**One-step synthesis of nonstoichiometric TiO₂ with designed (101) facets for
enhanced photocatalytic H₂ evolution**

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Abstract

Photocatalyst is widely applied in environmental remediation and energy conversion. Appropriately engineered band structures of semiconductor photocatalysts are beneficial for enhancing surface reactions under light irradiation. Exposing the highly reductive facets of TiO₂ crystals has been recognized as an efficient approach to promote photocatalytic reduction reaction. However, there is no report about the application of one-step solvothermal reaction for the synthesis of the TiO₂ crystals with (101) facets and *in-situ* doping. In this work, non-stoichiometric anatase TiO₂ microspheres with designed (101) facets were successfully synthesized by using one-step solvothermal reaction. The prepared non-stoichiometric anatase TiO₂ microspheres with designed (101) facets exhibited a great photocatalytic activity for H₂ evolution with a reaction rate of 3.4 times faster than that of anatase TiO₂ that was neither etched nor doped. The (101) facets of anatase TiO₂ were found to be able to generate and transmit more reductive electrons to promote the H₂ evolution in the photocatalytic reduction reaction. With the femtosecond time-resolved diffused reflectance measurement, the roles of self-doping Ti³⁺ as the photogenerated electrons trapping and (101) facets were further elucidated. Our findings might provide a new opportunity to develop an efficient, cost-effective and promising TiO₂-based catalyst for enhanced photocatalytic H₂ production.

Keywords: Self-doping, (001) facet etching, Photocatalytic reduction, Charge transfer dynamics

1. Introduction

Photocatalysis is an environmentally friendly process for environmental remediation and energy conversion [1]. Titania has been recognized as one of the most promising and suitable photocatalytic materials due to its abundant availability, nontoxicity, and high chemical stability [2]. In principle TiO_2 is an ideal photocatalyst. However, since photoinduced electron-hole pairs of anatase TiO_2 are easy to recombine, resulting in their lower photocatalytic activity, the capability to efficiently separate photoinduced electron-hole pairs needs substantial improvement [3]. So far, various approaches have been explored to improve the photocatalytic activity of TiO_2 .

Crystal facet is one of the most significant factors governing the photocatalytic performance of TiO_2 [4-6]. Some recent studies have demonstrated that the crystal facets play a critical role in improving photocatalytic activity of TiO_2 [7]. A new “surface heterojunction” concept was proposed based on the density functional theory calculations to highlight the effect of crystal facets on the photosynthetic activity of TiO_2 as a result of the transfer of photogenerated electrons and holes to (101) and (001) facets, respectively [8]. Single-molecule imaging and kinetic analysis of the fluorescence have further confirmed reaction sites by detecting reduced probe molecules located on the (101) facets, rather than the (001) facets of TiO_2 [9]. Meanwhile, strong evidence of charge separation on anatase TiO_2 crystals with selectively etched (001) facets was reported [10]. In this case, the appropriate corrosion on (001) facets could facilitate electron-hole separation and transfer.

Moreover, various experiments have shown that the (101) facets of TiO_2 with a higher thermodynamic stability exhibit a higher reactivity than the (001) facets in photocatalytic H_2 evolution [11, 12].

Recently, it has been reported that the reduced Ti^{3+} -containing TiO_2 (TiO_{2-x}), creates localized oxygen vacancy states, which are beneficial for the electron mobility [13]. Compared to the conventional doping, oxygen vacancy is facile self-doping without inducing any impurity elements. To date, several methods have been developed to synthesize the reduced TiO_2 with improved photocatalytic performance. For instance, a metallic zinc-assisted method has been used to synthesize Ti^{3+} doped TiO_{2-x} [14]. Some other methods such as plasma treatment [15], laser irradiation [16], or high-energy particle bombardment [17] have also been used to achieve the doping of Ti^{3+} into TiO_{2-x} . Although substantial progress on facet and doping has been made in preparing TiO_2 -based materials, exploration of one-step method to achieve in-situ Ti^{3+} self-doping TiO_2 with designed (101) facets for enhanced photocatalytic H_2 evolution is highly desired.

In this work, non-stoichiometric anatase TiO_2 microspheres with designed (101) facets were synthesized using a simple solvothermal method. Two strategies of facet-etching and doping were adopted to improve the photocatalytic reduction capacity of TiO_2 microspheres. Furthermore, the prepared non-stoichiometric anatase TiO_2 microspheres with (101) facets were used to produce H_2 under UV light irradiation to examine whether the facet etching and Ti^{3+} self-doping enhance its photocatalytic activity. The mechanisms behind the effects of self-doping Ti^{3+} as the

photogenerated electrons trapping and (101) facets were further elucidated using the femtosecond time-resolved diffused reflectance (TDR) measurement.

2. Materials and Methods

2.1 Sample preparation

All chemicals used in this work were analytical-grade reagents and used without further purification. The Ti^{3+} solution was synthesized following the method reported previously [18, 19]. Briefly, 0.15 g of NH_4F was dissolved in 15 mL of Ti^{3+} solution in 50 mL of beaker. After 15-min stirring, 25 mL of ethanol was added to the mixed solution. After additional 15-min stirring, the solution was transferred into a polytetrafluoroethylene (Teflon)-lined stainless autoclave with a total volume of 50 mL. The solvothermal synthesis was carried out at 160 °C for 4 h (denoted $\text{TiO}_2\text{-1}$) and 12 h (denoted $\text{TiO}_2\text{-2}$) in an electric oven respectively. The autoclave was cooled to room temperature after the growth process. Then, the obtained samples were ultrasonically cleaned using ethanol and water in sequence. Before the photocatalytic properties were measured, all the samples were treated with NaOH (0.1 M) to remove the adsorbed fluorine ions. The third sample ($\text{TiO}_2\text{-3}$) was obtained by annealing the sample ($\text{TiO}_2\text{-2}$) at 500 °C for 4 h.

To prepare Pt/ TiO_2 composites, the catalyst (2 mg) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.02 mg of Pt) were dispersed into an aqueous methanol solution (1 mL of CH_3OH and 4 mL of H_2O) in a glass tube. The mixture was under irradiation (UV light 365 nm) with

magnetic stirring for half an hour. Then, the Pt-loaded TiO₂ samples were cleaned with water.

2.2 Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were obtained by a diffractometer (TTR-III, Rigaku Co., Japan) using Cu K α radiation source ($\lambda=1.541841$ Å) at a scan speed of 8°/min to determine the crystal phase of the obtained samples. The accelerating voltage and the applied current were 40 kV and 200 mA, respectively. The morphology and microstructure of the TiO₂ nanostructures were characterized by field-emission scanning electron microscope (SEM, SIRION200, FEI Co., USA). The morphology and structure were characterized with a transmission electron microscope (TEM, JEM2100, JEOL Co., Japan). High-resolution transmission electron microscopy (HRTEM) images were obtained on a transmission electron microscope (JEM-2010, JEOL Co., Japan) with an accelerating voltage of 200 kV. The low temperature electron paramagnetic resonance (EPR) spectra of the samples were recorded at 150 K to confirm the presence of Ti³⁺ (JES-FA200, JEOL Co., Japan) (140 K, 9064 MHz, 0.998 mW, X-band). The g values were determined using a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard. The optical absorbance spectra of the samples were obtained using a UV-vis spectrophotometer (SOLID3700, Shimadzu Co., Japan). X-ray photoelectron spectroscopy (XPS) analysis was conducted to investigate the chemical state of samples (PHI 5600 XPS spectroscopy, Ulvac-Phi Co., Japan). The measurement of

surface area was conducted using the Brunauer-Emmett-Teller (BET) method on TriStar II 3020 V1.03 (Micromeritics Instrument Co., USA).

2.3 Photoelectrochemical measurements

Electrochemical measurements were all performed on an electrochemical station (ALS CH 660B, CH Instruments Inc., USA). The transient photocurrent and electrochemical impedance spectroscopy (EIS) were measured in a homemade three-electrode system, in which commercial glassy carbon electrode (GC, an effective area of 0.071 cm^2) deposited with TiO_2 samples was used as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. To determine the charge-transfer resistance at the electrode/electrolyte interface, EIS analysis was conducted at an open-circuit potential (OCP) by applying an AC voltage amplitude of 5 mV within the frequency range from 10^5 to 10^{-2} Hz in 0.2 M Na_2SO_4 solution.

2.4 Photocatalytic measurements

Photocatalytic H_2 evolution from methanol/water solution with the H_2PtCl_6 solution and TiO_2 catalyst was evaluated using a glass tube. The light source was a DC 12 V LED (POT-365, Asahi Spectra Co., Japan). The catalyst (2.0 mg) and 53 μL of H_2PtCl_6 solution (0.02 mg Pt) were dispersed into an aqueous methanol solution (1 mL of CH_3OH and 4 mL of H_2O) with magnetic stirring. The H_2 yield was quantified by a gas chromatograph (GC) (GC-8A, Shimadzu Co., Japan) equipped with a

thermal conductivity detector and Ar gas as the carrier.

2.5 Time-resolved diffuse reflectance spectral measurements

The TDR test was conducted by the pump and probe method using a regeneratively amplified titanium sapphire laser (Spectra-Physics, Spitfire Pro F, 1 kHz, Newport Inc., USA) pumped by a Nd:YLF laser (Spectra-Physics, Empower 15, Newport Inc., USA). The seed pulse was generated by a titanium sapphire laser (Spectra-Physics, Mai Tai VFSJW; fwhm 80 fs, Newport Inc., USA). The fourth harmonic generation (330 nm, 3 μ J pulse⁻¹) of the optical parametric amplifier (Spectra-Physics, OPA-800CF-1, Newport Inc., USA) was used as the excitation pulse. A white light continuum pulse generated by focusing the residual of the fundamental light on a sapphire crystal after the computer controlled optical delay, was divided into two parts and used as the probe and reference lights, of which the latter was used to compensate the laser fluctuation. Both probe and reference lights were directed to the sample powder coated on the glass substrate, and the reflected lights were detected by a linear InGaAs array detector equipped with the polychromator (Solar, MS3504, Newport Inc., USA). The pump pulse was chopped by the mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of spectra with and without the pump, from which the absorption change (% Abs) induced by the pump pulse was estimated. All measurements were carried out at ambient temperature around 25 °C.

3. Results and discussion

3.1 Structural, morphological and chemical characteristics of the TiO_{2-x} microspheres

The XRD patterns of the three samples in **Figure 1a** show similar diffraction peaks, indicating that the obtained samples were anatase TiO_2 and no overlapping of this peak with any other peaks from other phases occurred, in agreement with the standard anatase (JCPDS No. 21-1272). The morphologies of the as-obtained anatase TiO_2 microspheres with different solvothermal reaction times are shown in **Figures 1b and c**. The spheres are uniform with an average size of $\sim 3 \mu\text{m}$. In the high magnification micrographs (insets of **Figures 1b and c**), the constituent nanosheets and etching nanosheets are clearly observed. After etching, gaps and pores were formed on the self-assembly microsphere surface. As shown in **Figure 1d**, the morphology of sample TiO_{2-3} remains keeping the basic shape with forming small particles after annealing sample TiO_{2-2} . The XRD pattern, SEM images and energy-dispersive x-ray spectroscopies of Pt/ TiO_{2-2} sample are shown in Figure S1.

To further explore the morphological development and formation mechanism of the three dimensional hierarchical structures of anatase TiO_2 microspheres, more systematic experiments were carried out. **Figure 2** shows a schematic representation of the growth process of a microsphere, synthesized by solvothermal treatment at 433 K with different reaction times in a solution containing fluorine ions. From the SEM images of the serial samples, nanosheets and nanoparticles were produced in solution

at the initial stage of the reaction (**Figure 2a**). Then, the nanosheets and nanoparticles gathered to generate nanospheres (**Figure 2b**), and finally the nanospheres continued growing to form microspheres with exposed major (101) and (001) facets (**Figures 2c, d**) [20].

The SEM images of the products at different reaction times from 3 to 6 h (**Figures 2d–f**) show that the etched anatase microspheres in **Figure 1c** were developed from the selective etching of the anatase TiO₂, produced at the initial stage of the reaction (**Figure 2d**). Due to the etching effect of the excess HF in the reaction, numerous pits were generated simultaneously at the joint among the anatase TiO₂ nanosheets at the early stages. These pits were then enlarged gradually, and the center of the (001) facets almost disappeared by etching in the reaction. As a result, complex nanostructures were generated (**Figure 2f**). Interestingly, when the reaction time was prolonged to 12 h, more complex structures with an entirely etching (001) facets morphology was obtained (inset of **Figure 1d**). Such a formation process could be considered as the result of the continuous etching of the original structures [20, 21]. In this process, HF has an etching effect on the (001)-faceted anatase TiO₂ in the presence of water and the etching usually occurs on the (001)-faceted surfaces. Moreover, the degree of etching and the morphology of the resulting products vary remarkably by prolonging the reaction time.

The XPS analysis was used to probe the chemical state of Ti to gain more insight into the oxygen vacancies in the TiO₂ samples. The XPS spectrum of Ti 2p shown in **Figure 3b** exhibits two peaks at 458.6 and 464.3 eV with a spin–orbital doublet

splitting ($\text{Ti } 2p_{3/2}$ – $\text{Ti } 2p_{1/2}$) of 5.7 eV to be assigned to 4+ oxidation state of titanium as Ti^{4+} [22]. No peak corresponding to Ti^{3+} around 458.1 eV was detected. This result demonstrates that the surface of blue TiO_{2-x} was dominated by Ti^{4+} , ruling out the presence of Ti^{3+} on the sample surface, indicating that stoichiometric TiO_2 microspheres were formed on the surface of non-stoichiometric TiO_{2-x} core-microcrystals [23]. The radius of the TiO_2 microsphere was about 1.5 μm , larger than the detection limit of XPS [13]. The TiO_{2-x} microspheres were much stable than the previously reported TiO_{2-x} NPs, prepared through H_2 -reduction method and not stable due to the presence of oxygen vacancies on the surface of NPs [24].

The low temperature EPR was recorded at 130 K to identify the presence of Ti^{3+} in the TiO_{2-x} microspheres and the results are shown in **Figure 4**. At this temperature, the anisotropic g tensors for the sample could not be resolved. TiO_{2-2} had a very strong EPR signal at $g=1.97$ to be attributed to subsurface paramagnetic Ti^{3+} centers [25, 26]. Weak signals were seen for TiO_{2-1} and TiO_{2-3} , indicating that a great amount of Ti^{3+} was produced in the TiO_{2-x} microspheres by prolonging the solvothermal reaction time or annealing sample in air. In the annealing progress, Ti^{3+} can be oxidated to generate Ti^{4+} in air and the oxygen vacancy should decrease [27, 28].

The EPR spectra also exclude the presence of Ti^{3+} on the sample surface. Since the surface Ti^{3+} is prone to adsorb atmospheric O_2 , which would be reduced to O_2^- and show an EPR signal at $g=2.02$ [29]. However, no EPR signal at $g=2.02$ was observed.

The microstructures of the etching microspheres were further examined by using

TEM (**Figures 5a, b**), high-resolution TEM (**Figure 5c**), and selected-area electron diffraction (SAED) (inset of **Figure 5c**). The TEM image in **Figure 5a** shows that the obtained TiO_{2-x} microspheres had a uniform average size of ca. 3 μm , corresponding to the SEM (**Figure 2**) and the microstructure image of a representative microsphere respectively. The distinguished one-dimensional lattice fringes in **Figure 5c** indicate that the obtained etching TiO_{2-x} microspheres were well crystallized with a lattice fringe spacing of 0.36 nm (measured by Digital Micrograph in **Figure 5d**), corresponding to the (101) facets of anatase TiO_2 . More importantly, it provides direct evidence that (001) facets were etched and (101) facets remained. This is in agreement with the above analysis of the morphological development and formation mechanism.

Compared with etching and non-etching TiO_2 , the BET surface area is also important for photocatalytic activity. As shown in **Figure 6**, the obtained samples had normalized BET surface areas of 2.7 (TiO_2 -1), 3.2 (TiO_2 -2), and 2.5 (TiO_2 -3) m^2/g from nitrogen adsorption-desorption isotherm plots, respectively. There was a small difference in BET surface area for the three samples.

3.2 Optical and photoelectrochemical properties of the TiO_{2-x} microspheres

The optical response of Ti^{3+} self-doped TiO_{2-x} microspheres samples is shown in **Figure 7** with a comparison to that of other samples. For the Ti^{3+} self-doped TiO_{2-x} microspheres (**Figure 7**, red (TiO_2 -2)), a considerably large absorption tail in the visible regions was observed, in consistent with the change in color of the powder

solution (inset in **Figure 7**). This gives clear evidence that the non-stoichiometric TiO_{2-x} microspheres contained a large number of oxygen vacancies [23]. These results indicate that the Ti^{3+} -induced visible-light absorption is formed as isolated states between the forbidden gap in TiO_2 , as reported previously [13]. Theoretical studies also demonstrated that Ti^{3+} inside the bulk TiO_2 and the high oxygen vacancy concentration could form an electronic state vacancy band below the conduction band, which is responsible for the band-gap narrowing [25].

The responsive photocurrent intensity of the obtained samples under UV irradiation can reflect the overall photoelectron-conversion process (**Figure 8a**) [30]. The photocurrent on TiO_2 -2 was nearly 2 and 6 times higher those on TiO_2 -3 and TiO_2 -1, respectively. This revealed that the Ti^{3+} self-doped TiO_2 with designed (101) facet was beneficial for photoinduced charge separation and transport.

Correspondingly, EIS result can provide additional information and better understanding on the interfacial reactions of photoexcited electrons in photocatalysis [30]. **Figure 8b** shows the EIS spectra of the photocatalysis using TiO_2 -1, TiO_2 -2, and TiO_2 -3 respectively. The measured smaller arc radius on the TiO_2 -2 electrode clearly exhibited an enhanced electrochemical conductivity, reduced electron transfer resistance, and magnified separation and transfer ability of electro-generated carriers [31], compared to the other samples (**Figure 8b**).

3.3 Photocatalytic H_2 evolution over the TiO_{2-x} microspheres

The photocatalytic H_2 evolution from water/methanol (4:1 mL) by the TiO_2

catalysts (deposited with Pt as cocatalyst 1wt%) was investigated. **Figure 9** shows that the H₂ evolution rate was elevated by facet etching and Ti³⁺ self-doping. On one hand, the photocatalytic H₂ evolution of TiO₂-3 with (001) facet etching was 2.6 times higher than that for TiO₂-1. (001) and (101) facets are oxidation and reduction facets, respectively. Thus, the predominated presence of reductive (101) facet is beneficial for photocatalytic H₂ evolution. On the other hand, photocatalytic H₂ evolution of TiO₂-2 was 1.3 times higher than that for TiO₂-3, demonstrating that the changed electronic structure induced by Ti³⁺ self-doping lead to the enhanced h⁺/e⁻ separation and increased photocatalytic H₂ evolution. In this case, both Ti³⁺ self-doping and facet etching played important roles in charge separation and electron transfer [10]. Because of the small difference of BET for the samples (TiO₂-1, 2 and 3), their capability of H₂ evolution per unit surface area should be examined. The normalized H₂ evolution capacities of the Pt-loaded samples were 116, 334, and 326 μmol/(h·m²), respectively. This result also indicates that facet-etching played an important role in photocatalytic activity, but the effects of both BET surface and Ti³⁺-doping photocatalytic activity are limited. From the repeated runs of H₂ evolution (**Figure S3**), the Pt/TiO₂-2 sample exhibited a good stability. Moreover, the EPR spectra of the Pt/TiO₂-2 sample were similar to those of the TiO₂-2 sample (**Figure S4**). This result indicates that the TiO₂-2 sample was stable after the photocatalytic reaction.

3.4 Charge transfer dynamics and reaction mechanism on the TiO_{2-x} microspheres

As a powerful technique [32], the femtosecond TDR spectroscopic measurement was performed to clarify the charge carrier dynamics in the photocatalytic reaction under UV light irradiation (**Figure 10**). After 330 nm laser excitation of TiO₂-2 in ambient air (**Figure 10b**), a broad absorption band appeared in the near-infrared region, which was superimposed with trapped and free electrons in TiO₂-2. Similar absorption spectra were observed for TiO₂-1 and TiO₂-3 (**Figures 10a, c**). During the period of 0-10 ps, the transient absorption of TiO₂-2 decayed rapidly when compared with TiO₂-1 and TiO₂-3 (**Figure 10d**). After the sufficient generation of charge carriers upon the 330-nm laser excitation of TiO₂-1 and TiO₂-3, electrons were excited from valance band O 1s to the conduction band Ti 3d to be directly trapped ($\tau_1 = 6.1$ and 6.4 ps, respectively; **Table 1**). On the other hand, the generated holes were separated and localized at the O 1s state valance band at the same time [33]. After the equilibrium between electrons in the surface trap and the bulk ($\tau_2 = 41$ and 62 ps, respectively; **Table 1**), the favorable reduction pathway and charge recombination occurred ($\tau_3 = 472$ and 532 ps, respectively; **Table 1**) in TiO₂-1 and TiO₂-3. Therefore, TiO₂-3 with a higher efficiency exhibited a longer lifetime of two components ($\tau_2 = 62$ ps and $\tau_3 = 532$ ps) than those for TiO₂-1, exhibiting the similar photocatalytic efficiency under the UV irradiation. However, it is unusual that TiO₂-2 with a higher efficiency exhibited a shorter lifetime of the components ($\tau_2 = 33$ ps and $\tau_3 = 342$ ps) than both TiO₂-1 and TiO₂-3. It might be attributed to the fact that Ti³⁺ served as a midgap state and captured the position of carriers [13]. As a result, the shorter lifetime of TiO₂-2 (τ_1 3.8 ps) observed at the first decay component corresponded to Ti³⁺ at

midgap state compared with TiO₂-1 and TiO₂-3. Then, TiO₂-2 achieved the equilibrium between electrons in the surface trap and the bulk immediately ($\tau_2 = 33$ ps), and the favorable reduction pathway and charge recombination occurred more rapidly ($\tau_3 = 342$ ps) [34].

Conclusions

In summary, nonstoichiometric TiO₂ with desired (101) facets TiO_{2-x} microspheres was synthesized using a one-step solvothermal method. The obtained nonstoichiometric TiO₂ with designed (101) facets (TiO₂-2) exhibited the highest photocatalytic H₂ evolution (1.3 and 3.4 times higher those of TiO₂-3 and TiO₂-1, respectively). Experimental results show the presence of bulk Ti³⁺ defects generates mid gap electronic states within the band gap of TiO₂ microspheres, and significantly improve the efficiency of electron-hole separation, thus greatly enhance the photocatalytic activity and H₂ production. Moreover, the etching (101) facet in the TiO₂ microspheres was also beneficial for electron-hole separation and transfer and accordingly the H₂ evolution. This work provides a simple but efficient approach to prepare the TiO₂ with simultaneous facet-etching and self-doping. Our findings open up a new avenue for efficient hydrogen generation based on the earth-abundant, scalable TiO₂ catalysts, and may have implications in the optimization of other transition metal oxide electrocatalysts for energy conversion systems.

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445

Table 1 Kinetic parameters of decays for TiO₂ catalysts under the UV laser excitation

Sample	UV laser (330 nm, 3 $\mu\text{J pulse}^{-1}$)		
	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
TiO ₂ -1	6.1	41	471
TiO ₂ -2	3.8	33	342
TiO ₂ -3	6.4	62	532

Figure Legends

Figure 1. (a) XRD patterns of the products; (b-c) SEM images of the products at different solvothermal reaction times (b) TiO₂-1 (4 h), (c) TiO₂-2 (12 h), and (d) SEM image of TiO₂-3 after annealing. The scale bars are 10 μ m, and insets are 1 μ m.

Figure 2. SEM images of the products from the one-step solvothermal reaction at different reaction times (a) 1 h, (b) 1.5 h, (c) 2 h, (d) 3 h, (e) 4 h, and (f) 6 h. The scale bars are 2 μ m.

Figure 3. XPS spectra of the obtained TiO_{2-x} microspheres: a high resolution characteristic peak of Ti 2p recorded from the pristine surface layer prepared at different solvothermal reaction times.

Figure 4. The X-band EPR spectra of Ti³⁺ self-doped TiO_{2-x} microspheres samples TiO₂-1, TiO₂-2 and TiO₂-3 recorded at T = 130 K.

Figure 5. Structural characteristics of the as-prepared Ti³⁺ self-doped TiO_{2-x} sample (TiO₂-2) after 12-h solvothermal reaction at 160 °C: (a) Typical TEM images of several microspheres; (b) Magnified TEM image of a single representative microsphere, (c) HRTEM image of the etched surface from a microsphere, and SAED pattern (inset) showing single-crystal diffraction; and (d) Digital micrograph.

Figure 6. Nitrogen adsorption-desorption isotherm plot of the as-prepared TiO₂ samples.

Figure 7. UV-vis diffuse reflectance spectra of the as-prepared samples. The inset is the corresponding photographs.

Figure 8. Photocurrent versus time plots (a) and EIS Nyquist plots (b) of the obtained samples.

Figure 9. Time course of evolved H₂ under UV irradiation (70 mW/cm², 365-nm LED) by the TiO₂ catalysts.

Figure 10. The TDR spectra of the obtained samples (a) TiO₂-1, (b) TiO₂-2, and (c) TiO₂-3. (d) Normalized transient absorption traces observed at 900 nm for a range of samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Graphical Abstract