Fabrication of mixed-crystalline-phase spindle-like TiO_2 for enhanced photocatalytic hydrogen production

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The fabrication of heterojunction between different crystalline phases has been considered to be an effective strategy for promoting charge separation during photocatalytic process. Herein, the mixed-crystalline-phase (MC), spindle-like TiO_2 was prepared with a simple hydrothermal method, which was followed by a series of calcination processes. The final products are composed of two crystalline phases including anatase and brookite. The anatase/brookite ratio of the TiO_2 is tuned by varying the calcination temperature. The MC TiO_2 that consisted of 85.5% anatase and 14.5% brookite has the highest rate of photocatalytic hydrogen evolution ($290.2 \mu\text{mol h}^{-1}$) compared to the purely anatase TiO_2 . This is attributed to the mixed-phase heterojunction structure that improves electron-hole separation, and therefore, enhances the photocatalytic hydrogen production.

INTRODUCTION

With the increasing consumption of the world's limited reserves of fossil fuels, there has been a growing interest in finding renewable and clean energy sources. Hydrogen is believed to be the most promising source of clean energy, and the production of hydrogen from water via semiconductor-based photocatalysis is an ideal route [1–5]. Of the potential semiconductors, TiO_2 is considered to be the most suitable for photocatalytic water splitting because of its low cost, non-toxicity, and long-term stability [6–9]. However, TiO_2 -based photocatalysts currently show low photocatalytic activity for splitting water into H_2 and O_2 . One of the key issues related to this problem is the limited charge-separation efficiency upon photoexcitation, which largely depends on the intrinsic electronic and structural properties of TiO_2 [10–12]. To improve the photocatalytic activity of TiO_2 , it is highly desirable to develop approaches that can efficiently promote charge separation.

The fabrication of a heterojunction between different semiconductors has been demonstrated to be an effective strategy for promoting charge separation during photocatalytic processes [13,14]. For TiO_2 -based photocatalysts,

heterojunction structures, such as Ag- TiO_2 [13], C_3N_4 - TiO_2 [14], and TiO_2 -graphene [15], can provide a driving force for separating the photoinduced charge carriers by changing the band gap structure. A fully formed heterojunction could also lead to enhanced photocatalytic activity in either the production of hydrogen or degradation of pollutants. According to previous studies, composite semiconductor heterojunctions with a mixed phase have been demonstrated excellent photocatalytic performance [16,17]. TiO_2 commonly exists in three phases: rutile (tetragonal, $P4_2/mnm$), anatase (tetragonal, $I4_1/amd$), and brookite (orthorhombic, $Pbca$). Of these three phases, brookite nanocrystals exhibit higher photocatalytic activity than the rutile and anatase phases. Furthermore, compared to single-phase TiO_2 , mixed-phase TiO_2 , such as anatase/brookite, rutile/brookite, and anatase/rutile, has been proven to have higher photocatalytic activity [9,10]. For example, anatase/brookite TiO_2 nanocrystals were synthesized with a sonochemical sol-gel method, and the nanocrystals exhibited higher photocatalytic activity than single-phase anatase TiO_2 [18]. A brookite/rutile mixture of TiO_2 was synthesized through the thermolysis of TiCl_4 , and a brookite/anatase mixture of TiO_2 was obtained via the hydrolysis of titanium isopropoxide in the presence of nitric acid [19]. However, it remains a challenge to synthesize mixed-phase TiO_2 with a simple one-step process and tunable phase composition. More importantly, the essential relationship between the crystal phase of the heterojunction and photocatalytic activity is not well understood. An in-depth understanding of how the crystal phase of the heterojunction affects photocatalytic activity would be a great aid in the design and preparation of efficient semiconductor-based photocatalysts.

In this study, we investigated the synthesis of mixed-crystalline-phase (MC), spindle-like, anatase/brookite TiO_2 with a simple hydrothermal method. During the experimental process, titanium oxysulfate was selected as the Ti precursor to produce the spindle-like TiO_2 . The TiO_2 was

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then subjected to various calcination processes to obtain a series of products. The anatase/brookite ratio of the TiO_2 was tuned by varying the calcination temperature.

EXPERIMENTAL SECTION

Synthesis of MC TiO_2

The MC TiO_2 was fabricated with a hydrothermal method. Titanium oxysulfate (TiOSO_4 , 0.1 g) was dissolved in 30 mL of distilled water. Then, 4 mL of 80% hydrazine hydrate ($\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$) was added dropwise to the TiOSO_4 -containing solution under mechanical stirring. After being stirred for 0.5 h, the suspension was transferred to a Teflon-lined autoclave and heated to 150°C for 24 h. After the hydrothermal process, the resulting white products were separated with centrifugation, washed with distilled water and ethanol for three times, and dried for 24 h at 60°C in an oven. To improve the crystallinity and control the phase composition, the MC TiO_2 was heated at various temperatures (from 500 to 900°C) under N_2 atmosphere for 1 h. The samples obtained were denoted as MC-T, where T represents the calcination temperature. For example, the sample calcinated at 500°C was denoted as MC-500.

Characterization

X-ray powder diffraction (XRD) patterns were obtained by Bruker D8. Scanning electron microscopy (SEM) micrographs were taken with a Hitachi S-4800 operating at 5 kV. Transmission electron microscopy (TEM) micrographs were obtained with a JEM-2100 electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Raman spectra of the samples were obtained with a Jobin Yvon HR800 micro-Raman spectrometer equipped with a 457.9 nm light source. The Fourier transform infrared (FT-IR) spectra of the samples were collected with a PE Spectrum One B IR spectrometer. UV-vis diffuse reflectance spectra (DRS) were measured with a UV-vis spectrophotometer (Shimadzu UV-2550). X-ray photoelectron spectroscopy (XPS) analysis was performed with a VG ESCALAB MK II equipped with an Mg K α (1253.6 eV) achromatic X-ray source. The surface photovoltage (SPV) measurements of the samples were performed with a home-built apparatus. The powder samples were sandwiched between two indium tin oxide (ITO)-coated glass electrodes, and the changes in the surface potential barrier in the presence of light and in the dark were measured. The raw SPV data was normalized with a Model Zolix UOM-1S illuminometer.

Photocatalytic hydrogen production experiments

The photocatalytic hydrogen production experiments were conducted in an online photocatalytic hydrogen production system (AuLight, Beijing, CEL-SPH $_2$ N) at ambient

temperature (20°C). The catalyst (0.1 g) was suspended in a mixture of distilled water (80 mL) and methanol (20 mL) in the reaction cell under magnetic stirring. The 1 wt.-%-Pt-loaded photocatalysts were prepared with the standard *in situ* photodeposition method using an H_2PtCl_6 aqueous solution. Prior to the reaction, the mixture was deaerated by evacuation to remove any O_2 and CO_2 dissolved in the water. The reaction was initiated by irradiating the mixture with UV light from a 300 W Xe lamp equipped with a 200–400 nm reflection filter, i.e., the wavelength of light used was approximately 200–400 nm. The gas evolution was only observed under irradiation, and was analyzed with an online gas chromatograph (SP7800, TCD, 5 Å molecular sieve, N_2 carrier gas, Beijing Keruida Limited). To evaluate the photocatalytic stability, after the first 2.5 h hydrogen production run, the photocatalyst was separated from the suspension, washed with water, and dried at 60°C. The recovered photocatalyst was then used for the next hydrogen production run under the same conditions.

Measuring the photoelectric properties of the MC TiO_2

The photocurrent of the MC electrodes was measured in the three-electrode configuration with a BAS100B electrochemical analyzer (Bioanalytical Systems Inc. USA). The MC films were the working electrode, saturated Ag/AgCl was used as the reference electrode, and platinum foil (3 cm $\times$ 2 cm) was used as the counter electrode. A solution of 1 M NaOH (pH = 13.6) purged with N_2 was used as the electrolyte. A 70 mW UV lamp (OMRON ZUV-C30H, λ = 365 nm) provided the UV light, which penetrated the circular quartz window mounted in one side of the cell and illuminated the working electrode.

RESULTS AND DISCUSSION

The crystal structure and composition of the synthetic products were confirmed with XRD (Fig. 1). As can be seen, the diffraction peaks of the MC TiO_2 at 2θ = 25.3°, 37.8°, 48.2°, 53.9°, 55.1°, and 62.7° belong to the anatase phase of TiO_2 [20,21]. It is worth noting that the small peak at 2θ = 30.8° is the (121) reflection of the brookite phase of TiO_2 [22]. As the calcination temperature increases, the intensity of the characteristic brookite peak decreases. Once the calcination temperature reaches 900°C, the (121) peak has completely disappeared, and thus, the sample is composed of only the anatase phase. Furthermore, as the calcination temperature increases, the ratio of brookite to anatase changes. The phase composition of each sample is summarized in Table S1. The ratio of brookite is initially 8% for the as-prepared MC TiO_2 , but the ratio increases to approximately 14.5% for the MC-600 sample, which can be attributed to the calcination temperature. This further proves that both anatase and brookite phases were formed

Figure 1 XRD patterns of the as-prepared MC TiO₂ and samples calcined at different temperatures.

in the final products. Usually, the brookite is a metastable phase of TiO₂ that is converted into anatase or rutile structures upon calcination. However, in this work, the high ratio of brookite observed in the final products is because the amino group of the hydrazine hydrate may inhibit the crystal phase change, leaving the brookite structure unchanged. Interestingly, the surface area of the samples also changes from 47.3 m² g⁻¹ for the as-prepared MC TiO₂ to 59.4 m² g⁻¹ for the MC-500 sample (Table S1). The surface area then decreases as the calcination temperature increases. Raman spectroscopy was also used to confirm the presence of the mixed anatase/brookite phases in the samples; the detailed Raman spectra are shown in Fig. S1. For reference purposes, the peak at 153 cm⁻¹ corresponds to the E_{1g} mode of the anatase phase of TiO₂. The other peaks of TiO₂ are also present at 405, 525, and 648 cm⁻¹. These peaks are all characteristic peaks of the anatase phase of TiO₂ [23]. However, for the MC-T samples, it is clear that there are some changes in their Raman spectra after the thermal treatment. Even though increasing the calcination temperature does not change the intensity of all of the peaks, it changes the positions of all of the peaks. This shifting of the peaks towards lower wavenumbers is evidence of the presence of brookite in the calcined products.

We then studied the microscopic morphology and structure of the samples with TEM. TEM images of the as-prepared MC TiO₂ and MC-600 samples are shown in Fig. 2. The low-magnification image (Fig. 2a) demonstrates that the as-prepared MC TiO₂ has a unique spindle-like morphology. After the calcination process, the morphology of the MC-600 sample has slightly changed, resulting in the aggregation of the nanoparticles with a mean size of 40–70 nm (Fig. 2b). Highly detailed images of the struc-

tures were obtained with high-resolution TEM (HRTEM), as shown in Fig. 2c. It should be noted that the interplanar distance of 0.35 nm is close to the d-spacing of the (101) plane of anatase TiO₂ reported in the previous studies [24]. The other region was also analyzed, and the lattice fringes were found to be separated by 0.23 nm, which is close to the d-spacing of the (121) plane of brookite TiO₂ [25]. Thus, these experimental results confirm that brookite-phase TiO₂ is in contact with the anatase-phase TiO₂ to form two-phase heterojunction nanostructures, which is in good agreement with the XRD results. TEM images of the MC-900 sample are shown in Fig. S2. In addition, a possible structure of the brookite/anatase heterojunction is shown in Fig. 2d.

To investigate the composition of the MC TiO₂ in the final products, we performed XPS analysis on the MC-600 (brookite/anatase TiO₂) and MC-900 (anatase TiO₂) samples (Fig. 3). In Fig. 3a, the two peaks of the MC-900 sample at 458.72 and 464.45 eV are assigned to the Ti 2p_{3/2} and Ti 2p_{1/2} spin-orbit-split states of the photoelectrons in the Ti⁴⁺ chemical state, respectively [26]. Interestingly, in the MC-600 XPS spectrum, the Ti 2p states slightly shift towards lower binding energies compared to that of the MC-900. Normally, this kind of shift is attributed to the changes in the chemical environment, such as oxygen vacancies in this case. The oxygen vacancies are beneficial to improving the photocatalytic performance. The existence of oxygen vacancies is further validated by the differences in the O 1s XPS spectra of the samples (Fig. 3b). In the O 1s XPS spectrum of the MC-900 sample, the O 1s peak centered at 529.9 eV is mainly attributed to the oxygen in the TiO₂ crystal lattice, which agrees with the previous studies [27]. However, in the O 1s XPS spectrum of the MC-600 sample, the O 1s peak has slightly shifted by 0.3 eV from 529.9 to 529.6 eV. The origin of this downward shift is the well-known band bending effect, which is caused by the extra electrons from the oxygen defects in the TiO₂ crystal lattice. In addition, the oxygen vacancies will also influence the O₂ absorption performance of the composites. The O 1s signal at 531.5 eV is closely related to the hydroxyl groups of oxygen species adsorbed by the composites. A pronounced increase in this peak can be observed in the XPS spectrum of the MC-600 sample, which indicates the adsorption of additional oxygen species because of the high chemical reactivity of the surface. Therefore, the presence of an MC heterojunction can greatly enhance the adsorption of O₂, promoting the photogenerated electrons captured by the adsorbed O₂, and leading to a large increase in the charge separation. In addition, the Ti 2p XPS spectra, SPV spectra, and photocurrent responses of the other samples are shown in Fig. S3.

The brookite/anatase heterojunction could change the

Figure 2 TEM and HRTEM images of the (a) as-prepared MC TiO₂ and (b, c) MC-600 samples. (d) A diagram of a possible structure of the brookite/anatase heterojunction.

Figure 3 (a) High-resolution Ti 2p XPS spectra of the MC-600 and MC-900 samples. (b) O 1s XPS spectra of the MC-600 and MC-900 samples.

energy band structure of the final products. Therefore, the UV-vis absorption spectra of the samples were recorded to investigate the energy band structure and light-harvesting capabilities of the photocatalysts. Fig. S2 shows the UV-vis absorption spectra of the MC-600 and MC-

900 samples. The results indicate that the MC-600 sample has a strong absorption band in the short wavelength/high energy region of the light spectrum. The band gap energies are calculated by extrapolating the absorption edges with the equation $(h\nu F(R_{\infty}))^2 = A(h\nu - E_g)$. The band gap

energies of the samples were estimated to be approximately 3.4 eV (MC-900) and 3.5 eV (MC-600), with the slight difference caused by the different ratios of the brookite and anatase phases. Furthermore, with the higher energy of the electronic band structure of the MC-600 sample, it is expected that the MC-600 sample will possess thermodynamically enhanced reduction and oxidation abilities in photocatalytic reactions. The charge-transfer rate between the semiconductor catalyst and redox species in solution also depends on the energy level correlation. Therefore, it is expected that the MC-600 sample will possess a better photocatalytic performance for hydrogen evolution.

The rate of hydrogen production under a UV light was measured to evaluate the photocatalytic activity of the final products. Fig. 4a shows the photocatalytic hydrogen evolution of the different catalysts as a function of time. The as-prepared MC TiO_2 shows negligible activity, with an average hydrogen production rate of only $25 \mu\text{mol h}^{-1}$, which indicates that it has poor hydrogen evolution kinetics. Similarly, the hydrogen production rate of MC-900 sample is only $20 \mu\text{mol h}^{-1}$. However, the MC-600 sample shows a dramatic increase in the rate of hydrogen evolution, achieving a production rate of $290.2 \mu\text{mol h}^{-1}$. The high performance of MC-600 sample indicates that engineering the composite structure can induce synergistic effects. These results show that the MC-600 TiO_2 , which consists of 85.5% anatase and 14.5% brookite, has the highest rate of photocatalytic hydrogen evolution when compared to the purely anatase TiO_2 . A recycling test was performed to investigate the stability and reactivity of the MC-600 sample as a photocatalyst. Fig. 4b shows the measured hydrogen production under a UV light during five consecutive cycles. As can be seen from the first run to the fifth run, the MC-600 sample can be effectively recycled and repeatedly used without any obvious decrease in ac-

tivity. This is attributed to the effective electron-hole separation that results from the transfer of charges from the brookite conduction band to the anatase conduction band [19,20]. The 1 wt.-%Pt-loaded photocatalysts were characterized after the photocatalytic measurements with TEM micrographs (Fig. S5), which show a uniform distribution of particles that contribute to the enhanced hydrogen evolution stability.

The introduction of heterojunctions between the anatase and brookite phases is the main reason for the high photocatalytic activity. Therefore, the SPV spectra of the samples were measured to understand the heterojunction effect. SPV spectroscopy is a rapid and non-destructive measurement technique for obtaining information about the separation rate of photoinduced charge carriers, and is based on the differences in the SPV before and after the sample is irradiated [28]. Fig. 5a shows the SPV responses of the MC-600 and MC-900 samples in air. According to the principles of SPV, the SPV signal mainly results from the photogenerated charges, followed by the separation of charges under the built-in electric field or diffusion processes. Interestingly, compared to the MC-900 sample, the MC-600 sample has a weak SPV response. It is thought that the oxygen vacancies in the MC-600 sample can easily capture the photoinduced electrons, inhibiting the recombination of photogenerated charges, resulting in a low net surface charge, and therefore, a weak SPV response. These experimental results also show that the mixture of crystalline phases allows photogenerated electrons to be extracted and stored, reducing the electron-hole pair recombination rate, and thus, improves the quantum yield and lifetime of the charge carriers. Another type of photocurrent measurement was conducted to understand the conductivity and charge transport properties of the MC-600 and MC-900 samples (Fig. 5b). As can be seen, a fast and uniform

Figure 4 (a) The photocatalytic hydrogen production of the different samples under a UV light. (b) The recyclability of the MC-600 sample.

Figure 5 The SPV spectra and the photocurrent responses of the MC-600 and MC-900 samples.

photocurrent response is obtained for each switch-on and switch-off event of both electrodes. However, the photocurrent of the MC-600 electrode is approximately 7-times higher than that of the MC-900 electrode, indicating that the enhanced photocurrent and good stability is achieved through the electronic interactions between the brookite and anatase phases. Thus, for the MC-600 sample, the photoinduced electron-hole pairs are easily transferred to the sample's surface because of the interfacial interactions between the brookite and anatase phases. Furthermore, the MC-600 sample has the highest concentration of the brookite phase and one of the highest surface areas compared to that of the other products, which are possibly responsible for the excellent photocatalytic performance for hydrogen evolution.

Conclusions

In summary, the spindle-like MC TiO₂ samples were prepared with a simple method. During the experimental process, titanium oxysulfate was selected as the Ti precursor to produce the spindle-like MC TiO₂. A mixture of the anatase and brookite phases of TiO₂ produced higher rates of photocatalytic hydrogen evolution compared to that of purely anatase TiO₂. The mixed-phase heterojunction structures decreased the electron-hole pair recombination rate, and subsequently increased the lifetime of the charge carriers.

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Author contributions Fu H and Jiang B designed and engineered this work. Hao R performed the experiments. Jiang B and Hao R wrote this paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary data are available in the online version of the paper.

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中文摘要 本文采用一种简单的方法制备了混晶相（锐钛矿/板钛矿）纺锤形二氧化钛。首先，硫酸氧钛被选择为前驱体，通过水热合成以及惰性气氛下的热处理过程，得到一系列混晶相（锐钛矿/板钛矿）二氧化钛，其中，组成为85.5%锐钛矿、14.5%板钛矿的二氧化钛具有最优异的光催化分解水制氢活性，产氢速率为 $290.2 \mu\text{mol h}^{-1}$ 。研究发现锐钛矿/板钛矿晶相间异质结的存在能够有效的分离光生载流子，同时进一步提高对电子的捕获，实现光催化分解水制氢效率的显著提高，这种基于硫酸氧钛水热合成方法得到的高活性光催化剂在制氢领域具有潜在的应用价值。