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Nitrogen-doped TiO₂ microsheets with enhanced visible light photocatalytic activity for CO₂ reduction

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ABSTRACT

Nitrogen-doped anatase TiO₂ microsheets with 65% (001) and 35% (101) exposed faces were fabricated by the hydrothermal method using TiN as precursor in the presence of HF and HCl. The samples were characterized by scanning electron microscopy, X-ray diffraction, N₂ adsorption, X-ray photoelectron spectroscopy, UV-visible spectroscopy, and electrochemical impedance spectroscopy. Their photocatalytic activity was evaluated using the photocatalytic reduction of CO₂. The N-doped TiO₂ sample exhibited a much higher visible light photocatalytic activity for CO₂ reduction than its precursor TiN and commercial TiO₂ (P25). This was due to the synergistic effect of the formation of surface heterojunctions on the TiO₂ microsheet surface, enhanced visible light absorption by nitrogen-doping, and surface fluorination.

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1. Introduction

Nowadays, human society relies on fossil fuels for energy. However, the depletion of fossil resources and increasing environmental concerns about the emission of large amounts of CO₂ during the combustion of fossil fuels have emphasized the need to develop renewable and clean energy resources. Therefore, great efforts have been made to reduce the use of fossil fuels that increase the concentration of CO₂ in the atmosphere. Photocatalytic CO₂ reduction to produce valuable organic fuels, such as methane, formic acid, and methanol, is of particular interest because of its environmental friendliness and ability to

mimic natural photosynthesis to transform solar energy into chemical energy [1–11]. Among the semiconductors, TiO₂ has been studied worldwide and proven to be the most promising due to its biological and chemical inertness, strong oxidation power, and low cost [12–25]. However, the practical application of TiO₂ is limited by low visible light absorption ability and fast electron-hole recombination, which significantly reduce the photoconversion efficiency. Recently, it has been reported that the photocatalytic properties of TiO₂ greatly depend on its structure and morphology [26,27]. Therefore, tailoring the TiO₂ morphology, crystal architecture, and surface and textural properties is effective strategies to modify and improve its

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photocatalysis for practical applications [28].

The design of the TiO_2 morphology with specific efforts to control exposed crystal faces is receiving a lot of attention. Crystal face engineering is an efficient way to improve photocatalytic performance. Since the first successful preparation of single crystal anatase TiO_2 sheets with 47% (001) faces by Yang et al. [29], many methods have been developed to fabricate anatase TiO_2 dominated by the (001) face, including hydrothermal, solvothermal, and high temperature gas phase reactions. Han et al. [30] demonstrated that nano-sized titania sheets with 89% (001) faces can be synthesised by an aqueous synthesis route. The formation of mainly (001) crystal faces was achieved by using a capping agent, which facilitated the formation of these crystal faces by lowering their free energy and making them more stable [30–32]. A report by Selloni [33] indicated that there was a strong preferential interaction between fluorine and the (001) faces of anatase TiO_2 crystals. Meanwhile, the formation of anatase (001) faces largely depended on the presence of plentiful fluorine under acidic conditions. This was attributed to the strong coordination between Ti^{4+} and F^- , which was enhanced by the acid and which preserved the TiO_2 (001) faces [33,34]. It was reported that fluorine enhanced the crystallization and promoted the growth of the anatase phase of TiO_2 nanosheets with mainly (001) faces for higher photocatalytic activity [34].

Recently, it was revealed that the co-existence of exposed (001) and (101) faces on anatase TiO_2 had specific synergetic effects, which showed a higher photocatalytic activity than that of TiO_2 with mainly (001) or (101) faces. This is because the difference in the energy levels of the (001) and (101) faces drives the electrons and holes to diffuse to different crystal faces [34], resulting in faster charge separation rates. Further, Yu et al. [34] proposed a novel “surface heterojunction” concept based on density functional theory (DFT) calculations, which explained the superior photocatalytic activity of TiO_2 with both (001) and (101) faces. Here, we report the fabrication of visible light responsive N-doped TiO_2 microsheets (N- TiO_2 MS) with exposed (101) and (001) faces that formed surface heterojunctions by a simple hydrothermal method. Compared with commercial TiO_2 (P25) and the precursor TiN, the N-doped TiO_2 sample exhibited a higher photocatalytic CO_2 reduction activity. The surface heterojunction formed by the (001) and (101) faces enhances electron-hole separation, which was shown by electrochemical impedance spectroscopy (EIS) analysis. This work provides new insight into the design and preparation of new highly efficient visible light responsive photocatalytic materials.

2. Experimental

2.1. N- TiO_2 MS sample preparation

The TiO_2 sample was synthesised by the hydrothermal method. TiN (0.9 g) was mixed with 1 mL HF, 3 mL HCL, and 26 mL deionized water under constant stirring for 1 h. The mixture was transferred into a dry Teflon-lined stainless steel autoclave and heated at 200 °C for 18 h. The resulting suspension

was cooled to room temperature. Then, the sample was washed three times with deionized water and ethanol. Finally, the sample was dried in an oven at 80 °C for 10 h and labelled N- TiO_2 MS. For comparison, the precursor TiN was treated under the same condition without HF and HCL. In addition, another N-doped TiO_2 nanoparticle (N- TiO_2 NP) sample was prepared using tetrabutylorthotitanate as precursor with 1 wt% $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution according to a previous study [35] for visible light comparison.

2.2. Characterization

The surface morphology of the as-prepared samples was characterized by a JSM-6510 microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV. The crystalline structure of the samples was analyzed by an XRD diffractometer (Rigaku, Japan) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at a scanning rate of $0.04^\circ/\text{s}$. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) of the samples were determined by nitrogen adsorption data obtained on a Micromeritics ASAP 3020 nitrogen adsorption apparatus (USA). All the samples were degassed at 180 °C prior to the nitrogen adsorption measurement. A desorption isotherm was used to determine the pore size distribution by the Barret-Joyner-Halender (BJH) method, by using a cylindrical pore model [36]. The nitrogen adsorption volume at the relative pressure (p/p_0) of 0.994 was used to calculate the pore volume and average pore size. The XPS measurement was performed in an ultrahigh vacuum VGESCALAB 210 electron spectrometer equipped with a multichannel detector using $\text{Mg } K_\alpha$ (1253.6 eV) radiation (operated at 200 W) of a twin anode in the constant analyzer energy mode with a pass energy of 30 eV. All the binding energy was referenced to the C 1s peak at 284.8 eV of surface adventitious carbon. Survey scans and detailed scans of the Ti 2p, C 1s, O 1s, F 1s, and N 1s photoelectron peaks were recorded for the samples. Optical absorption by the samples was characterized by a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). BaSO_4 was used as a reflectance standard in the UV-visible diffuse reflectance experiment.

2.3. Photoelectrochemical measurements

The electrochemical behavior of the samples was determined by EIS. EIS was performed in a three electrode system (CH1660C instruments, CHI, China) using Ag/AgCl as the reference electrode, Pt wire as the counter electrode, and FTO as the working electrode. Na_2SO_4 aqueous solution (0.5 mol/L) was used as the electrolyte. The samples were coated on a 2 cm $\times$ 1.5 cm fluorine-tin oxide (FTO) glass electrode and dried at room temperature for 24 h. The Nyquist plot was used out to analyze the measured results.

2.4. Photocatalytic CO_2 reduction activity

The photocatalytic reduction of CO_2 was carried out in a 200 mL capacity homemade Pyrex reactor at room temperature and atmospheric pressure described in our recent reports [37,38]. In a typical photocatalytic CO_2 reduction experiment,

0.1 g of the sample was suspended in 20 mL of deionized water in the reactor and ultra-sonicated and dried in an oven at 80 °C to form a thin film at the bottom of the Pyrex reactor. Prior to illumination, the reactor was tightly sealed and fastened using a rubber septum. Then, ultra-pure nitrogen gas was blown through the system for 30 min to remove air and put the reaction system into an anaerobic condition. A chemical reaction between 0.12 g NaHCO_3 (added into the reactor before sealing) and 0.3 mL HCl aqueous solution (4 mol/L), which was added into the reactor by a syringe, was used to produce CO_2 and H_2O vapour in situ. Then, the reactor was irradiated for 2 h with a Xe arc lamp with a power of 300 W without (as a UV-visible full spectrum light source) and with a cut filter of 400 nm as a visible light source, which was placed 10 cm above the photocatalytic reactor. After the photocatalytic CO_2 reduction reaction, 1 mL of mixed gas was taken out from the reactor and analyzed by a gas chromatograph (GC2014C, Shimadzu, Japan) equipped with a flame ionization detector (FID) and methanizer. Products were analyzed on the basis of the retention time of the standard gaseous sample. The amount of methanol produced after the reaction was quantified as a major product of the reaction.

3. Results and discussion

3.1. Phase structure and morphology

The phase structure of the TiO_2 sample is important for determining its photocatalytic activity. Figure 1 shows the XRD patterns of the different samples. The XRD pattern of the N- TiO_2 MS sample showed the formation of pure anatase (JCPDS No. 21-1272) with no residual TiN phase. Further analysis of the pattern indicated that the intensity of the diffraction peak of the N- TiO_2 MS sample was more intense and sharper than that of P25, suggesting the formation of well-crystallized TiO_2 . This result is in good agreement with previous reports that surface fluorination and an acidic synthesis condition improved the growth and crystallization of TiO_2 crystallites [39].

According to the Wulff construction, the high surface energy (001) faces grow and diminish rapidly, and thus a conventional anatase TiO_2 grows into a unique octahedral bipyramid shape, and 90% of the exposed faces are the thermodynamically stable (101) face [29]. The morphology of our samples was studied by SEM. As shown in Fig. 2, N- TiO_2 MS exhibited a characteristic microsheet morphology with a high percentage of the

Fig. 1. XRD patterns of TiN, as-prepared N- TiO_2 MS, and P25 samples.

(001) face. It has an average side length of 3.5 μm and thickness of 0.3 μm , indicating the formation of larger crystallites and an enhanced crystallization in comparison to P25. The percentage of the exposed (001) faces on as-prepared N- TiO_2 MS was determined to be 65% from the FESEM image (Fig. 2(c)) using Eqs. (1)–(3) below [40]. This is significantly higher than that on natural TiO_2 (around 10%). Note that this exposed percentage of (001) faces (65%) is very close to that reported recently (58%) for the optimized formation of a surface heterojunction [34]. This is an indication that a properly exposed ratio of (001) and (101) faces was achieved. Therefore, a good photocatalytic activity can be expected.

The percentage of exposed (001) faces was calculated from Eqs. (1)–(3) [40]:

$$S_{001} = 2 \left(l - \frac{d}{\tan \theta} \right)^2 \quad (1)$$

$$S_{101} = \frac{2d}{\sin \theta} \left(2l - \frac{d}{\tan \theta} \right) \quad (2)$$

$$P = \frac{S_{001}}{S_{001} + S_{101}} \quad (3)$$

where l and d are the average length and average thickness, respectively, of the sheets measured from SEM images, S_{001} is the area of the (001) face, S_{101} is the area of the (101) face, P is the percentage of exposed the (001) face, and θ is the value for the angle between the (001) and (101) faces of anatase TiO_2 .

Fig. 2. SEM images of as-prepared N- TiO_2 MS (a) and TiN (b), and FESEM image of N- TiO_2 MS showing (001) and (101) faces (c).

Table 1

Physical properties and estimated band gap energy of the samples.

Sample	(001) face (%)	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)	Band gap energy (eV)
TiN	—	1.6	6.2	< 0.012	—
N-TiO ₂ MS	65	5.0	7.8	< 0.010	3.2

3.2. BET surface area and pore size distribution

It is well-known that a high surface area and large pore structure are beneficial for improving photocatalytic activity. This is because of more surface active sites for the adsorption of reactant molecules and ease of transport of reactant molecules and products through the interconnected pore network [41,42]. The specific surface area and pore structure of the as-prepared N-doped TiO₂ samples were investigated by nitrogen adsorption isotherms. The results are shown in Table 1 and Fig. 3. The isotherm of the as-prepared N-TiO₂ MS sample was type IV of the BDDT (Brunauer-Deming-Deming-Teller) classification, indicating the presence of mesopores. Moreover, the isotherm with an H3 hysteresis loop suggested that there were slit-shaped pores formed within aggregates of plate-like particles [43–45]. The pore size distribution determined from the desorption branch of the nitrogen isotherm by the BJH (Barrett-Joyner-Halenda) method is shown in the inset of Fig. 3. This indicated a wide pore diameter distribution in a range of 10–100 nm centered at 40 nm for the as-prepared N-TiO₂ MS sample. This mesoporous structure would be useful as the transport pathway during the photocatalytic reaction by allowing the rapid diffusion of reactant molecules in the pores.

3.3. XPS analysis

The XPS measurements were carried out to investigate the chemical state and surface chemical composition of the samples. Figure 4(a) shows the XPS survey spectra of the as-prepared N-TiO₂ MS and precursor TiN samples. Sharp photoelectron peaks appeared at the binding energy of 458 (Ti 2p), 531 (O 1s), 684 (F 1s), and 285 eV (C 1s). The C 1s peak

Fig. 3. Nitrogen adsorption isotherms of TiN and as-prepared N-TiO₂ MS. The inset shows the pore size distribution curves.

resulted from residual carbon on the sample and adventitious hydrocarbon from the XPS instrument itself.

Two characteristic peaks at the binding energy of 458.8 and 464.5 eV (Fig. 4(b)) were observed for Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, indicating that the oxidation state of the Ti element in the as-prepared N-TiO₂ MS sample was the same as that of bulk TiO₂. The high resolution spectrum of O 1s showed a core level peak at 530 eV, which corresponded to the lattice oxygen associated with Ti–O–Ti linkages in TiO₂, and a shoulder peak at 531.4 eV, which came from the hydroxyl group (–OH) of adsorbed water molecules (not shown here). An important feature was that one characteristic high resolution F 1s XPS peak at the binding energy of 684.5 eV appeared for the as-prepared N-TiO₂ MS sample, as shown in Fig. 4(c). This peak indicated that F ions were adsorbed on the surface of the TiO₂. More significantly, the high resolution N 1s XPS peak of as-prepared N-TiO₂ MS, shown in Fig. 4(d), showed one wide N 1s peak centered at 395 eV, which was attributed to nitrogen doping in the TiO₂ microsheets with a moderate doping content (surface atomic concentration of 1.98% from XPS) derived from the TiN precursor. Usually, N doping is very hard to achieve in highly crystalline TiO₂ microsheets, yet, it is crucial for visible light absorption.

Fig. 4. XPS survey spectra (a) of as-prepared N-TiO₂ MS and TiN, and high resolution XPS spectra of Ti 2p (b), F 1s (c), and N 1s (d) of as-prepared N-TiO₂ MS.

3.4. UV-visible diffuse reflection spectroscopy

The UV-visible spectra provide insightful information into the interactions of the photocatalytic materials (i.e., TiO_2 samples) with photons of different energy. Figure 5 shows the comparison of the optical absorption spectra of TiN, as-prepared N- TiO_2 MS, and reference P25. The TiN precursor showed strong visible light absorption with an obvious decrease around 500 nm. In contrast, the reference P25 exhibited almost no detectable visible light absorption above 400 nm. Notably, as-prepared N- TiO_2 MS showed an obvious red shift in the absorption edge as compared to the reference P25. Moreover, strong absorption in the whole visible light spectrum was observed for as-prepared N- TiO_2 MS, which is consistent with its dark colour inherited from the TiN precursor. Therefore, it was not surprising that the prepared N- TiO_2 MS sample exhibited visible light photocatalytic activity.

3.5. EIS analysis

Many studies have demonstrated that charge recombination versus separation and transport is an important factor in the performance of a photocatalyst. In order to develop a photocatalyst with a high photoconversion efficiency, a reduced e^-/h^+ recombination rate and enhanced electron transport are desirable. In this study, EIS was carried out to investigate the interfacial charge transport process. Figure 6 depicts the Nyquist plot of the three samples, where the radius of each arc correlated with the charge transport ability of the corresponding photocatalyst. Generally, a larger radius of the arc indicates a lower ability to transport charges [46,47]. It can be seen that as-prepared N- TiO_2 MS showed a much smaller arc than that for the TiN precursor or reference P25 samples. Several reasons account for the higher separation and transport efficiency of charge carriers in N- TiO_2 MS. First, the exposure of (001) and (101) faces with a proper ratio on N- TiO_2 MS facilitated the formation of surface heterojunctions and significantly enhance charge separation and transport. Second, the highly crystalline feature of N- TiO_2 MS favored the separation and transport of charge carriers. Finally, the F^- ions

Fig. 5. UV-visible diffuse reflection spectra of TiN, as-prepared N- TiO_2 MS, and P25.

Fig. 6. Nyquist plots of the TiN, as-prepared N- TiO_2 MS, and P25 samples.

on the surface of TiO_2 were responsible for a reduction of the recombination rate of photogenerated electrons and holes [48].

3.6. Photocatalytic CO_2 reduction

The photocatalytic CO_2 reduction activity of the samples was investigated under both full spectrum light irradiation and visible light (with 400 nm cutoff filter) irradiation. The detected product over the N- TiO_2 MS sample is shown in Fig. 7. The control experiment showed that no hydrocarbon compound was detected in the absence of either photocatalyst or light irradiation, suggesting that the resulting hydrocarbon compounds were produced by a photocatalytic reaction on the photocatalyst. In particular, under both full spectrum light irradiation and visible light irradiation, CO_2 was mainly transformed into methanol on the N- TiO_2 MS sample during the photocatalytic reduction reaction (Fig. 7(a) and (b)). In contrast, no product was detected for reference P25 under visible light irradiation, and the dominant product was methane for reference P25 under full spectrum light irradiation.

Figure 8 shows a comparison of the photocatalytic methanol production rates by the TiN precursor, N- TiO_2 MS, reference P25, and N- TiO_2 NP samples as photocatalyst. TiN showed no UV or visible light photocatalytic activity because of its very high charge recombination rates (based on the EIS analysis). P25 also showed no methanol production under visible light irradiation because it has no visible light absorption ability (Fig. 5). In contrast, N- TiO_2 MS and N- TiO_2 NP exhibited obvious photocatalytic activity for methanol production under visible light irradiation because of the nitrogen doping. Also, the UV activity under full spectrum light irradiation for producing methanol was considerable on N- TiO_2 MS relative to reference P25 and N- TiO_2 NP (Fig. 8). The high photocatalytic activity of the N- TiO_2 MS sample was attributed to the exposed 65% (001) and 35% (101) faces on the TiO_2 , which helped build surface heterojunctions on the TiO_2 microsheet surface that favored charge separation and transport. In particular, the photogenerated electron migrated through the surface heterojunction to (101) faces for the photoreduction process, while the photogenerated hole was transferred through the surface hetero-

Fig. 7. GC chromatograms for the photocatalytic CO_2 reduction over TiN, N-TiO₂ MS, and P25 under full spectrum light irradiation (a) and visible light irradiation (b) for 2 h.

Fig. 8. Comparison of CH_3OH production rates over TiN, N-TiO₂ MS, P25, and N-TiO₂ NP under full spectrum light irradiation (1) and visible light irradiation (2) for 2 h.

junction to (001) faces for a photooxidation process. As a result, the electron-hole recombination rate was greatly reduced. Moreover, the existence of the F^- ions on the TiO₂ sample acted as a mediator of interfacial charge transfer, which significantly reduced the electron-hole recombination. In summary, the N-TiO₂ MS sample exhibited superior visible light photocatalytic performance due to the synergistic effect of the N doping, surface heterojunction, and surface fluorination.

4. Conclusions

N-doped anatase TiO₂ microsheets with both exposed (101) and (001) faces that formed surface heterojunctions were fabricated by a simple hydrothermal method using TiN as precursor in the presence of HF as capping agent and HCl for pH control. The prepared TiO₂ sample exhibited 65% (001) and 35% (101) exposed faces, high crystallinity, a large surface area, and desirable wide spectrum optical response. The prepared TiO₂ sample was chemically modified by N doping and surface fluorination. As a result, the prepared N-doped TiO₂ sample showed significantly higher photocatalytic activity than TiN

and P25 under visible light. This was due to the synergistic effect of the surface heterojunction, N doping, and surface fluorination. In particular, the surface heterojunctions improved electron-hole separation. N doping favored visible light absorption. Surface adsorbed F^- ions act as a mediator for interfacial charge separation. The surface fluorinated N-doped TiO₂ with exposed (001) and (101) faces has potential applications in gas sensors, photocatalysts, solar cells, biomedical engineering, and photonic and optoelectronic devices.

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Anatase nitrogen self-doped TiO₂ microsheets with formed surface heterostructure between exposed (001) and (101) faces were fabricated for high efficient charge separation and visible-light-driven photocatalytic CO₂ reduction to methanol.

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氮自掺杂暴露(001)晶面TiO₂微米片的可见光光催化CO₂还原性能增强

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摘要: 化石能源的使用可产生大量CO₂, 带来严重的温室效应. 光催化CO₂还原生产太阳燃料技术既有望缓解温室效应, 又可以将低能量密度的太阳能转化为高能量密度的化学能储存起来方便使用. 高效光催化材料的开发是发展光催化技术的关键. 迄今, 在已开发的所有半导体光催化材料中, TiO₂仍是广泛研究的明星材料. 在实际使用中, TiO₂的光催化效率仍受限于其极弱的可见光利用率和较高的电子-空穴复合几率. 近年来, 越来越多的研究表明TiO₂的结构与形貌特征极大地影响其光催化效率. 尤其, TiO₂的外露晶面设计与晶面效应研究引起了广泛关注. 由于具有较高表面能和较多表面不饱和键, 起初大多数理论和实验研究认为

锐钛矿 TiO_2 (001)晶面是光催化活性晶面。后来,越来越多研究表明并非锐钛矿 TiO_2 (001)晶面的暴露比例越高其光催化活性就越高。

最近,我们发现锐钛矿 TiO_2 (001)晶面与(101)晶面在调控光催化 CO_2 还原性能上具有良好的协同效应。密度泛函理论计算表明,锐钛矿 TiO_2 的(001)晶面与(101)晶面的能带结构有差异,(001)晶面的导带位置相对于(101)晶面而言较高,而(101)晶面的价带位置相对于(001)晶面而言较低。基于此我们提出,具有合适比例的锐钛矿 TiO_2 的(001)晶面与(101)晶面的交界处可以形成最佳的表面异质结或晶面异质结。表面异质结的形成导致光生电子倾向于向(101)扩散,光生空穴倾向于向(001)扩散,从而促进光生电子-空穴分离,降低光生电子-空穴复合几率。在此工作基础上,我们直接以氯化钛为原料,氢氟酸为添加剂,通过简单的水热反应一步合成了氮自掺杂的 TiO_2 微米片。利用X射线粉末衍射、扫描电镜、X射线光电子能谱、紫外-可见漫反射光谱、氮气吸附-脱附以及电化学阻抗谱等方法手段对所制备的光催化剂进行了基本结构与理化性质表征分析,并研究了其可见光光催化 CO_2 还原性能。

电镜照片结果表明,我们所制备的氮自掺杂锐钛矿 TiO_2 微米片的(001)晶面与(101)晶面比例分别为65%和35%。基于我们前期研究结果, TiO_2 微米片的(001)晶面与(101)晶面可以形成表面异质结,具有良好的电荷分离效率,这也得到了电化学阻抗谱研究结果的证明。同时,由于N的原位掺杂,所制备的 TiO_2 微米片具有优异的可见光捕获能力。由于可见光利用效率增强与光生电子-空穴分离效率提高这两方面的综合作用,所制备的氮自掺杂 TiO_2 微米片具有非常好的可见光光催化 CO_2 还原制甲醇性能,比商用P25及氮掺杂 TiO_2 纳米粒子等参考样品的可见光光催化性能更优异。研究表明,通过原位自掺杂方法与晶面设计方法相结合,可以同时改善 TiO_2 的可见光利用效率和光生电子-空穴分离效率,优化 TiO_2 的可见光光催化性能,这也为后续开发新型高效光催化材料提供了新思路。

关键词: 氮自掺杂; 二氧化钛; (001)晶面; 二氧化碳还原; 表面异质结

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