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Building surface defects by doping with transition metal on ultrafine TiO₂ to enhance the photocatalytic H₂ production activity

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ABSTRACT

Inefficient charge separation and limited light absorption are two critical issues associated with high-efficiency photocatalytic H₂ production using TiO₂. Surface defects within a certain concentration range in photocatalyst materials are beneficial for photocatalytic activity. In this study, surface defects (oxygen vacancies and metal cation replacement defects) were induced with a facile and effective approach by surface doping with low-cost transition metals (Co, Ni, Cu, and Mn) on ultrafine TiO₂. The obtained surface-defective TiO₂ exhibited a 3–4-fold improved activity compared to that of the original ultrafine TiO₂. In addition, a H₂ production rate of 3.4 μmol/h was obtained using visible light (λ > 420 nm) irradiation. The apparent quantum yield (AQY) at 365 nm reached 36.9% over TiO₂-Cu, significantly more than the commercial P25 TiO₂. The enhancement of photocatalytic H₂ production activity can be attributed to improved rapid charge separation efficiency and expanded light absorption window. This hydrothermal treatment with transition metal was proven to be a very facile and effective method for obtaining surface defects.

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1. Introduction

TiO₂ has been extensively used in bio-separation, sensors, energy storage, solar cells, catalysis, and photocatalysis [1,2]. It has several advantages, such as lower cost, lower toxicity, higher chemical and biological stabilities, and higher photocatalytic activity than other semiconductors [3]. Since the first report on photoelectrochemical water splitting on TiO₂ electrode [4], extensive research has been conducted on photocatalytic or photoelectrochemical splitting of water into H₂ and O₂ by TiO₂. The photocatalytic splitting of water using TiO₂ offers a promising way for clean, low-cost, and environ-

ment-friendly production of hydrogen by solar energy.

However, TiO₂ is a wide-bandgap semiconductor photocatalyst ($E_g = 3.0\text{--}3.2$ eV), which can only absorb UV light. The photoproduction electron-hole pairs rapidly recombine leading to low quantum efficiency of solar energy to hydrogen production by photocatalytic water splitting catalyzed by TiO₂. Over the past few years, considerable efforts have been devoted to improving the photocatalytic activity of TiO₂. Generally, several techniques have been used, such as doping with different elements [5–8], combining with narrow-bandgap semiconductor, and sensitizing with quantum dots or dye molecules [9–12], to increase visible light absorption and charge separation effi-

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ciency.

The recombination of photogenerated electrons and holes is one of the most critical factors degrading the photocatalytic activity. Introducing surface defects into photocatalyst materials within a certain concentration range have been demonstrated to improve photocatalytic activity [13–18]. The surface defects result in the formation of a defect energy band located below the conduction band and/or above the valence band. These surface defects can effectively capture the photogenerated charges and promote charge transfer to surface defects, preventing charge recombination. Moreover, the defect energy band narrows the bandgap and expands light absorption that results in the visible light activity. These factors greatly promote charge separation and expand the light absorption window in the entire photocatalytic reaction.

A more pressing issue is developing a facile and effective method to treat low-activity TiO_2 and enhance its photocatalytic activity [19–22]. Among various morphologies of TiO_2 , ultrafine TiO_2 have attracted immense attention. Ultrafine TiO_2 has several advantages including high surface area, multiple surface-reactive sites, and easy transport of photogenerated carriers to the surface. However, it shows poor activity due to the presence of less defects, a strong fluorescence emission, and susceptibility to radiation recombination [23]. Transition metals are low-cost and doping with their ions enhances the photocatalytic activity of TiO_2 [24–28]. Although several similar studies have been reported, most of these reports describe bulk doping of TiO_2 , while reports on surface doping are relatively few. In addition, works concerned with surface doping focus on the process itself, rather than the formation of defects. For M^{x+} (M refers to transition metal) doped TiO_2 , when one M^{x+} ion is present instead of Ti^{4+} , it produces one $\text{M}_{\text{Ti}}^{(4-x)+}$ and $(4-x)/2 V_{\text{O}}$ defect. Thus, the surface defects on ultrafine TiO_2 can be constructed by surface doping with transition metal.

In our work, we successfully demonstrated that the surface-defective (oxygen vacancies and metal cation replacement defects) ultrafine TiO_2 exhibited enhanced photocatalytic activity. The surface defects were built using a facile and effective hydrothermal method with low-cost transition metal (Co, Ni, Cu, and Mn) as dopants. The surface -defective TiO_2 exhibited an observably improved full-spectrum and visible light activity, significantly more than that of the commercial P25 TiO_2 . Low-temperature electron spin resonance (ESR) studies confirmed the existence of surface defects. Steady-state and transient fluorescence, transient absorption, and photocurrent and surface photovoltage (SPV) results indicate faster charge separation efficiency for defective TiO_2 . This hydrothermal treatment with transition metal was proven to be a very facile and effective method for building surface defects.

2. Experimental

2.1. Chemicals and materials

Pluronic®F-127 (F127) were purchased from Sigma-Aldrich. Tetrabutyl titanate (TBT, AR, 98%), ethanol (AR, 99.7%), HCl (AR, 36%–38%), and acetic acid (AR, 99.5%) were

purchased from Beijing Chemical Reagent Company. $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR, 99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, 98%), $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, 99%), and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (AR, 99%) were purchased from Aladdin Reagent Company. P25 TiO_2 was purchased from Degussa AG, Germany. All chemicals were used without further purification.

2.2. Synthesis

At room temperature, 8 g of F127, 11.5 mL of HCl, and 3.7 mL of hydrochloric acid were dissolved in 150 mL of ethanol and then added to 17.5 mL of TBT. The mixture was agitated vigorously for 2 h, then subsequently evaporated at 40 °C in an electric oven for 12 h. Thereafter, the reaction was aged for 24 h. The as-prepared samples were annealed at 450 °C for 4 h at a heating rate of 2 °C/min to remove the remaining organic impurities. Finally, the ultrafine crystal phase of TiO_2 was obtained.

At room temperature, 1 g of ultrafine TiO_2 was dispersed into 15 mL of deionized water and then added with transition metal salt. The molar ratio (transition metal element/Ti element) of each element in the starting solution was fixed at 0.5%. The solution was then transferred into a 25 mL Teflon lined stainless steel autoclave and was heated at 200 °C for 24 h in an electric oven. Subsequently, the mixture was air-cooled to room temperature. The as-prepared samples were washed with deionized water to remove free remaining transition metal ions and dried at 70 °C for 12 h in an electric oven. The samples were labeled as $\text{TiO}_2\text{-Co}$, $\text{TiO}_2\text{-Ni}$, $\text{TiO}_2\text{-Cu}$, $\text{TiO}_2\text{-Mn}$, respectively, according to the added transition metal salt. $\text{TiO}_2\text{-H}$ was synthesized by a similar procedure without adding any transition metal salt.

2.3. Characterization

Scanning electron microscopy (SEM) images were obtained by JEOL SU8010, while transmission electron microscopy (TEM) images were taken using an FEI Tecnai G2 F20 operated at 200 kV. The crystalline structure was recorded using an X-ray diffractometer (XRD) (Bruker AXS D8 Focus), using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The Brunauer-Emmett-Teller (BET) specific surface area was measured using a ASAP2460 Surface Area and Pore Size Analyzer. Furthermore, the ultraviolet-visible (UV-Vis) absorption spectra were recorded on a UV-3600 UV-Vis-NIR scanning spectrophotometer (Shimadzu). The fluorescence emission spectra were recorded on a LabRAM HR Evolution spectrograph. The electron paramagnetic resonance (EPR) spectra were recorded using a Bruker EMX-8 spectrometer at 9.857 GHz at 100 K. X-ray photoelectron spectrum (XPS) analyses were performed on an ESCALAB 250Xi spectrometer with an $\text{Al-K}\alpha$ (1486.6 eV) achromatic X-ray source.

2.4. Photocatalytic activity measurements

10 mg of sample photocatalysts loaded with 1.0 wt% Pt was placed into an aqueous methanol solution (120 mL, 25 vol%) in

a closed gas circulation system. The full spectrum light and visible-light irradiations were provided by a 300-W Xe lamp (Perfect Light Company Solaredge 700) without and with a UVCUT-420 nm filter (Newport). The evolved gases were detected in situ using an online gas chromatograph (GC-2014C, Shimadzu) equipped with a thermal conductivity detector (TCD).

2.5. Quantum efficiency calculations

10 mg of the TiO₂-Cu sample loaded with 1.0 wt% was placed into an aqueous methanol solution (120 mL, 25 vol%) in a closed gas circulation system. The catalyst solution was irradiated by a LED Light (2 W) source centered at 365 nm for 5 h. The evolved gases were detected in situ by an online gas chromatograph (GC-2014C, Shimadzu) equipped with a TCD detector. The average intensity of irradiation is determined by an FZ-A spectroradiometer (Photoelectric Instrument Factory of Beijing Normal University). The quantum efficiency was calculated from the equation:

$$QE = \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

2.6. SPV measurements

A SPV measurement system consists of a source of monochromatic light, lock-in amplifier (SR 830-DSP) with a light chopper (SR 540), and sample chamber. Monochromatic light was provided by a 300-W Xe lamp (Perfect Light Company Solaredge 700) and a monochromator (SBP500, Zolix). All measurements were performed at room temperature and under ambient pressure. Furthermore, samples were not pre-treated prior to the SPV measurement.

2.7. Photoelectrode preparation

50 mg of the sample was dispersed in a 100 mL of I₂/acetone solution (0.2 mg/mL) under ultrasonic treatment. A two-electrode process was used to deposit the samples at an applied potential of 30 V for 5 min. FTO glass substrates coated over an area of approximately 1 × 3 cm² was used for both electrodes. Lastly, the deposited electrode was dried at 200 °C for 30 min to remove I₂ residues.

2.8. Photoelectrochemical measurements

A conventional three-electrode process was used to investigate the photoelectrochemical properties of the samples in a quartz cell. An FTO photoanode deposited with samples, Ag/AgCl, and Pt foil electrode were considered as the working electrode, reference electrode, and counter electrode, respectively. A NaOH aqueous solution (1.0 mol/L) was used as the electrolyte. The photoanode was illuminated by a 300-W Xe lamp (Perfect Light Company Solaredge 700) with a monochromator.

3. Results and discussion

A large amount of ultrafine TiO₂ were synthesized following a sol-gel method by introducing a surfactant, F127, to maintain the size of TiO₂ below 10 nm [29]. Figs. 1A and B show field-emission scanning electron microscopy (FE-SEM) images of the as-synthesized ultrafine TiO₂ with good dispersion and relatively uniform size distribution. Low-resolution TEM (Fig. 1C) and high-resolution TEM images (HR-TEM, Fig. 1D) confirm that the ultrafine TiO₂ are nanoparticles with a diameter of ~10 nm and a lattice fringe space of 0.35 nm, characteristic of anatase TiO₂ at (101). The XRD pattern (Fig. 1E) exhibits a typical anatase crystalline phase pattern with diffraction peaks at 25.3°, 37.8°, and 48.0°, which are related to the (101), (004), and (200) facets of the anatase phase TiO₂, respectively (JCPDS NO. 21-1272). The ultrafine TiO₂ has a high BET surface area of 112 m²/g, calculated from the N₂ adsorption-desorption curves (Fig. 1F).

A large surface area is beneficial for photocatalytic activity. Our ultrafine TiO₂ has a surface area 2 to 3 times larger than that of commercial P25 TiO₂ (~50 m²/g). Therefore, it is expected to exhibit good photocatalytic performance. However, the ultrafine TiO₂ presents a general activity H₂ production rate of 64 μmol/h (Fig. S1), significantly below our expectations and appreciably less than P25 (132 μmol/h). Fig. S2 shows the FE-SEM images of the ultrafine TiO₂ treated with transition metal salts (Co(NO₃)₃, Ni(NO₃)₂, Cu(NO₃)₂ and MnCl₂) under hydrothermal condition at 200 °C for 24 h. After treatment, the morphology shows no significant change with original ultrafine TiO₂. The energy dispersive spectroscopy (EDS, Fig. S3) analysis indicates trace amounts of transition metal element. To in-

Fig. 1. FE-SEM images (A, B), low resolution TEM image (C), HR-TEM image (D), XRD pattern (E), and N₂ adsorption-desorption isomers (F) of the original ultrafine TiO₂. Inset is the pore size distribution curve.

investigate the content of the transition metal elements for treated TiO_2 , ICP tests were further employed. The molar ratio of the transition metal with TiO_2 are 0.012%, 0.017%, 0.009%, and 0.014% for $\text{TiO}_2\text{-Co}$, $\text{TiO}_2\text{-Ni}$, $\text{TiO}_2\text{-Cu}$, and $\text{TiO}_2\text{-Mn}$, respectively (Table S1). The signal of the XPS (Fig. S4) for Co, Ni, Cu, and Mn also detected trace amounts, consistent with the EDS results. We suspect that these exist mainly in the form of Co^{3+} , Ni^{2+} , Cu^{2+} , or Mn^{2+} ions, if the valence state of a transition metal does not change during hydrothermal treatment. The low resolution TEM image (Fig. S5A) clearly shows that the particles of $\text{TiO}_2\text{-Cu}$ are well dispersed, and the particles size does not grow nor aggregate. Only the lattice fringe spacing of TiO_2 was observed in the HR-TEM image (Fig. S5B), signifying that no CuO_x or complexes Cu was formed during the hydrothermal process. The diffraction peaks at 25.3° , 37.8° , and 48.0° were assigned to the (101), (004), and (200) of anatase phase TiO_2 (JCPDS NO. 21-1272) respectively. No additional diffraction peaks of other species were observed (XRD, Fig. 2A). According to the Scherrer equation, the nanocrystal sizes were calculated to be 10.1, 10.4, 10.6, 10.4, and 10.6 nm for the original ultrafine TiO_2 , $\text{TiO}_2\text{-Co}$, $\text{TiO}_2\text{-Ni}$, $\text{TiO}_2\text{-Cu}$, and $\text{TiO}_2\text{-Mn}$, respectively, using the (101) reflection peaks. These values were consistent with the diameter values observed from the TEM images, which indicates that the particles size does not increase after treatment. UV-Vis diffuse reflection spectrum (DRS, Fig. 2B) represents weak visible-light absorption after treatment, likely caused by the surface being doped with transition metal ions. The BET surface area and pore size of the samples are characterized using the nitrogen adsorption-desorption isotherm shown in Fig. S6. The BET surface areas were determined to be 104, 109, 106, and 108 m^2/g for $\text{TiO}_2\text{-Co}$, $\text{TiO}_2\text{-Ni}$, $\text{TiO}_2\text{-Cu}$, and $\text{TiO}_2\text{-Mn}$, respectively. These values displayed no observable variation after the hydrothermal treatment. The photocatalytic activity for H_2 evolution was tested under full spectrum and visible light irradiation. All the treated TiO_2 displayed an enhanced activity (Fig. 2C). $\text{TiO}_2\text{-Ni}$ and $\text{TiO}_2\text{-Cu}$ exhibited the highest H_2 production rates of 279 and 287 $\mu\text{mol}/\text{h}$, respectively, while $\text{TiO}_2\text{-Co}$ and $\text{TiO}_2\text{-Mn}$ gave moderate rates of 186 and 132 $\mu\text{mol}/\text{h}$, respectively (full spectrum, 10 mg of samples). The full

spectrum activity for $\text{TiO}_2\text{-Ni}$ and $\text{TiO}_2\text{-Cu}$ exhibited a 3- to 4-fold improved activity than that of the original ultrafine TiO_2 , and greatly more than that of commercial P25 TiO_2 . Unlike the original ultrafine TiO_2 and P25, $\text{TiO}_2\text{-Cu}$ exhibited an H_2 production rate of 3.4 $\mu\text{mol}/\text{h}$. $\text{TiO}_2\text{-H}$ synthesized via similar hydrothermal procedures, except without adding any transition metal salt, presented a similar activity with the original ultrafine TiO_2 . These results indicate that the photocatalytic H_2 production activity can be improved treating not with the deionized water but with transition metal salts. The apparent quantum yield (AQY) of 36.9% at 365 nm was attained by synthesized $\text{TiO}_2\text{-Cu}$. Continuous hydrogen evolution was observed during the entire process, even when the reaction prolonged for more than 40 h (Figs. 2D and S7). Even after the samples were washed with deionized water multiple times, the activity was retained. Furthermore, the comparison of XRD patterns and SEM images of $\text{TiO}_2\text{-Cu}$ before and after photocatalytic reaction showed no observable signs of change (Fig. S8), indicating excellent stability.

Encouraged by this improved photocatalytic activity and to gain more insight into the drastic variations in the activity of treated TiO_2 , we conducted a low-temperature ESR, steady-state and transient photoluminescence, transient absorption, and photocurrent and SPV experiments. The ESR signal at $g = 1.95$ can be attributed to the oxygen vacancies in the $\text{TiO}_2\text{-Cu}$ samples (Fig. 3A) [30]. When Cu^+ or Cu^{2+} ions were surface doped on ultrafine TiO_2 , oxygen vacancies were introduced simultaneously. For example, a surface with Cu^{2+} instead of Ti^{4+} produces one $\text{Cu}_{\text{Ti}}^{\bullet}$ and one $\text{V}_\text{O}^{\bullet}$ defect, correspondingly. $\text{TiO}_2\text{-Cu}$ exhibits a significantly low fluorescence emission, even fluorescence quenching (Fig. 3B), that promotes charge separation. In addition, a slow decay of transient fluorescence and absorption, observed in Fig. 3C, indicates a significant increase in the lifetime of photogenerated carriers. Importantly, longer lifetime of photogenerated carriers is very beneficial for photocatalysis. The photocurrent and surface photovoltage spectra are powerful tools for the characterization of the photoelectric response and charge separation [31]. As shown in Fig. 3E and F, $\text{TiO}_2\text{-Cu}$ exhibits markedly increased photocurrent and surface photovoltage signals.

Based on the experimental results, the influence of surface defects on the photocatalytic activity of TiO_2 is proposed on the following defect-assisted mechanism shown in Fig. 4. The original ultrafine TiO_2 , despite of a high BET surface area (112 m^2/g), has poor activity due to the presence of less defects, a strong fluorescence emission, and susceptibility to radiation recombination. When surface dopants were introduced, defects (oxygen vacancies and metal cation replaced defects) were formed simultaneously. For $\text{TiO}_2\text{-M}$, the surface defects result in the formation of a defect energy band located below the conduction band. These surface defects can effectively capture the photogenerated charges, promote charge transfer to the surface defects, and prevent charge recombination [32]. The defect levels in $\text{TiO}_2\text{-Cu}$ can be calculated by subtracting the bandgap (E_g) from the valence band position (VB). To ensure that the defect levels in $\text{TiO}_2\text{-Cu}$ meet the conditions for thermodynamics-driven force for H_2 production, we further meas-

Fig. 2. XRD patterns (A), UV-Vis DRS (B), and H_2 production rate under full spectrum light (C) of original ultrafine TiO_2 and surface-doped TiO_2 . (D) recycle measurements of photocatalytic H_2 production for $\text{TiO}_2\text{-Cu}$.

Fig. 3. The ESR (A), photoluminescence (B), time resolution of photoluminescence (C), transient absorption (D), photocurrent (E), and surface photovoltage spectra (F) results of the original ultrafine TiO₂ and TiO₂-Cu, respectively.

Fig. 4. Possible photocatalytic H₂ production mechanism of ultrafine TiO₂ (A) and after surface doping (B) under full spectrum light.

ured the VB and the E_g . The valence band position was unchanged at 1.7 eV below the fermi level for both TiO₂ and TiO₂-Cu (Fig. S9A)), while the E_g was changed by approximately 0.02 eV, decreasing from 3.24 to 3.22 (Fig. S9B). We conclude that the defect levels located about 0.02 eV below the conduction band (CB) meet the conditions for thermodynamics-driven force for H₂ production. On the other hand, the defect energy band narrows the bandgap and expands light absorption, resulting in the visible light activity [33]. These factors greatly promote charge separation and expand light absorption in the entire photocatalytic reaction [34].

4. Conclusions

In summary, we have developed a facile and effective treatment for creating surface defects (oxygen vacancies and metal cation replace defects) by surface doping with transition metal (Co, Ni, Cu and Mn) on ultrafine TiO₂. The surface defec-

tive TiO₂ exhibited the highest H₂ production rate of 287 $\mu\text{mol/h}$ (full spectrum), a 3- to 4-fold improved activity than that of the original ultrafine TiO₂ and significantly more than that of the commercial P25 TiO₂. Unlike the original ultrafine TiO₂ and P25, defective TiO₂ showed a visible light ($\lambda > 420$ nm) H₂ production rate of 3.4 $\mu\text{mol/h}$ and an AQY at 365 nm of up to 36.9%. The promotion of photocatalytic H₂ production activity can be attributed to improved rapid charge separation efficiency. This hydrothermal treatment with transition metal was proven to be a very facile and effective method for inducing surface defects.

Author contributions

Liu Q performed the experiments; Liu Q wrote this manuscript under the guidance of Ma J and S Li. All authors contributed to the general discussion and article revision.

Conflict of interest

The authors declare that they have no conflict of interest.

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Building surface defects by doping with transition metal on ultrafine TiO₂ to enhance the photocatalytic H₂ production activity

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Surface defects (oxygen vacancies and metal cation replace defects) were induced with a facile and effective method by surface doping with low-cost transition metal (Co, Ni, Cu and Mn) on ultrafine TiO₂.

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过渡金属掺杂构建超细二氧化钛的表面缺陷以提升光催化产氢活性

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摘要: 载流子分离效率低和光吸收范围窄是制约二氧化钛光催化产氢活性的两个关键因素。研究表明, 一定浓度的表面缺陷既有利于光生载流子传递到表面缺陷位点, 抑制载流子的复合, 又可以扩展光催化剂的光谱吸收范围, 从而提高光催化活性。本文利用低成本过渡金属(Co, Ni, Cu和Mn)掺杂在超细二氧化钛表面, 构建了表面缺陷(氧空位和金属阳离子取代缺陷)。相对于原始的缺陷很少的二氧化钛, 表面缺陷的二氧化钛活性可以提升3–4倍, 而且可见光产氢速率高达3.4 μmol/h, 在365 nm处的表观量子效率达到36.9%, 这些结果都远远高于商业的P25 TiO₂。我们认为, 光催化产氢活性的明显提升可以

归结为更快速的电荷分离和更好的光吸收。可见,利用过渡金属进行热液处理来实现表面掺杂是一种非常简便有效构建表面缺陷的方法。

关键词: 构建表面缺陷; 超细二氧化钛; 低成本过渡金属; 表面掺杂; 光催化产氢

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