Hydrogenated TiO₂/SrTiO₃ porous microspheres with tunable band structure for solar-light photocatalytic H₂ and O₂ evolution

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ABSTRACT The production of H₂ and O₂ from solar-light photocatalytic water splitting has attracted significant research attention as a clean and renewable source of energy. In this study, hydrogenated TiO₂/SrTiO₃ porous microspheres were prepared as a high-performance photocatalyst. Titanium glycerolate and then strontium complex precursors were first prepared via a two-step solvothermal process, then, after calcination in air and subsequent H₂/Ar reduction treatments, hydrogenated TiO₂/SrTiO₃ porous microspheres with controllable defects and band positions were prepared. Several characterization techniques were used to demonstrate that the catalyst heterostructures, the oxygen-vacancy content, and the unique porous structures synergistically enhanced the visible-light harvesting abilities and photogenerated charge separation, and resulted in improved photocatalytic efficiency for H₂ and O₂ evolution. As expected, the optimum treatment conditions provided hydrogenated TiO₂/SrTiO₃ porous microspheres that showed excellent photocatalytic activity with H₂ and O₂ evolution rates of 239.97 and 103.79 $\mu\text{mol h}^{-1}$ (50 mg catalyst, under AM 1.5 irradiation), respectively, which were ca. 5.9 and 6.6 times higher, respectively, than those of solid TiO₂/SrTiO₃ materials. Thus, this type of hydrogenated TiO₂/SrTiO₃ porous microsphere catalyst shows great potential as a photocatalyst for solar-energy conversion applications.

Keywords: TiO₂/SrTiO₃, heterostructure, oxygen vacancy, visible-light absorption, photocatalysis

INTRODUCTION

Semiconductor photocatalysis provides environmentally friendly methods for splitting water to produce clean H₂ and O₂ energy and the decomposition of organic contaminants with the assistance of solar light, and it is therefore considered to be a promising strategy for mitigating energy

shortages and realizing environmental remediation [1,2]. In this context, H₂ and O₂ have attracted remarkable interest as promising energy carriers as they do not produce the greenhouse gas CO₂ [3,4]. The synergistic effects of the two related half-reactions, i.e., photoinduced electron reduction and hole oxidation, are very important for H₂ and O₂ evolution from water splitting, and inherently determine photocatalysis efficiency [5]. Since the pioneering work by Fujishima and Honda on water splitting to produce H₂ and O₂ under UV illumination utilizing TiO₂ photoelectrodes, many photocatalysts, such as TiO₂ and SrTiO₃, have been widely investigated for water splitting applications owing to their non-toxicity, low cost, chemical and optical stability, and biocompatibility [6–9]. However, rapid recombination of photogenerated charge carriers and low visible-light utilization because of their wide band gap have limited their practical application.

Constructing heterostructure semiconductor composites has proved to be an effective approach to accelerate the transfer and separation of photogenerated charge carriers due to the existence of an interfacial potential gradient between the two components of the composite. The improved photocatalytic activity of these semiconductor composites originates from the rapid transfer of photogenerated electrons and holes from one component to the other. For TiO₂/SrTiO₃ composites, their significantly enhanced catalytic activities compared to those of TiO₂ or SrTiO₃ alone have also been reported in several studies [10–14]. However, TiO₂/SrTiO₃ composites do not absorb visible light because of their wide band gaps. The visible-light photocatalytic performance of a catalyst strongly depends on the nature of the catalyst in terms

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of defect states, components, etc. Various strategies have been proposed to shift the photoabsorption region of wide-band-gap photocatalysts toward the visible-light region, such as doping with metals (e.g., Cr or Fe) and nonmetal ions (e.g., N or S) [15–19] or coupling with other narrow-band-gap semiconductors [20,21]. Furthermore, recent studies have shown that, through the partial reduction method, semiconductors modified by hydrogen treatment (e.g., TiO_2 and CeO_2) present oxygen vacancies and exhibit visible-light response for robust charge generation [22–24]. Annealing the semiconductors in a H_2 atmosphere creates oxygen vacancy sites, thus forming donor states below the conduction band, leading to an improvement in light absorption and water oxidation performance. Furthermore, the disordered layer produced can significantly enhance visible-light absorption [25]. The exploitation of oxygen vacancies in hydrogenated semiconductors provides new strategies to control their charge separation process and electronic structures [26,27]. Thus, this methodology can be used to maximize the advantages of the wide range of semiconductor photocatalysts while minimizing their disadvantages.

In addition, much effort has been dedicated to realizing the potential of semiconductor photocatalysis by controlling the size, morphology, and structure of photocatalytic nanomaterials, which strongly affect their photocatalytic properties and applications [28,29]. Compared with their bulk counterparts of the same size, porous nanoparticles exhibit superior performance owing to their high surface area, multiple channels, and lower resistance to mass transfer in catalytic systems, all of which endow them with multifunctional capabilities [30,31]. Until now, there have been no reports on the synthesis of $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres. For most of these kinds of composites, homogeneous component distribution is difficult to achieve, which hinders their catalytic application. Moreover, low visible-light utilization limits their efficiency under sunlight [32–34]. Thus, there is an urgent need to prepare $\text{TiO}_2/\text{SrTiO}_3$ composites with homogeneous component distribution and multichannel synergistic effects in order to provide photocatalysts with enhanced visible-light absorption and photocatalytic performance.

In this study, hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres were synthesized via a two-step solvothermal route. Flower-like titanium glycerolate (Ti-Gly) complex precursors were first prepared based on the methodology from our previous study [35]. In the subsequent solvothermal process, the addition of a strontium salt allowed further solvothermal reaction, leading to the formation of homo-

geneous Ti-Gly-Sr complexes. Spherical, flower-like, or irregular bulk morphologies were selectively obtained by changing the ratio of water and ethanol in the reaction solvent. The component and surface oxygen vacancy concentration of the composites were adjusted by changing the reactant ratio (Ti and Sr) and hydrogenation conditions, respectively. We also demonstrated the synergistic effects of the well-designed multichannel structure of the $\text{TiO}_2/\text{SrTiO}_3$ composite photocatalysts, including the heterojunction effect, surface defect effects, and the effects of the unique structure, which synergistically promote the production of photoinduced charge carriers and visible-light absorption. As expected, the optimized hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ porous microsphere photocatalytic system exhibited significantly higher photocatalytic activity than that of irregular $\text{TiO}_2/\text{SrTiO}_3$ solid composites.

EXPERIMENTAL SECTION

Preparation of hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres

The synthesis process was divided into two steps. The first step was the preparation of Ti-Gly complexes, which was achieved according to our previously reported procedures [35]. Specifically, 1 mL tetrabutyl titanate (TBOT) and 5 mL glycerin (Gly) were added to 20 mL ethanol to form a stable and clear solution, and then the solution was transferred to a Teflon-lined autoclave and heated at 180°C for 12 h. The resultant mixture was centrifuged. In the second step, the obtained precipitate was added to a mixed solution containing a predetermined amount of strontium nitrate, 5 mL Gly, and 17 mL mixed solvent (ethanol and water), and stirred for 30 min at room temperature. By changing the solvent proportions of ethanol and water, different morphologies were obtained, and the composition of the product was also altered by changing the molar proportion of Ti and Sr (the molar ratios 1:0.2, 1:0.4, 1:0.6, 1:0.8, and 1:1 were used). Then the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, heated to 180°C for 12 h and then cooled to room temperature. The obtained Ti-Gly-Sr precursor was washed several times by centrifugation using ethanol and finally dried at 60°C in air for 6 h. The obtained products were calcined at 1000°C for 4 h at a heating rate of 3°C min^{-1} to form $\text{TiO}_2/\text{SrTiO}_3$ composites. Finally, the hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ composites were obtained by calcination in a H_2 (10%)/Ar (90%) mixed gas flow at 800°C for 2 h under normal pressure conditions with a constant heating rate of 5°C min^{-1} . The samples are denoted as H- $\text{TiO}_2/\text{SrTiO}_3$.

Characterization

Powder X-ray diffraction (XRD) data for the samples were recorded with a Bruker D8 Advance using a Cu K α radiation source (40 kV, 44 mA). Scanning electron microscopy (SEM) characterizations were performed on a Hitachi S-4800 electron probe microanalyzer. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) studies were carried out with a JEOL 2100 TEM microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCALABMK II with a Mg K α achromatic X-ray source (1253.6 eV). The electron spin resonance (ESR) spectra were measured at room temperature with a Bruker EMX-8/2.7 ESR spectrometer. UV-Vis diffuse reflectance spectra (DRS) were obtained using a Shimadzu UV-2550 UV-Vis spectrophotometer. The N₂ adsorption-desorption isotherms of the as-prepared samples were obtained using a Micromeritics Tristar II apparatus. The photoluminescence (PL) spectra of the samples were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan) at room temperature (ca. 25°C). The excitation wavelength was 325 nm induced from a He-Cd laser source.

Electrochemical tests

Photocurrent measurements were performed using a three-electrode configuration, with the different sample films as the working electrode, saturated Ag/AgCl as the reference electrode, and platinum foil (1 cm $\times$ 1.5 cm) as the counter electrode. The electrolyte was 0.5 mol L⁻¹ Na₂SO₄ purged with N₂. A 300 W Xe lamp (Au Light, CEL-HXF-300, Beijing) coupled with an AM1.5 filter with a working current of 15 A was used as the light source. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by sequential sonication in water, acetone, and ethanol for 30 min each and dried at 333 K. Five milligrams of catalyst was mixed with 1 mL of ethanol by sonication to give a slurry mixture, which was spread onto the pretreated FTO glass. After air drying, the working electrode was further calcined at 573 K for 2 h to improve adhesion. Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.5 mol L⁻¹ Na₂SO₄ solution at open circuit voltage over a frequency range from 105 to 0.05 Hz with an alternating current (AC) voltage of 5 mV. The Mott-Schottky plots were obtained at a fixed frequency of 1 kHz in the dark. The scan rate was 50 mV s⁻¹. The reference was calibrated against a reversible hydrogen electrode (RHE). All the tests were carried out at room temperature (ca. 25°C).

Photocatalytic activity for H₂ and O₂ evolution

The photocatalytic water splitting activity was evaluated through the measurement of either H₂ or O₂ evolution in a closed gas circulation and evacuation system. A 50 mg sample of catalyst powder was well dispersed in an aqueous methanol solution (20 v.%). Pt (0.3 wt.%) and 0.01 mol L⁻¹ AgNO₃ were used as sacrificial agents to generate H₂ and O₂, respectively, in separate experiments. The reactions were carried out by irradiating the suspensions with light from a 300 W Xe lamp (Au Light, CEL-HXF-300, Beijing) with a working current of 15 A. The wavelength of the incident light was controlled by applying the appropriate long-pass cutoff filters. Gas evolution was observed only under photoirradiation, and was analyzed by an on-line gas chromatograph (SP7800, TCD, molecular sieve 5 Å, N₂ carrier, Beijing Keruida, Ltd.). The apparent quantum efficiency (QE) was calculated according to the following equation:

$$\begin{aligned} \text{EQ}(\%) &= \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100 \\ &= \frac{\text{the number of evolved H}_2 \text{ molecules} \times 2}{\text{the number of incident photons}} \times 100 \\ &= \frac{\text{the number of evolved O}_2 \text{ molecules} \times 4}{\text{the number of incident photons}} \times 100. \end{aligned}$$

RESULT AND DISCUSSION

The XRD patterns of TiO₂, SrTiO₃, TiO₂/SrTiO₃, and H-TiO₂/SrTiO₃ are shown in Fig. 1. All the diffraction peaks are consistent with rutile TiO₂ (JCPDS 75-6082) [6] and cubic perovskite SrTiO₃ (JCPDS 35-0734) [10]. The typical diffraction peaks of rutile TiO₂ and cubic perovskite SrTiO₃ are observed in the XRD pattern of the TiO₂/SrTiO₃ sample. It is evident from the TiO₂/SrTiO₃ diffraction patterns that there are no characteristic peaks for impurities, confirming the purity of the synthesized samples. XRD patterns of the three samples used in the experiments and the fitting results based on Le Bail analysis are shown in Fig. S1. The lattice parameters for rutile TiO₂ were determined based on Le Bail fitting analysis (see in Fig. S1A). This phase has been indexed with a tetragonal system (space group *P4₂/mmm*, *a* = 4.59067 Å, *b* = 4.59067 Å, *c* = 2.95767 Å). This is in good agreement with the parameters obtained from X-ray single crystal diffraction data, i.e., *a* = 4.593 Å, *b* = 4.593 Å, *c* = 2.958 Å. The lattice parameters for pure SrTiO₃ were determined to belong to a cubic system (space group *Pm3m*) based on Le Bail fitting analysis (see in Fig. S1B). The lattice constants (*a* = *b* = *c* =

Figure 1 XRD patterns of the different samples.

3.9029 Å) are consistent with the values ($a = b = c = 3.9051$ Å) determined for the pure SrTiO_3 single crystal in this study. Fig. S2 shows the differences before and after the fitting of samples. No other phase is found in the products. The strong and sharp peaks also indicate the highly crystalline nature of the photocatalysts. The synthesis conditions for the $\text{TiO}_2/\text{SrTiO}_3$ samples with different molar ratios of Ti and Sr are illustrated in Fig. S3. The XRD peak intensity for TiO_2 gradually decreases and the corresponding characteristic peaks of SrTiO_3 gradually increase with

an increasing amount of Sr source, indicating the formation of $\text{TiO}_2/\text{SrTiO}_3$ composites with different Ti and Sr proportions. Moreover, there is no obvious shift in the diffraction peaks between the pristine $\text{TiO}_2/\text{SrTiO}_3$ and the corresponding hydrogenated sample ($\text{H-TiO}_2/\text{SrTiO}_3$), implying that no significant hydrogen-induced distortion occurs under the hydrogenation conditions employed.

The morphology and structure details of the as-prepared $\text{TiO}_2/\text{SrTiO}_3$ and $\text{H-TiO}_2/\text{SrTiO}_3$ samples were investigated by SEM and TEM. As shown in Fig. 2a, a typical porous microsphere structure with a mean particle size of ca. 1 μm is obtained. These porous microspheres are composed of small nanoparticles (20–30 nm). The TEM image in Fig. 2b confirms the results of the SEM observation in Fig. 2a. Moreover, a heterojunction interface is visible in the HRTEM image (Fig. 2c). The lattice fringes with interplanar distances of 0.352 nm and 0.276 nm correspond to the (101) plane of rutile TiO_2 [34] and the (110) plane of cubic perovskite SrTiO_3 [11], respectively. The SEM image (Fig. 2d) and TEM images (Figs 2e and 2f) indicate that the morphology and size of these porous microspheres undergo no detectable change upon hydrogenation. A previous study reported that vacuum or hydrogen treatment can induce surface disorder in oxides [22]. Similarly, in the present work, a disordered surface layer is observed in the HRTEM image of $\text{H-TiO}_2/\text{SrTiO}_3$ (as shown in Fig. 2g). This de-

Figure 2 SEM (a), TEM (b) and HRTEM (c) images of the $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres; SEM (d), TEM (e,f) and HRTEM (g) images of the $\text{H-TiO}_2/\text{SrTiO}_3$ porous microspheres.

monstrates that the hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres have a disordered crystalline structure. The HRTEM image in Fig. 2g clearly shows different lattice fringe phases for TiO_2 and SrTiO_3 besides the disordered layer, indicating the formation of a heterostructure.

In this study, different catalyst morphologies were obtained by adjusting the water/ethanol volume ratio (Table S1 and Fig. 3) in the second solvothermal step. When the water/ethanol volume ratio is lower than 2:15, the prepared $\text{TiO}_2/\text{SrTiO}_3$ catalyst exhibits flower-like structures that are composed of small tightly packed nanoparticles (Fig. 3a). The $\text{TiO}_2/\text{SrTiO}_3$ catalyst presents both flower-like and porous structures (Fig. 3b), when prepared under mixed solvothermal conditions ($0 < V_{\text{Water}}:V_{\text{Alcohol}} < 2:15$), and an irregular bulk morphology (Fig. 3d) is obtained when the water/ethanol volume ratio is $> 2:15$. Porous microsphere structures can be prepared when the water/ethanol volume ratio is 2/15 (Fig. 3c). The textural parameters, such as the surface area, pore diameter, and pore volume of the $\text{TiO}_2/\text{SrTiO}_3$ composite materials with different morphologies are summarized in Table S2. As revealed in Table S2 and Fig. S4, the $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres have the largest surface area of $5.924 \text{ m}^2 \text{ g}^{-1}$ and a pore size distribution centered at 1.3 nm. However, the flower-like and irregular bulk samples exhibit surface areas of $2.64 \text{ m}^2 \text{ g}^{-1}$ and $1.365 \text{ m}^2 \text{ g}^{-1}$, respectively.

According to the above experimental results, an illustration of the formation mechanism for the H- $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres is shown in Scheme 1. The formation

Figure 3 SEM images showing the morphological evolution of the precursors prepared in the second solvothermal reaction with different solvents: ethanol-thermal (a), mixed solvothermal ($0 < V_{\text{Water}}:V_{\text{Alcohol}} < 2:15$) (b), mixed solvothermal ($V_{\text{Water}}:V_{\text{Alcohol}} = 2:15$) (c), and hydrothermal (d).

process involves a two-step sequential solvothermal reaction. In the initial step of the solvothermal synthesis, the reaction between TBOT and glycerol in ethanol forms flower-like Ti-Gly complexes (Fig. S5), similar to our previous study [35]. In the subsequent solvothermal process, with the addition of the strontium salt and mixed solvent, further solvothermal reaction leads to the formation of homogeneous Ti-Gly-Sr complexes. Furthermore, three different morphologies, i.e., flower-like, porous microspheres,

Scheme 1 Schematic formation process of H- $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres.

and irregular bulk, are formed by changing the ratio of water and ethanol in the mixed solvent. Flower-like morphology is obtained when alcohol alone is used as the solvent, and the petals are made up of many particles. When the volume of water used increases from 0 to 2 mL, the flower-like Ti-Gly precursor hydrolyzes and reacts with the strontium salt, leading to a portion of the small particles reassembling into microspheres. When the volume of water is increased to 2 mL, all of the flower-like precursors are transformed into porous microspheres. However, when the volume of water in the solvent is larger than 2 mL, excess hydrolysis leads to the formation of irregular bulk morphology. After calcination in air and subsequent hydrogenation treatment, these Ti-Gly-Sr precursors transform into hydrogenated $\text{TiO}_2/\text{SrTiO}_3$ ($\text{H-TiO}_2/\text{SrTiO}_3$) porous microspheres without changes in the original morphology.

The XPS spectra of the as-obtained samples are shown in Fig. 4. As shown in Fig. 4a, the Ti 2p XPS spectrum of

$\text{TiO}_2/\text{SrTiO}_3$ shows peaks at binding energies of 458.2 eV ($\text{Ti } 2\text{p}^{3/2}$) and 463.8 eV ($\text{Ti } 2\text{p}^{1/2}$) and these values correspond to the binding energy of Ti^{4+} . However, after hydrogenation treatment, the $\text{Ti } 2\text{p}^{3/2}$ peak of $\text{TiO}_2/\text{SrTiO}_3$ shifts from 458.2 eV to the lower binding energy of 457.7 eV, indicating the presence of Ti^{3+} in the $\text{H-TiO}_2/\text{SrTiO}_3$ [24,28]. The wide peak (Fig. 4b) in the Sr 3d region can be divided into two peaks for $\text{Sr } 3\text{d}^{5/2}$ and $\text{Sr } 3\text{d}^{3/2}$, located at around 132.84 and 134.56 eV, respectively. The peak at 132.84 eV is in accordance with those reported for perovskite SrTiO_3 , and the peak at 134.56 eV can be attributed to SrO complexes [12]. Clearly, the Sr 3d binding energy for $\text{TiO}_2/\text{SrTiO}_3$ is higher than that for SrTiO_3 , which is due to electron transfer from SrTiO_3 to TiO_2 . In addition to Ti^{3+} , oxygen vacancies are also produced during the reduction process. The O 1s XPS spectra of the samples before and after H_2 treatment are shown in Fig. 4c. For $\text{H-TiO}_2/\text{SrTiO}_3$, the stronger peak at 531.8 eV is ascribed to the formation of oxygen vacancies neighboring Ti^{3+} [23]. In addition to

Figure 4 High-resolution Ti 2p (a), Sr 3d (b), and O 1s (c) XPS scans of the different samples. (d) EPR results for the different samples measured at 273 K.

the surface defects, hydrogenation also induces defects in the bulk, such as Ti^{3+} and oxygen vacancies. For the hydrogenated samples H- TiO_2 , H- SrTiO_3 , and H- $\text{TiO}_2/\text{SrTiO}_3$, the presence of Ti^{3+} and oxygen vacancies were further investigated by room temperature electron paramagnetic resonance (EPR) (Fig. 4d). Based on the ESR spectrum, no signal can be detected for the $\text{TiO}_2/\text{SrTiO}_3$ sample. However, the sharp strong EPR signal at $g = 1.96\text{--}1.99$ for the as-synthesized hydrogenated samples is assigned to a paramagnetic Ti^{3+} center. Another small broad weak peak at around $g = 2.00\text{--}2.02$ is generally attributed to O^- species, which may be generated from the interaction of O_2 with the surface Ti^{3+} species associated with surface oxygen vacancies [25]. Therefore, the hydrogenation of $\text{TiO}_2/\text{SrTiO}_3$ generates surface oxygen vacancies and Ti^{3+} species.

Fig. 5a shows the UV-Vis absorption spectra of the different samples. TiO_2 and SrTiO_3 have an absorption edge around 400 nm, which is consistent with traditional rutile TiO_2 [27,25] and perovskite SrTiO_3 [26] semiconductors, suggesting that the light irradiation for photocataly-

sis should derive mainly from UV light. The $\text{TiO}_2/\text{SrTiO}_3$ composite exhibits absorption up to ca. 600 nm. However, the strength of the absorption is weak. The H- $\text{TiO}_2/\text{SrTiO}_3$ porous microspheres exhibit stronger absorptive capacity in the visible-light region at above 420 nm, and a clear red-shift of the optical absorption edge is observed. This phenomenon is very common and widely developed for hydrogenated semiconductors [35,36], and the photoabsorption tail rising in the visible-light region is a good indication of oxygen vacancies [37]. As shown by the plot of the Kubelka-Munk function *versus* the energy of the incident light, the band gaps of the pristine TiO_2 , SrTiO_3 , $\text{TiO}_2/\text{SrTiO}_3$, and H- $\text{TiO}_2/\text{SrTiO}_3$ heterostructured porous microspheres are 3.11, 3.04, 2.98, and 2.87 eV, respectively (Fig. 5b). The enhancement of visible-light absorption and band gap shrinkage are due to the disordered layer-induced band tail states merging with the valence band. The enhanced light absorption of the H- $\text{TiO}_2/\text{SrTiO}_3$ heterostructured porous microspheres leads to the production of more electron-hole pairs under the same visible-light irradiation.

Figure 5 (a) UV-Vis diffusive reflectance curves of the different samples; (b) corresponding plot of the transformed Kubelka-Munk function *versus* the energy of light; (c) and (d) are the room-temperature photoluminescence spectra of the different samples.

Furthermore, the surface-localized oxygen vacancies strongly influence the electronic structure, which results in higher photocatalytic activity [26].

PL spectroscopy reveals details related to the surface states, oxygen vacancies, defects, and stoichiometry of semiconductor materials. Thus, using this technique one can obtain information regarding the effectiveness of capture, migration, and transfer of charge carriers, as well as the fate of the electron-hole pairs, in semiconductor materials [36]. For TiO_2 and SrTiO_3 , the PL peaks at 450 and 448 nm are attributed to the band edge free excitons (Fig. 5c). $\text{TiO}_2/\text{SrTiO}_3$ has a similar PL spectrum to those of TiO_2 and SrTiO_3 , but the intensity is lower than those of TiO_2 and SrTiO_3 , indicating that the formation of a heterostructure promotes the separation of charge carriers. It is worth noting that the peak intensity for $\text{H-TiO}_2/\text{SrTiO}_3$ is lowest and the separation efficiency of electron-hole pairs is much higher than that of $\text{TiO}_2/\text{SrTiO}_3$. However, the PL intensities observed in the case of the H-TiO_2 and H-SrTiO_3 nanostructures are also higher than that of $\text{H-TiO}_2/\text{SrTiO}_3$ (Fig. 5d). This is because the formation of a heterostructure accelerates the charge carrier transfer

rate and thus inhibits the recombination of photogenerated electrons and holes, which contributes to the improvement of photocatalytic activity [37].

To further investigate the charge-transfer properties at the semiconductor interfaces, photoelectrochemical analyses, including transient photocurrent response (TPR) and EIS, were performed [38]. According to the TPR analysis, all the catalysts show significant photocurrent generation under AM1.5 irradiation. The $\text{H-TiO}_2/\text{SrTiO}_3$ porous microspheres exhibit a maximum photocurrent density of 0.025 mA cm^{-2} , suggesting a low recombination rate of electrons and holes in the $\text{H-TiO}_2/\text{SrTiO}_3$ heterostructured porous microspheres. EIS analysis can evaluate the charge transport and recombination properties of a photocatalyst, which is presented in the form of Nyquist plots. A smaller arc diameter in a Nyquist plot indicates lower resistance of the interfacial charge transfer.

As shown in Figs 6a and b, the $\text{H-TiO}_2/\text{SrTiO}_3$ heterostructured porous microspheres exhibit higher instant photoresponse to visible-light irradiation in the TPR analysis, and a smaller charge transfer resistance (R_{ct}) of 17.15Ω in the EIS analysis than those of $\text{TiO}_2/\text{SrTiO}_3$ (45.2Ω),

Figure 6 (a) Photoelectrochemical TPRs of different samples. (b) Nyquist plots of electrochemical impedance spectra. (c) Mott-Schottky analysis of photocatalysts at a frequency of 1 kHz and direct current potential range of -1.0 to $+0.8 \text{ V}$ (saturated calomel electrode voltage).

SrTiO₃ (145.9 Ω), and TiO₂ (186.3 Ω), indicating that the introduction of oxygen vacancies and Ti³⁺ defect sites promotes the separation of photoinduced charges and benefits interfacial charge transfer [18,20]. This reveals that H-TiO₂/SrTiO₃ porous microspheres are a promising catalyst for photocatalytic water splitting. The Mott-Schottky plots of the TiO₂, SrTiO₃, TiO₂/SrTiO₃, and H-TiO₂/SrTiO₃ heterostructured porous microsphere samples all show positive slopes (Fig. 6c), indicating that they are typical n-type semiconductors [39]. Moreover, the TiO₂/SrTiO₃ composite has a smaller slope than those of pure TiO₂ and SrTiO₃, indicating a higher carrier density. In addition, the H-TiO₂/SrTiO₃ porous microspheres show a much smaller slope in the Mott-Schottky plot compared to that of TiO₂/SrTiO₃. The charge-carrier densities of TiO₂, SrTiO₃, TiO₂/SrTiO₃, and H-TiO₂/SrTiO₃ calculated from their slopes according to the Mott-Schottky equation [40] are 2.76×10^{17} , 2.96×10^{17} , 6.75×10^{17} , and 7.78×10^{17} cm⁻³, respectively. This reveals the further enhancement of carrier densities upon hydrogenation treatment, which contributes to an improvement in photocatalytic performance.

As is well known, the composition, morphology, and surface area of a catalyst have significant effects on its photocatalytic activity [41]. In this study, the photocatalytic H₂ and O₂ production activities over TiO₂, SrTiO₃, and TiO₂/SrTiO₃ composite photocatalysts with different molar ratios of Ti and Sr (Ti:Sr = 1:0.2, 1:0.4, 1:0.6, 1:0.8, 1:1) were evaluated under xenon arc lamp irradiation (AM1.5). It can be seen from Fig. 7 that TiO₂ and SrTiO₃ alone show relatively low photocatalytic activities owing to the rapid recombination of photogenerated electrons and holes. The introduction of SrTiO₃ results in a significant improvement in the photocatalytic H₂ and O₂ production activity compared to that of TiO₂ alone. Furthermore, the

TiO₂ and SrTiO₃ contents of the composite catalysts have a significant influence on photocatalytic activity. When the molar ratio of Ti and Sr is 1:0.8, the photocatalytic H₂ and O₂ production of the TiO₂/SrTiO₃ composite is 58 and 44 $\mu\text{mol h}^{-1}$, respectively, which is the best photocatalytic water splitting performance of all these catalysts. This suggests that there is a strong interaction between TiO₂ and SrTiO₃, which plays an important role in the transfer and separation of photogenerated carriers. After selecting the optimal molar ratio (Ti:Sr = 1:0.8) in TiO₂/SrTiO₃, photocatalytic water splitting tests using TiO₂/SrTiO₃ with three different morphologies were conducted (Fig. S6). The TiO₂/SrTiO₃ with porous microsphere morphology shows a higher catalytic activity than those of the irregular bulk morphology and flower-like TiO₂/SrTiO₃ composites. Moreover, the photocatalytic activities of the H-TiO₂/SrTiO₃ porous microspheres hydrogenated at different temperatures (700, 800, and 900°C) under H₂ (10%)/Ar (90%) mixed gas flow were determined, revealing that the H-TiO₂/SrTiO₃ obtained from 800°C hydrogenation treatment exhibits the highest photocatalytic performance (Fig. S7A). The H-TiO₂/SrTiO₃ heterostructured porous microsphere sample obtained under these hydrogenation conditions exhibits suitable oxygen-vacancy content. By comparing the EPR spectra (Fig. S7B) of the H-TiO₂/SrTiO₃ samples prepared at different hydrogenation temperatures, it can be seen that the intensity of the EPR spectrum of the H-TiO₂/SrTiO₃ obtained at 800°C is higher than those of the H-TiO₂/SrTiO₃ samples obtained at 700 and 900°C. Thus, the oxygen-vacancy content of the TiO₂/SrTiO₃ obtained at 800°C is moderate, which indicates that the charge separation and transfer in TiO₂/SrTiO₃ obtained at 800°C are more efficient, leading to enhanced photocatalytic H₂ and O₂ production activity.

Figs 8a and c show a comparison of the photocatalytic

Figure 7 The hydrogen (a) and oxygen (b) generation of the different catalysts under simulated sunlight (AM1.5) irradiation: (1) TiO₂, (2) SrTiO₃ (Ti:Sr = 1:1), (3) TiO₂/SrTiO₃ (Ti:Sr = 1:0.2), (4) TiO₂/SrTiO₃ (Ti:Sr = 1:0.4), (5) TiO₂/SrTiO₃ (Ti:Sr = 1:0.6) and (6) TiO₂/SrTiO₃ (Ti:Sr = 1:0.8).

H₂ and O₂ production activities of H-TiO₂/SrTiO₃ and TiO₂/SrTiO₃ under simulated sunlight and visible light (> 420 nm), respectively. The initial evolution rates for H₂ (239.97 $\mu\text{mol h}^{-1}$) and O₂ (103.79 $\mu\text{mol h}^{-1}$) generated over H-TiO₂/SrTiO₃ under AM 1.5 irradiation are higher than those of the pristine TiO₂/SrTiO₃ (38.24 $\mu\text{mol h}^{-1}$ for H₂ and 17 $\mu\text{mol h}^{-1}$ for O₂). We also measured photocatalytic H₂ and O₂ generation using H-TiO₂/SrTiO₃ and TiO₂/SrTiO₃ as the photocatalyst under visible-light irradiation by cutting off the UV light at wavelengths shorter than ca. 420 nm. It is worth noting that the H₂ and O₂ evolution rates are 95.25 and 53.42 $\mu\text{mol h}^{-1}$, respectively. However, the H₂ and O₂ evolution rates for TiO₂/SrTiO₃ are only 3.44 and 2.68 $\mu\text{mol h}^{-1}$, respectively. Clearly, the addition of Ti³⁺ and presence of oxygen vacancies in the H-TiO₂/SrTiO₃ porous microspheres cause significant improvement of visible-light absorption [34]. Additionally, the photocatalytic performance of the H-TiO₂, H-SrTiO₃, and H-TiO₂/SrTiO₃ samples was evaluated under visible-light irradiation (> 420 nm). As shown in Fig. S8, the H₂ and O₂ evolution over H-TiO₂/SrTiO₃ exceed those over H-TiO₂ and H-SrTiO₃, implying that the formation of a

heterojunction significantly improves the catalytic activity. This result is also supported by the results of the photoelectrochemical tests. The higher photocurrent density, lower onset potential, and extended photoresponse range of the H-TiO₂/SrTiO₃ heterostructured porous microspheres provide a strong indication of the more efficient charge separation and transport.

In addition, to evaluate the solar energy conversion efficiencies of the catalysts, the apparent QEs for different single wavelengths were also measured. In the UV light region, the apparent QEs at 365 nm are 72.95% and 35.43% for H₂ and O₂ generation, respectively, implying a high utilization of photogenerated charges in the TiO₂/SrTiO₃ composite (Figs 8b and d) [42,43]. In the visible-light region, the apparent QEs for H₂ and O₂ generation are 21.99% and 9.70% at 400 nm, respectively, which is a high apparent quantum yield for an oxide semiconductor photocatalyst. The apparent quantum yield decreases with increasing incident light wavelength. This indicates that the water-splitting reaction over the samples is associated with the DRS absorption spectra [44]. Compared with other typical TiO₂/SrTiO₃ nanostructures with different

Figure 8 Photocatalytic H₂ (a) and O₂ (c) generation over H-TiO₂/SrTiO₃ (1) and TiO₂/SrTiO₃ (3) under AM1.5 irradiation, and H-TiO₂/SrTiO₃ (2) and TiO₂/SrTiO₃ (4) under visible-light irradiation. The photocatalytic H₂ (b) and O₂ (d) generation rates of the H-TiO₂/SrTiO₃ porous microspheres under single-wavelength light and the corresponding QEs.

morphologies [26,30–34], the H-TiO₂/SrTiO₃ heterostructured porous microspheres present much higher photocatalytic activity. This can be attributed to the synergistic effect of the unique porous sphere structure, heterostructure, and appropriate oxygen-vacancy and Ti³⁺ contents, which serve as trapping sites, preventing the rapid recombination of charge carriers and improving the interfacial electron-transfer rate and the migration efficiency of photoinduced electrons.

In order to evaluate the stability of the H-TiO₂/SrTiO₃ porous microsphere composites, cycling runs of the H₂ and O₂ evolution reactions over the H-TiO₂/SrTiO₃ porous microsphere (Ti:Sr = 1:0.8) under simulated sunlight (AM1.5) were performed. As shown in Fig. S9, the efficiency for photocatalytic water splitting exhibits no obvious change after 5 cycles (20 h). Moreover, according to XRD and SEM analyses, the structure and morphology of the catalyst remain intact during cycle testing (Fig. S10). These results indicate that H-TiO₂/SrTiO₃ heterostructured porous microspheres not only have high photocatalytic activity for the water-splitting reaction, but also good stability.

Based on the results of UV-Vis spectroscopy (Figs 5a and b), XPS valence band spectroscopy (Fig. S11), and the above photocatalytic results, an energy band diagram and charge transfer mechanism schematic for the efficient H₂ and O₂ evolution activity of H-TiO₂/SrTiO₃ heterostructured porous microspheres are presented in Fig. 9. As described in previous reports [24,26], hydrogenation leads to the formation of an isolated band within the band gap, which causes the band edge to red-shift toward the longer wavelength region, indicating a narrowing of the band gap [25,45]. Under visible-light irradiation, the photogenerated electrons in the covalence band of H-TiO₂ and H-SrTiO₃ are both excited and transferred to the corresponding conduction band (CB) (process 4). Some of the electrons approaching the edge of H-SrTiO₃ directly react with adsorbed H⁺ in water to produce H₂ under the co-catalytic activity of CH₃OH molecules (process 3), which can accept electrons and act as active sites for H₂ generation. Other electrons generated from H-SrTiO₃ transfer to the CB of H-TiO₂. Together with the electrons already in the CB of H-TiO₂, they participate in H₂ generation. It can be seen that the formation of the heterostructure is beneficial for the separation of electrons and holes. Compared to the reduction half-reaction, the oxygen evolution reaction is relatively difficult because it involves a four-electron transfer process and the formation of O–O bonds [46]. Fig. 9 shows that a portion of holes generated from the covalence band of H-TiO₂ are transferred to that of H-SrTiO₃ (processes 3

Figure 9 Schematic illustration of the charge transfer in the hydrogenated TiO₂/SrTiO₃ porous microsphere under visible light irradiation.

and 5), and along with the holes generated from H-SrTiO₃, which can participate in photocatalytic water oxidation to generate O₂. At the same time, the recombination of electrons and holes can also occur between H-TiO₂/SrTiO₃ particles (process 1) and prolong the charge separation life of a single heterojunction. Thus, the heterostructure, oxygen vacancies, and porous structure act synergistically to promote the separation and transfer of electrons and holes, increasing the photocatalytic activity.

CONCLUSIONS

In conclusion, we demonstrated a targeted strategy for the controllable synthesis of hydrogenated TiO₂/SrTiO₃ porous microsphere composites. The composition and morphology of the composites were easily controlled by changing the reaction conditions. From the structure and surface characterization of the prepared samples, it can be deduced that the synergistic effects of oxygen vacancies, Ti³⁺ species, and the heterostructure contribute to visible-light harvesting over a broad range, improve electron transport ability, and prolong lifetime of charge carriers, all of which are directly related to superior water-splitting performance. As a result, by tuning the ratio of TiO₂ and SrTiO₃, morphology, and defects (Ti³⁺ species and oxygen vacancies), relatively high photocatalytic activities were achieved for the hydrogenated TiO₂/SrTiO₃ porous microspheres, with H₂ and O₂ evolution rates reaching 239.97 and 103.79 μmol h⁻¹, respectively, which are ca. 5.9 and 6.6 times higher than those of bulk TiO₂/SrTiO₃ materials. The construction of such hydrogenated TiO₂/SrTiO₃ porous microsphere composite systems may be expected to facilitate their use in practical applications.

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氢化能带可调的TiO₂/SrTiO₃多孔微球用于光催化制备氢气和氧气

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摘要 氢气和氧气是清洁的和可再生的能源材料, 光催化分解水制备氢气和氧气受到了广泛的关注. 本文通过一个前驱体合成路线得到了氢化的TiO₂/SrTiO₃多孔微球高效光催化剂, 首先, 通过两步连续的溶剂热方法形成了Ti-Gly-Sr前驱体, 然后, 经过空气气氛下的煅烧以及氢气和氩气混合气体的还原, 得到了氢化的TiO₂/SrTiO₃多孔微球光催化剂. 在反应过程中, 通过调节反应条件可以对缺陷以及催化剂的带隙进行调控. 通过进行各种表征发现, 异质结构、合适的氧空位以及特殊的多孔结构, 可以有效地促进催化剂对可见光的吸收以及光生电荷的分离效率. 氢化的TiO₂/SrTiO₃多孔微球光催化剂的产氢和产氧速率可以达到239.97 $\mu\text{mol h}^{-1}$ 和103.79 $\mu\text{mol h}^{-1}$, 比普通的TiO₂/SrTiO₃分别高出5.9和6.6倍. 在光催化转换太阳能的应用中, 氢化的TiO₂/SrTiO₃多孔微球复合物是一种有前景的光催化剂.