ti³⁺, O₂⁻, and V_O, suggesting the formation of a new species of defects. Moreover, the Ti2p XPS spectrum (Figure 2c) is well symmetrical, no shoulder band appeared at 456.9 eV that is associated with Ti³⁺ defect,⁵⁴ supporting that there is no Ti³⁺ and O₂⁻ species. In addition, the absence of peak at 457.3 eV in the Ti2p XPS spectrum rules out the existence of Ti-H bonds,⁵⁵ and the presence of other doped impurities (mainly C atoms) is excluded by EDX and XPS analysis (Figure S6, SI).

To determine the defect structure of defected TiO₂, DFT calculations on the cell structure were conducted.

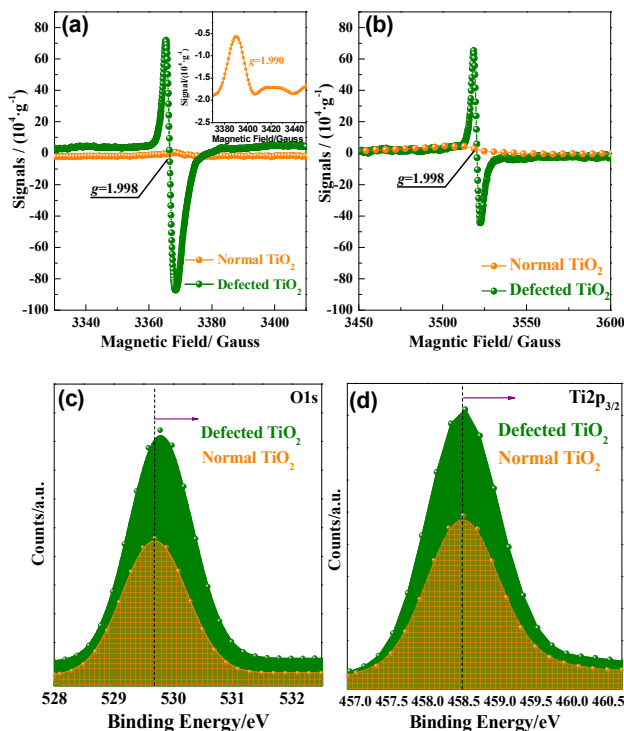


Figure 2. (a) Low temperature (120 K) and (b) room temperature (298 K) EPR spectra of defected and normal TiO₂. Inset in (a): enlarged EPR spectrum of normal TiO₂. (c) O 1s and (d) Ti2p_{3/2} XPS spectra of defected and normal TiO₂.

The optimized cell units containing V_{Ti} (Ti₁₅O₃₂, Ti/O=0.469) and O_{int} (Ti₁₆O₃₃, Ti/O=0.485) are shown in Figure 3, with the lattice constants summarized in Table 1. Calculation predicts that the presence of V_{Ti} makes the *c* axis to shrink heavily whereas the *a* and *b* axes to expand slightly. On the contrary, the presence of O_{int} makes *c* axis to expand. Actually in the XRD pattern (Inset in Figure 1b), the (101) peak of defected TiO₂ is shifted towards higher angle compared with that of normal TiO₂, suggesting the lattice constants are changed. As shown in Table 1,

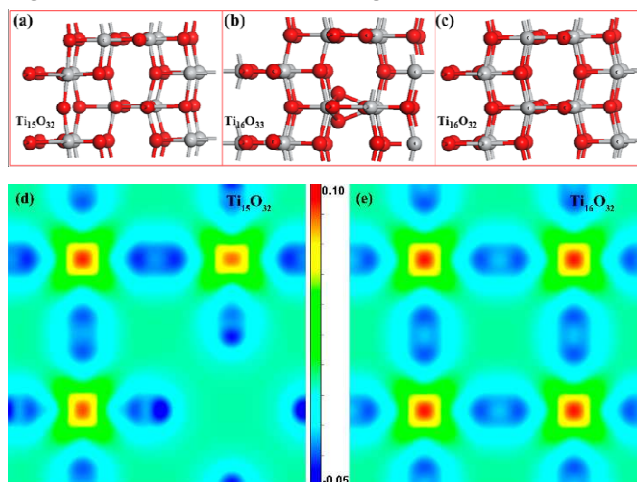


Figure 3. (a), (b), (c) Optimized cell structures of Ti-defected (Ti₁₅O₃₂), O-interstitial (Ti₁₆O₃₃) and normal anatase (Ti₁₆O₃₂) TiO₂, respectively. (d), (e) Charge density difference of Ti-defected (Ti₁₅O₃₂) and normal (Ti₁₆O₃₂) TiO₂, respectively.

Table 1. Lattice constants, molar ratio and electrical properties of normal and defected TiO₂.

Samples	a/ Å	b/ Å	c/ Å	Ti/O ratio		Resistivity×10 ⁻⁴ /(Ω cm)	Mobility×10 ⁻⁴ /(cm ² /V.s)	Hall coefficient /(cm ³ /C)	Carrier type
				Bulk	Surface				
26-1272 ^a	3.785	3.785	9.514	0.500	0.500	-	-	-	-
Normal TiO ₂	3.787	3.787	9.513	0.496 ^c	0.498 ^d	1.497	0.223	-33.3	n
Defected TiO ₂	3.790	3.790	9.487	0.452 ^c	0.456 ^d	0.967	1.390	+134	p
Ti ₁₆ O ₃₂ ^b	3.804	3.804	9.481	0.500	0.500	-	-	-	-
Ti ₁₅ O ₃₂ ^b	3.811	3.811	9.372	0.469	0.469	-	-	-	-
Ti ₁₆ O ₃₃ ^b	3.811	3.807	9.511	0.485	0.485	-	-	-	-

^a Standard JCPDS card of anatase TiO₂; ^b cluster calculated using DFT; ^c calculated from chemical titration; ^d calculated from XPS measurement.

the *c* axis of defected TiO₂ is shortened whereas the *a* and *b* axes are elongated compared with those of normal TiO₂. This experimental result is in agreement with the computed V_{Ti} mode instead of the O_{int} mode. We further calculated the charge density of V_{Ti} mode. The neighboring O and Ti atoms of V_{Ti} get less electrons compared with those on normal sites (Figure 3d,e), which is consistent with the increased binding energy in O 1s and Ti 2p XPS spectra of defected TiO₂ (Figure 2c,d). Based on the experiment and calculation, the un-stoichiometry of defected TiO₂ is attributed to the presence of Ti vacancies in the lattice.

The defects in TiO₂ were further characterized by positron annihilation. As shown in Figure S7 (SI) and Table 2, four positron lifetime components are observed for normal and defected TiO₂. The shorter lifetime component (τ_1) is caused by the free annihilation of positrons in defect-free crystal.⁵⁶ In a disordered system, small vacancies or shallow positron traps can reduce the surrounding electron density and thus increase the lifetime of τ_1 .⁵⁶⁻⁵⁹ The τ_1 for normal and defected TiO₂ is 264 ps and 287 ps, respectively, longer than that of defect-free TiO₂ crystal (178 ps),⁵⁶ indicating the existence of monovacancies or point defects in TiO₂.^{16, 56-59} The very low intensity (3.0%) for normal TiO₂ corresponds to the existence of small amount of oxygen vacancies. Interestingly, the intensity of I_1 for defected TiO₂ reaches 48.5%, which indicates the crystals have many monovacancies or point defects. Hahn et al pointed out that metal vacancies in metal oxides exist in form of point defect.⁶⁰ In defected TiO₂, metal vacancies are the major defects. Therefore, the lifetime component of τ_1 in defected TiO₂ is attributed to Ti point vacancies. Additionally, the longer lifetime components of τ_2 and τ_3 are resulted from the positrons trapped by larger size defects, and the longest component (τ_4) is pos-

sibly due to the annihilation of orthopositronium atoms formed in the large voids present in TiO₂.^{16,56}

In our recent work, Zn-defected ZnO was synthesized by calcining zinc glycerolate (ZnGly),³⁹ where the lamelleted structure of ZnGly plays crucial role in constructing the metal defected crystals. Actually, TiGly has parallel chains built up from edge-sharing Ti⁴⁺O₆ octahedrals,^{47,61} similar to the structure of ZnGly, so the formation mechanism of Ti vacancies should be similar to that of Zn vacancies. During calcination, inter-chains organic groups of TiGly is gradually removed, and the remaining Ti-O-Ti parallel lattice chains simultaneously conjunct with each other to form TiO₂ crystals. It has been reported the defects in metal oxides are sensitive to the circumstance (O-rich or metal-rich) of synthesizing process.⁶²⁻⁶⁴ In particular, theoretical calculations predicted that metal vacancies can be formed easily under O-rich environment.^{6,8} In the present case, the removal of inter-chains glycerin groups may result in O-rich environment between the Ti-O-Ti parallel lattice chains, and thus metal defects are formed.

3.3. *p*-Type conductivity and room-temperature ferromagnetism

TiO₂ is intrinsic n-type semiconductor without any ferromagnetism. As mentioned above, V_{Ti} is acceptor-type defects, so defected TiO₂ may show p-type conductivity if the concentration of V_{Ti} is high enough. As shown in Figure 4a, the valence band of defected TiO₂ starts from 1.96 eV, which is closer to the Fermi level (0.0 eV in the valence band spectrum) compared with that of normal TiO₂ that starts from 2.12 eV, suggesting defected TiO₂ possesses p-type characteristic.^{25,65}

Hall Effect measurement was conducted to get direct evidence for the type of electrical conductivity, see Table 1. The Hall coefficient is positive for defected TiO₂, which

Table 2. Positron lifetime parameters (lifetime (τ), and intensity (I)) of normal and defected TiO₂.

Samples	τ_1 /ps	I_1 /%	τ_2 /ps	I_2 /%	τ_3 /ps	I_3 /%	τ_4 /ns	I_4 /%
Normal TiO ₂	264	3.0	326	79.1	405	17.4	1.07	0.483
Defected TiO ₂	287	48.5	320	4.1	364	47.4	4.17	0.020

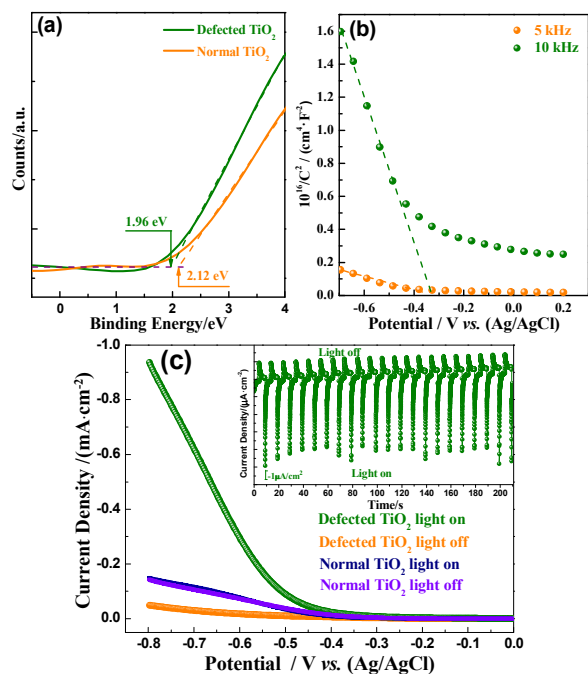


Figure 4. (a) XPS valence band spectra of defected and normal TiO₂. (b) Mott-Schottky plots measured in a standard three-electrode setup using defected TiO₂ electrode as working electrode. (c) Current-voltage (I-V) curve of defected and normal TiO₂, inset in (c): transient photocurrent (chronoamperometric) curve of defected TiO₂ at -0.45 V vs. Ag/AgCl.

confirms this material is truly p-type and conducts *via* holes.⁶⁶⁻⁶⁸ As contrast, normal TiO₂ is n-type with negative Hall coefficient. Furthermore, the presence of V_{Ti} increases the charge mobility ($1.39 \times 10^4 \text{ cm}^2/\text{V}\cdot\text{s}$ for defected TiO₂ vs. $2.23 \times 10^3 \text{ cm}^2/\text{V}\cdot\text{s}$ for normal TiO₂). It was reported that the mobility of Mn-doped p-TiO₂ is lower than that of pure TiO₂.²⁸ Unlike foreign p-type dopants, V_{Ti} has no deteriorating effect on the charge transfer.

The electrochemical impedance measurements and photoelectrochemical characterizations were also performed to determine the conductivity of defected TiO₂. The evidence for p-type conductivity comes from the negative slope of linear part of Mott-Schottky plots (Figure 4b).⁶⁹ Correspondingly, defected TiO₂ photocathode shows obvious cathodic current under illumination (Figure 4c) with the photocurrent increasing progressively with the increase of negative potential applied (due to increased band bending), also see the transient current ($I-t$) curves (Inset in Figure 4c) with a sharp cathodic current peak appears upon the turn-on of light. On the contrary, normal TiO₂ exhibits positive slope in the Mott-Schottky plots (Figure S8, SI) and do not show any cathodic current under similar measurement conditions (Figure 4c). Besides, the photocurrent onset potential (-0.40 V vs. Ag/AgCl) of defected TiO₂ is more negative than the V_{FB} , which is also consistent with the feature of p-type photoelectrode.⁷⁰

DFT calculations indicate that the presence of V_{Ti} in TiO₂ causes ferromagnetism (Table S1, SI). The magnetic response was measured as a function of magnetic field

strength ($M-H$) at 300 K (Figure 5a). Well-defined hysteresis loop is observed, indicating the defected TiO₂ crystal is ferromagnetic at room temperature. From the $M-T$ curve in a field of 4000 Oe (Figure 5b), the Curie temperature is higher than 300 K. The spontaneous magnetic moment deduced from the saturated magnetization value is $0.025 \text{ emu}\cdot\text{g}^{-1}$ and the coercivity is about 18 Oe, which is significantly higher than the reported magnetization of Co-doped TiO₂ nanocrystalline (Ti_{0.985}Co_{0.015}O₂, $1.57 \times 10^{-3} \text{ emu}\cdot\text{g}^{-1}$).⁷¹ In addition, according to DFT calculation (Table S1, SI), the O_{int} mode does not have any ferromagnetism.

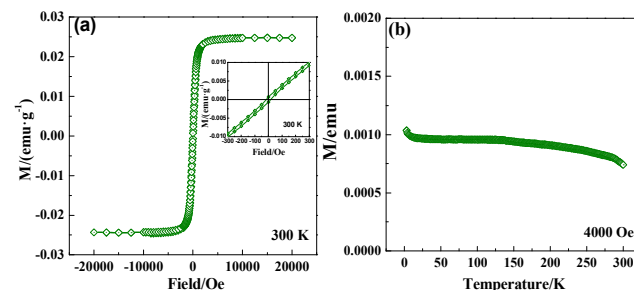


Figure 5. (a) Magnetization ($M-H$) curves of defected TiO₂ measured at 300 K. (b) $M-T$ curve of defected TiO₂ in the field of 4000 Oe.

3.4. Photocatalytic performance

TiO₂ is the most widely studied photocatalyst in energy and environment fields. Here we tested the photocatalytic activity of defected TiO₂ in three types of reactions: H₂ generation under UV light, organic pollutant (RhB, MO and phenol) degradation under UV light, and self-sensitized RhB degradation under visible light. The photoreaction under UV light involves the formation, separation and transfer of electron-hole pairs, surface reaction, with charge recombination as the major side process.²⁴ The sensitized reaction under visible light involves the excitation of dye, injection of electron from dye to TiO₂, and then surface reaction, with the electron back-injection as the side process.¹⁵ No matter what type of photocatalysis is, the charge transfer in TiO₂ crystal is one key factor determining the efficiency.

The reaction rate shown in Figure 6a derived from pseudo-first-order fitting of data in Figure S9 (SI) is used to evaluate the degradation photoactivity. Obviously, defected TiO₂ is much more active than normal TiO₂ under both UV and visible illumination. The phenol degradation rate of defected TiO₂ is 7.0-fold of normal TiO₂. Figure 6b shows the time course of H₂ evolution, defected TiO₂ exhibits stable H₂ release rate of $29.8 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, whereas normal TiO₂ produces only $6.8 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under the same conditions.

Defected and normal TiO₂ are both pure anatase phase, and have similar morphology (Figure S10, SI), comparable BET surface area ($59 \text{ m}^2\cdot\text{g}^{-1}$ and $72 \text{ m}^2\cdot\text{g}^{-1}$ for normal and defected TiO₂, respectively) and identical optical absorption (Figure S11, SI), so the influences of

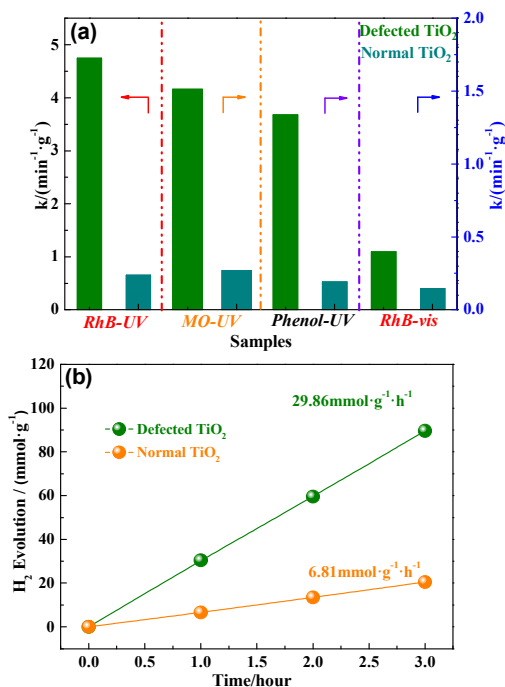


Figure 6. (a) Reaction rate of photodegradation of organic pollutants. (b) Time course of hydrogen generation.

morphology, surface area and optical property on the photoactivity are excluded. The only difference is the presence of metal defects in defected TiO₂. Actually, it has been reported that increasing the concentration of Ti vacancies can increase the electrical conductivity and the mobility of electronic charge carriers.²⁹ More specifically, as shown in Figure 7a, the calculated density of states (DOS) of defected TiO₂ has a new band transition above the top of original VB, which means the VB width is raised. The VB width intrinsically controls the mobility of holes, and wider VB results in higher mobility of holes generated.⁷²⁻⁷³ Therefore, the charge transfer and separation in defected TiO₂ is improved.

The more efficient charge transfer and separation of defected TiO₂ is confirmed by experiments. Photoluminescence (PL) emission signal caused by charge recombination can reflect the charge separation in bulk. As shown in Figure 7b, defected TiO₂ has smaller PL intensity than normal TiO₂, which indicates a more efficient transfer and separation of photo-induced charge pairs. In electrochemical impedance spectroscopy, the radius of arc of Nyquist plots can be used to evaluate the charge transfer resistance at the semiconductor/electrolyte interface, and smaller arc radius implies smaller charge transfer resistance.⁷⁴ Figure 7c shows that defected TiO₂ exhibits smaller radius, so the charge in defected TiO₂ can be quickly transferred to reactant through the solid/liquid interface and consumed by chemical reaction. The quick consumption of surface charges in turn retards the charge recombination or back charge transfer side processes.

The stability of surface defects is important because photocatalysis is very sensitive to them. XPS analysis reveals the surface Ti/O ratio, binding energies of Ti and lattice O of defected TiO₂ do not change after 4 months

storage under atmosphere (Figure S12, SI). Moreover, defected TiO₂ shows stable activity in 5 recycles of photocatalytic reactions (Figure S13, SI), and the surface defects are well retained after the recycling as evidenced by XPS analysis (Figure S12, SI). These results indicate that the surface defects are stable under the reaction conditions and long-term storage.

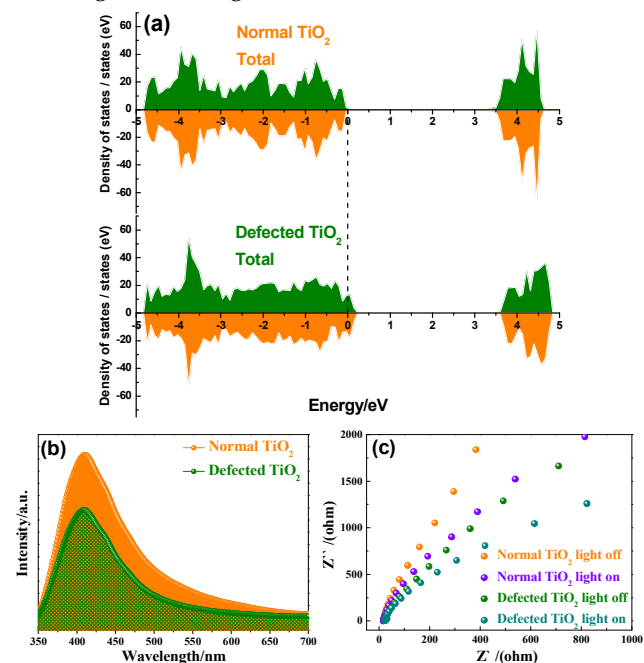


Figure 7. (a) Calculated total density of states of normal TiO₂ (Ti₁₆O₃₂) and defected TiO₂ (Ti₁₅O₃₂), (b) Steady state PL spectra of defected and normal TiO₂, (c) EIS Nyquist plot of defected and normal TiO₂.

4. CONCLUSIONS

We successfully synthesized undoped anatase TiO₂ with large amount of (9.5 mol%) Ti vacancies using a facile solvothermal treatment method. The presence of abundant V_{Ti} makes the *c* axis of anatase shrunk heavily whereas *a* and *b* axes elongated slightly, produces a strong EPR signal at $g=1.998$ even under room temperature, and widens the valence band top edge. V_{Ti} switches TiO₂ conductivity from n-type to p-type with higher charge mobility, and endows room temperature ferromagnetism higher than Co-doped TiO₂ nanocrystalline. Moreover, defected TiO₂ exhibits remarkably higher photocatalytic activity compared with normal TiO₂ because of the more efficient charge transfer in bulk and at semiconductor/electrolyte interface. It indicates that the metal vacancies can change the structure characteristics and physiochemical properties of undoped semiconductor and thus produce new kind of functional materials for chemical and physical devices.

ASSOCIATED CONTENT

Supporting Information.

Details of composition analysis, XRD pattern of intermediated powders, NMR spectra of TiGly, XPS spectrum, positron annihilation spectra, EDS spectra, Raman spectra, computed ferromagnetism of defected TiO₂, UV-vis DRS spectra, pho-

1 todegradation data, stability test, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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