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Nitrate-group-grafting-induced assembly of rutile TiO₂ nanobundles for enhanced photocatalytic hydrogen evolution

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ABSTRACT

In this study, an acid-induced assembly strategy for a rutile TiO₂ photocatalyst was proposed on the basis of the treatment of lamellar protonated titanate with a concentrated HNO₃ solution. Nitrate groups were successfully grafted onto a TiO₂ surface and induced the assembly of rutile TiO₂ nanorods into uniform spindle-like nanobundles. The resulting TiO₂ product achieved a photocatalytic hydrogen evolution rate of 402.4 μmol h⁻¹, which is 3.1 times higher than that of Degussa P25-TiO₂. It was demonstrated that nitrate group grafting caused the rutile TiO₂ surface to become negatively charged, which is favorable for trapping positive protons and improving charge carrier separation, thereby enhancing photocatalytic hydrogen production. Additionally, surface charges were crucial to structural stability based on electrostatic repulsion. This study not only developed a facile surface modification strategy for fabricating efficient H₂ production photocatalysts but also identified an influence mechanism of inorganic acids different from that reported in the literature.

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1. Introduction

The rapid consumption of fossil fuels has accelerated the global energy crisis and various environmental issues that threaten societal development. Photocatalytic hydrogen production has been recognized as a promising technique based on its direct utilization of clean and sustainable solar energy to realize solar-to-chemical fuel conversion [1–4]. Among various semiconductor photocatalysts, titanium dioxide (TiO₂) has been extensively investigated as one of the most promising candidates for photocatalytic water splitting based on its several advantages, including matched band energy, nontoxicity, low cost, and stability against photocorrosion [5–11]. TiO₂ crystals have three main polymorphs of rutile, anatase, and

brookite. It is widely recognized that anatase TiO₂ generally possesses higher photocatalytic activity than that of rutile TiO₂ because of its high reactivity [12]. Recently, nanoscale rutile crystals have also been developed as promising photocatalysts since it was discovered that they play an active role in certain cases [13,14]. Furthermore, rutile TiO₂ is a more thermodynamically stable state compared to the anatase and brookite phases [15]. However, rutile TiO₂ photocatalysts suffer from the same major issue as anatase photocatalysts, namely high recombination loss of photogenerated electron-hole pairs. Many attempts have been made to improve the separation efficiency of charge carriers to reduce recombination loss, including functional group grafting, construction of surface heterojunctions, and co-catalyst loading [16–25].

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Since photocatalytic reactions typically occur on the surface active sites of photocatalysts, surface properties have a significant influence on photocatalytic activity based on their modification of charge transfer pathways [26,27]. It has been well established that the grafting of inorganic acids, such as phosphoric, sulfuric, boric, and hydrochloric acid, can modify the surface properties of photocatalysts to enhance their photocatalytic activity [28–32]. The influence mechanisms of these inorganic acids have been examined from two main perspectives. One generally accepted mechanism is that acidification enhances the surface protonation of oxygen atoms to promote the formation of hydroxyl groups and oxygen adsorption, thereby improving charge carrier separation to boost reactivity [28–30]. For example, Cao et al. [28] reported that phosphoric acid treatment modifies phosphate groups on the surface of TiO_2 nanocrystals to form $-\text{Ti}-\text{O}-\text{P}-\text{OH}$, which improves photocatalytic degradation efficiency. He et al. [29] treated TiO_2 nanosheets with sulfuric acid to form surface hydroxyl groups and oxygen vacancies/ Ti^{3+} species, which extended the lifetime of electron-hole pairs. Wu et al. [30] introduced phosphoric and boric acids to co-modify rutile TiO_2 nanorods using residual chlorine, leading to the formation of $-\text{Ti}-\text{O}-\text{P}-\text{OH}$ and $-\text{Ti}-\text{Cl}-\text{B}-\text{OH}$ group ends. Their results confirmed that the promotion of adsorption of O_2 facilitates the capture of photo-generated electrons based on acid co-modification. Dhandole et al. [31] proposed a synergistic effect between the OH-rich surfaces of HCl-treated rutile TiO_2 nanorods and metal oxide co-catalysts that contributes to enhanced charge transfer. The second mechanism is based on electrostatic interactions between surface functional groups and reactive species. Li et al. [32] demonstrated that modification using phosphate groups creates a negative field effect on the surface of BiOCl , which effectively traps positive holes to suppress charge recombination. Based on the research above, it can be concluded that inorganic acid treatment has a significant effect on the enhanced photocatalytic degradation of organic pollutants based on the generation of surface hydroxyl groups and inorganic oxyanions. Despite the remarkable merits of such surface modification strategies, their effects on the photocatalytic production of clean solar fuels have not been extensively studied thus far. Therefore, it remains a considerable challenge to develop efficient photocatalysts for hydrogen production using acid treatments.

In this paper, we report the facile synthesis of spindle-like rutile TiO_2 nanobundles via nitric-acid-induced assembly. First, lamellar protonated titanate (LPT) was prepared as a TiO_2 precursor based on our previous research [33,34]. Subse-

quently, concentrated nitric acid was introduced to induce the assembly of rutile TiO_2 nanorods. The first three hours of light irradiation revealed an average hydrogen evolution of $402.4 \mu\text{mol h}^{-1}$ for the as-prepared TiO_2 photocatalysts, which is 3.1 times higher than that of a Degussa P25- TiO_2 reference. The mechanism for enhanced hydrogen production was determined to be related to the loss and recovery of photocatalytic efficiency. The synthesis strategy and the role of surface-grafted nitrate groups in hydrogen production are illustrated in Scheme 1. The proposed surface modification strategy with inorganic acid was confirmed to be an effective method to improve photocatalytic hydrogen production based on a novel mechanism of pollutant degradation reactions.

2. Experimental

2.1. Synthesis of LPT as a precursor

LPT was prepared as a TiO_2 precursor based on our previous studies [33,34]. In a typical procedure, 9 mL of tetrabutyl titanate is first dispersed into 66 mL of absolute ethanol. This solution is then added into 90 mL of deionized water dropwise under vigorous stirring. The resulting suspension is then heated to 70°C for 2 h under mechanical stirring to evaporate most of the solvent. Next, 300 mL of 1-M NaOH aqueous solution is added to the suspension. After continuous stirring for another 12 h, the precipitate is washed with deionized water and ethanol several times to obtain a wet LPT precursor.

2.2. Synthesis of nitric-acid-treated TiO_2 photocatalysts

The acid treatment process was conducted by directly mixing 6.2 g of wet LPT with 60 mL of 65 wt% concentrated HNO_3 in a 150 mL flask. The mixture was refluxed at 80°C for 4 h under continuous stirring. The final precipitate was collected via centrifugation and washed with ethanol and deionized water, then dried in a vacuum oven at 60°C for 4 h. The as-obtained product was denoted as rutile TiO_2 nanobundles (R- TiO_2).

To clarify the effects of nitrate group grafting, a series of samples were synthesized for comparison. First, LPT was treated with 1-M dilute HNO_3 and the product was labelled as R- TiO_2 -1M. Another controlled synthesis was conducted by employing a conventional hydrothermal method to produce anatase TiO_2 without the addition of concentrated HNO_3 , which was labelled as A- TiO_2 -No [33,34]. The concentrated HNO_3 treatment was then applied under the same conditions to yield

Scheme 1. The fabrication process for R- TiO_2 nanobundles and proposed photocatalytic mechanism for hydrogen evolution.

a post-treated sample labelled as A-TiO₂-acid.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected using a powder XRD instrument (SmartLab-SE) operating at 40 kV and 45 mA. The morphologies of the samples were examined using field emission scanning electron microscopy (FESEM, SU8010). Field emission transmission electron microscopy (FTEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai G² F30 instrument (FEI, Holland). N₂ adsorption-desorption isotherms were acquired at 77 K using a Micrometrics ASAP24600 instrument. Fourier transform infrared (FT-IR) spectra were obtained using a Bruker INVENIO R instrument with the KBr disk method. X-ray photoelectron spectroscopy (XPS) data were analyzed using an Escalab Xi+ instrument. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) were obtained using a UV-vis spectrophotometer (UV-3600, Shimadzu, Japan) with BaSO₄ powder as a reflectance standard. Photoluminescence (PL) spectra were measured using a fluorescence spectrometer (RF-5301PC, Shimadzu, Japan) with an excitation wavelength of 360 nm. Photoelectrochemical measurements were carried out in a 1-M Na₂SO₄ solution using an electrochemical workstation (CHI650E, Chenhua Com., China) with a standard three-electrode system. Electrochemical impedance spectroscopy (EIS) was performed in a frequency range of 10⁵–1 Hz with an open potential (AC voltage of 5 mV in amplitude) in a 0.1-M KCl solution containing 5 mM of Fe(CN)₆^{3−}/Fe(CN)₆^{4−}. Zeta potential analysis was performed using a Malvern Zetasizer Nano ZS.

2.4. Photocatalytic H₂ production activity

Photocatalytic H₂ evolution reactions were carried out in a closed circulation system using a CEL-HXF300 lamp. The light intensity incident on the photocatalyst surface was measured to be 0.38 W/cm². In a typical photocatalytic test, 100 mg of the as-prepared photocatalyst is uniformly suspended in 100 mL of aqueous solution containing 90 mL of deionized water and 10 mL of methanol in a reaction cell. Next, 1.5 wt% Pt is photodeposited from an H₂PtCl₆·6H₂O aqueous solution. Next, 50 mg of photocatalyst is dispersed into 90 mL of deionized water and 10 mL of triethanolamine (TEOA). The resulting suspension is then bubbled with N₂ for 10 min to remove any residual air. Photocatalytic H₂ evolution is analyzed using an online gas chromatographer (FULI GC9790, TCD) with N₂ as a carrier gas. The apparent quantum yield (AQY) for H₂ production is measured using a 300-W Xe lamp equipped with a 365 ± 15-nm band-pass filter as a monochromatic light source. The average energy density of the proposed photocatalyst was determined to be 15.3 mW/cm². AQY can be calculated using the following equation:

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

3. Results and discussion

Fig. 1. XRD patterns of a series of TiO₂ samples.

3.1. Structural characterization

The crystallinities and phase compositions of a series of TiO₂ samples were characterized using XRD. As shown in Fig. 1, the R-TiO₂ and R-TiO₂-1M samples present distinct diffraction peaks at $2\theta = 27.5^\circ, 36.1^\circ, 41.2^\circ, 43.8^\circ, 54.3^\circ, 56.4^\circ, 62.9^\circ$, and 69.1° , corresponding to the (110), (101), (111), (210), (211), (220), (002), and (301) reflection planes of rutile TiO₂ (JCPDS 21-1276), respectively. In contrast, the A-TiO₂ product obtained from the conventional hydrothermal method is a typical anatase crystal according to the standard JCPDS 21-1272 pattern. The A-TiO₂-acid product also exhibits an anatase structure, indicating that post treatment using concentrated HNO₃ under the same conditions used for the proposed photocatalyst does not induce a transition of the crystal phase. These results indicate that HNO₃ treatment during the formation of TiO₂ crystals induces the transition of LPT into a rutile TiO₂ structure [35,36]. The surface area and pore distribution of R-TiO₂ nanorods were determined using N₂ adsorption-desorption isotherms (Fig. S1). One can see that the R-TiO₂ photocatalyst possesses a large specific surface area of 221.3 m² g^{−1} with a pore diameter of approximately 1.4 nm. This large surface area can provide many reaction sites, which are beneficial for reacting with protons to produce H₂ gas. The FESEM images in Fig. 2(a) and (b) reveal the uniform spindle-like morphology of the R-TiO₂ sample. The FTEM images clarify the fine morphology of the spindles as bundles of TiO₂ nanorods (Fig. 2(c)). The R-TiO₂-1M sample treated with a diluted HNO₃ solution also produces rutile TiO₂ nanobundles, but they are smaller than the bundles in the R-TiO₂ sample (Fig. S2(a)). In contrast, the A-TiO₂ sample prepared in the absence of a HNO₃ solution is composed of nanoparticles (Fig. S2(b)). The magnified FTEM image in the inset of Fig. 2(c) and HRTEM image in Fig. 2(d) indicate that each bundle consists of a dozen of nanorods with dimensions of approximately 300 nm in length and 100 nm in width. Regular lattice fringes can be clearly observed in the HRTEM image and the d-spacing of 0.320 nm can be attributed to the (110) crystallographic planes of rutile TiO₂. The lattice fringes are parallel to the axial direction of the nanorods, indicating that nitric acid treatment induces TiO₂ nanorods to grow along the (110) plane and adhere to each other to form bundles.

Fig. 2. FESEM (a, b), FTEM (c), and HRTEM (d) images of the R-TiO₂ catalyst.

The chemical structures of the as-prepared TiO₂ samples were investigated using FT-IR spectroscopy, as shown in Fig. 3. All of the spectra exhibit strong and broad bands below 1000 cm⁻¹, which are attributed to the stretching mode of Ti–O bonds in TiO₂ networks. The peak at 1383 cm⁻¹, which corresponds to the bending mode of nitrate groups [37], can only be observed in the FT-IR spectra of the R-TiO₂ and R-TiO₂-1M samples, indicating the grafting of nitrate groups onto the TiO₂ surfaces during the nitric-acid-induced assembly process. One can see that the signal of nitrate groups of R-TiO₂ is much stronger than that of the nitrate groups of R-TiO₂-1M. The peak at approximately 1634 cm⁻¹ originates from the bending vibrations of adsorbed H₂O on the sample surfaces. Another broad peak in the range of 3100–3600 cm⁻¹ corresponds to the stretching vibrations of O–H groups. One can see that the R-TiO₂ sample exhibits the most intense O–H stretching. These results indicate that nitrate group grafting promotes the formation of hydroxyl groups to produce an OH-rich surface, which is consistent with other inorganic acid treatments described in the literatures [28–31]. To clarify the chemical states of the TiO₂ samples, the XPS technique was employed. The results are presented in Fig. 4. All spectra were calibrated using the binding energy of standard C 1s of 284.6 eV. The high-resolution Ti 2p XPS spectrum of R-TiO₂ exhibits two major peaks at 458.5 and 464.3 eV, corresponding to the 2p_{3/2} and 2p_{1/2} peaks, respectively, of Ti⁴⁺ in the TiO₂ structure (Fig.

Fig. 3. FT-IR spectra of R-TiO₂, R-TiO₂-1M, A-TiO₂-No, and A-TiO₂-acid.

4(a)). The binding energy of Ti 2p displays a clear shift to higher values relative to R-TiO₂-1M, indicating electronic interactions between surface Ti atoms and nitrate groups. Accordingly, R-TiO₂ possesses an N content of 0.55 at%, while the surface N of R-TiO₂-1M is undetectable (Fig. 4(b)). The high-resolution N 1s XPS spectrum exhibits a nearly symmetric peak at 399.6 eV, suggesting that N atoms largely exist as surface-bonded N-containing groups, rather than doped states [38]. These results confirm the successful grafting of nitrate groups onto the rutile TiO₂ surface via concentrated nitric acid treatment.

3.2. Optical properties

The light absorption levels and band edges of photocatalysts are important properties that affect their performance. Fig. 5(a) presents the UV-vis DRS of the as-obtained samples. One can see that the rutile phase displays a red shift at the absorption edge compared to the anatase phase, indicating a wider light absorption range for rutile TiO₂ compared to that for anatase. The energy gap (E_g) values of the photocatalysts were calculated based on the converted Tauc plot presented in Fig. 5(b). The E_g values of both A-TiO₂ and A-TiO₂-acid were determined to be 3.22 eV, which is consistent with the results in the literature. The results also indicate that post treatment with nitric acid has a negligible influence on band energy. It should be noted that R-TiO₂ has a lower band gap (3.10 eV) compared to that of anatase, and this band gap narrowing can improve light absorption ability over a wider range. The PL spectra are presented in Fig. 5(c) to provide additional evidence for the noted

Fig. 4. High-resolution XPS spectra of R-TiO₂ and R-TiO₂-1M. (a) Ti 2p; (b) N 1s.

Fig. 5. UV-vis diffuse reflectance spectra (a), converted Tauc plot of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$) (b), and PL spectra (c) of R-TiO₂, A-TiO₂-No, and A-TiO₂-acid.

optical properties and charge transfer efficiency. The emission band originates from band-band electronic transitions and excitonic PL from surface vacancies and defects [39,40]. Similar to the UV-vis DRS results, post treatment with nitric acid has little influence on PL spectra. Compared to anatase TiO₂, an evident decrease in PL intensity can be observed in the rutile TiO₂ catalysts. These results demonstrate that the nitric-acid-induced assembly of rutile TiO₂ nanobundles results in an extended light absorption range and reduced charge recombination loss.

3.3. Photocatalytic activity and stability

Photocatalytic efficiency in terms of hydrogen production was evaluated in a TEOA aqueous solution under 300-W xenon arc lamp irradiation. Fig. 6(a) presents a comparison of different types of TiO₂ samples with 1.5 wt% of Pt loading. The rutile TiO₂ photocatalyst R-TiO₂-1M exhibits a higher H₂ evolution rate compared to that of A-TiO₂, indicating that the rutile structure can function as an efficient photocatalyst. Post treatment of TiO₂ crystals with concentrated nitric acid increases the average H₂ evolution rate from 52.0 to 92.6 μmol h⁻¹. In contrast, introducing concentrated nitric acid during the formation of TiO₂ crystals dramatically improves the H₂ evolution rate from 110.8 to 402.4 μmol h⁻¹, which is 3.1 times higher than that of the P25-TiO₂ reference photocatalyst. The apparent quantum efficiency of R-TiO₂ for H₂ production was calculated to be $57.5 \pm 0.2\%$ at $\lambda = 365 \pm 15$ nm, which is very high among recently reported results for pure TiO₂ photocatalysts. The

influence of acid treatment on the charge carrier separation of the TiO₂ photocatalyst was investigated based on photocurrent measurements. Comparisons of photocurrent signals revealed similar tendencies in terms of the improvement based on acid treatment (Fig. 6(b)). The photocurrent density of R-TiO₂ is higher than that of the comparative samples, which suggests that the most efficient charge separation can be achieved under light irradiation. A smaller semicircle diameter at high frequencies of EIS confirmed reduced charge transfer resistance across the interface of the R-TiO₂ electrode and electrolyte, resulting in reduced charge recombination loss (Fig. 6(c)). As evidenced by the characterizations discussed above, the direct treatment of LPT precursor with concentrated nitric acid can induce a transformation into rutile TiO₂ nanorods and attach them to form discrete nanobundles with nitrate-group-grafted surfaces. Post-acid treatment of TiO₂ crystals cannot initiate such assembly or surface grafting. Therefore, the improved charge separation efficiency and photocatalytic performance of R-TiO₂ can be attributed to surface modification by nitrate groups.

In addition to activity, stability is also an important factor for evaluating the performance of photocatalysts. Fig. 7(a) presents the results of cyclic photocatalytic H₂ production for four consecutive cycles. One can see that the R-TiO₂ photocatalyst exhibits a tendency to gradually decrease in terms of efficiency after each cycle, indicating the instability of rutile TiO₂ nanobundles. To clarify the reason for this instability, changes in structure before and after the photocatalytic reactions were analyzed using XRD and FT-IR characterizations. The comparison in Fig. 7(b) confirms that the crystal phase is

Fig. 6. (a) Photocatalytic H₂ production rates of R-TiO₂, R-TiO₂-1M, A-TiO₂-No, A-TiO₂-acid, and P25-TiO₂ photocatalysts. Experimental conditions: 50 mg of photocatalyst with 1.5 wt% of Pt loading in a mixture of 90 mL of deionized water and 10 mL of TEOA with an irradiance of 0.38 W/cm². Transient photocurrent responses during three on-off cycles (b) and EIS Nyquist plots (c) of as-prepared samples.

Fig. 7. (a) Photocatalytic cycling tests for H₂ production using the R-TiO₂ photocatalyst; XRD patterns (b) and FT-IR spectra (c) of R-TiO₂ before and after cyclic photocatalytic experiments; (d) zeta potential of R-TiO₂ before and after the first and fourth H₂ evolution tests, as well as the refreshed catalyst after the fourth H₂ evolution test.

well-maintained during the H₂ production reactions. However, the signal of nitrate bending appears to weaken after cyclic testing (Fig. 7(c)), suggesting that proton reduction was accompanied by the consumption of nitrate groups on the R-TiO₂ surface. Because this loss in photocatalytic activity is related to the number of surface nitrate groups, the R-TiO₂ photocatalyst was refreshed after four cycles by repeating the concentrated nitric acid treatment process. As expected, the performance in the fifth cycle partially recovered to match the efficiency of the second cycle. Changes in the amount of adsorbed nitrate groups can be investigated using zeta potential measurements. Fig. 7(d) reveals that the R-TiO₂ photocatalyst is negatively charged with a zeta potential value of -9.56 mV based on surface modification by nitrate anions. The surface charge gradually decreases after each cycle and nearly all charges are lost after the fourth cycle. It should be noted that the surface becomes negatively charged again after recovery of the used R-TiO₂ photocatalyst. It can be deduced that nitrate group grafting is crucial to photocatalytic H₂ production efficiency. As mentioned previously, in the literature, the enhancement mechanisms of inorganic acids are largely discussed from two perspectives, namely the promotion of hydroxyl group formation and interactions between oppositely charged holes, both of which contribute to oxygenic radical production for pollutant degradation [28–32]. Apparently, the influence mechanism of nitrate group grafting on photocatalytic H₂ production is completely different. Based on the above analysis, a reaction mechanism for this photocatalyst can be proposed (Scheme 1). Because holes are consumed by the sacrificial reagent as TEOA, the negative field effects of nitrate groups facilitate the trapping of positive protons to yield hydrogen gas. Additionally, changes in morphology before and after cyclic

testing were studied based on FESEM observations. In contrast to the fresh catalyst in Fig. 2(a) and (b), the crystals are partially aggregated after the first cycle, as shown in Fig. 8(a). After four cycles, the catalyst largely lost the original spindle-like morphology and experiences significant agglomeration, as shown in Fig. 8(b). Fig. 8(c) verifies the recovery of the used R-TiO₂ photocatalyst (product after four cycles) by repeating the acid treatment process, although the original uniform morphology cannot be recovered. The fifth cycling test caused further aggregation of the refreshed crystals, as shown in Fig. 8(d). Morphology changes can also be explained by reduced surface charges. Based on the existence of zeta potential, the electrostatic repulsion resulting from the nitrate-group-grafted surface suppresses the aggregation of crystals. The consumption of nitrate during H₂ production gradually weakens the electrostatic repulsion and causes the structures of the rutile TiO₂ nanobundles to become unstable.

4. Conclusions

In summary, we developed a facile nitric-acid-induced assembly strategy for the synthesis of spindle-like rutile TiO₂ nanobundles. Structural characterizations demonstrated that the proposed strategy is effective for surface modification using nitrate groups. The R-TiO₂ sample exhibited the highest photocatalytic H₂ evolution rate of $402.4 \mu\text{mol h}^{-1}$, which is 3.1 times higher than that of Degussa P25-TiO₂. In contrast, the anatase and rutile TiO₂ photocatalysts without sufficient nitrate group grafting only yielded H₂ evolution rates of 52.0 and $110.8 \mu\text{mol h}^{-1}$, respectively. The enhanced photocatalytic efficiency of R-TiO₂ can be attributed to the negative field effects of nitrate groups, which favor the trapping of positive protons on the

Fig. 8. FESEM images of R-TiO₂ photocatalyst after the first (a) and fourth (b) cyclic tests of H₂ evolution. (c) FESEM image of the refreshed R-TiO₂ photocatalyst after the fourth cycling test based on repeating the acid treatment process. (d) FESEM image of the R-TiO₂ photocatalyst in (c) after the fifth cycling test.

surface to improve charge carrier separation. Photocatalysts before and after photocatalytic reactions were compared from the perspectives of crystal and chemical structures, morphology, and surface charge properties. It can be deduced that surface charges are crucial for structural stability based on electrostatic repulsion. Overall, this work is of considerable significance for developing highly efficient photocatalysts for H₂ production based on different influence mechanisms of inorganic acids from those reported in the literatures.

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Graphical Abstract

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Nitrate-group-grafting-induced assembly of rutile TiO₂ nanobundles for enhanced photocatalytic hydrogen evolution

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Nitrate group grafting induced the assembly of rutile TiO₂ nanorods into spindle-like nanobundles. The grafted photocatalyst exhibited a significantly enhanced H₂ evolution rate based on the improved proton trapping efficiency of the negatively charged surface.

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硝酸根接枝诱导组装金红石相TiO₂纳米束以增强光催化产氢

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摘要: 化石燃料的快速消耗加速了全球能源危机和环境污染等问题。光催化产氢直接利用清洁和可持续的太阳能实现向化学燃料的转化, 因而成为一种有前景的技术。众多半导体光催化剂中, 二氧化钛因其高光催化活性、稳定的化学性质、低成本和无毒等优势而被广泛用作分解水产氢的光催化剂。最近, 金红石相TiO₂纳米晶体在某些情况下被证明具有光催化的潜力, 然而其光生电子-空穴对的快速复合显著抑制了光催化效率。表面修饰、构建异质结和负载助催化剂等策略被用来提高光生载流子的分离效率以减少复合损失, 从而提升光催化活性。

由于光催化反应通常发生在光催化剂的表面活性位点上, 因此通过改善表面性质改变电荷转移途径对光催化活性具有重要影响。磷酸、硫酸、硼酸和盐酸等无机酸的修饰可以改变光催化剂的表面基团, 分别通过促进表面羟基的形成和氧气的吸附以及改变表面电荷性质更有效地捕获空穴, 实现光生电子和空穴的分离, 有助于光催化降解有机污染物。然而, 这种影响机制显然不适用于光催化产氢体系, 目前对无机酸修饰用于分解水产氢的研究鲜有报道。因此, 通过酸改性策略制备高效产氢的光催化剂仍然是一个相当大的挑战。

本文利用硝酸诱导策略合成纺锤状金红石相二氧化钛纳米束(R-TiO₂)。首先, 制备层状质子化钛酸盐(LPT)作为TiO₂的前体, 随后, 加入浓硝酸以诱导向金红石相TiO₂的转变, 并组装形成纺锤状纳米束。对照实验显示, 硝酸的酸化可以诱导LPT向金红石相TiO₂的转变, 而相同条件下浓硝酸后处理不会引起晶相的转变。纺锤形纳米束的形成源于, 硝酸诱导R-TiO₂沿(110)方向生长并彼此粘附, 硝酸诱导组装过程成功在TiO₂表面修饰上硝酸根, 同时扩大了光吸收范围, 有效减少了电荷复合损失。光催化产氢测试证明了R-TiO₂光催化剂具有高效的产氢性能, 产氢速率为402.4 μmol h⁻¹, 是Degussa P25的3.1倍, 并且显著高于未经浓硝酸处理的锐钛矿(52.0 μmol h⁻¹)或金红石相(110.8 μmol h⁻¹)光催化剂。为了说明表面硝酸根的影响, 分别从晶体和化学结构、形态以及表面电荷性质方面比较了光催化反应前后的变化, 结果表明, R-TiO₂增强的光催化效率可归因于硝酸根基团的负场效应, 有利于在表面上捕获带正电的质子以促进载流子分离, 提高光催化产氢的效率。

总之, 本工作不仅对于发展表面修饰策略制备高效产氢光催化剂的研究具有重要意义, 而且提出了一种不同于文献报道的无机酸影响机制。

关键词: 酸改性; 金红石相TiO₂; 表面修饰; 产氢; 光催化

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