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Article

Prolonging charge-separation states by doping lanthanide-ions into {001}/{101} facets-coexposed TiO₂ nanosheets for enhancing photocatalytic H₂ evolution

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ABSTRACT

Ultrathin TiO₂ nanosheets with coexposed {001}/{101} facets have attracted considerable attention because of their high photocatalytic activity. However, the charge-separated states in the TiO₂ nanosheets must be extended to further enhance their photocatalytic activity for H₂ evolution. Herein, we present a successful attempt to selectively dope lanthanide ions into the {101} facets of ultrathin TiO₂ nanosheets with coexposed {001}/{101} facets through a facile one-step solvothermal method. The lanthanide doping slightly extended the light-harvesting region and markedly improved the charge-separated states of the TiO₂ nanosheets as evidenced by UV-vis absorption and steady-state/transient photoluminescence spectra. Upon simulated sunlight irradiation, we observed a 4.2-fold enhancement in the photocatalytic H₂ evolution activity of optimal Yb³⁺-doped TiO₂ nanosheets compared to that of their undoped counterparts. Furthermore, when Pt nanoparticles were used as cocatalysts to reduce the H₂ overpotential in this system, the photocatalytic activity enhancement factor increased to 8.5. By combining these results with those of control experiments, we confirmed that the extended charge-separated states play the main role in the enhancement of the photocatalytic H₂ evolution activity of lanthanide-doped TiO₂ nanosheets with coexposed {001}/{101} facets.

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1. Introduction

With the rapid depletion of fossil fuels, the world is facing an unprecedented energy-shortage crisis [1]. A promising strategy to overcome this issue is the development of sustainable clean

energy sources to replace the conventional fossil fuels. Owing to its high energy capacity and environmental friendliness, hydrogen is considered as one of the ideal “green” energy sources [2,3]. The discovery of photoelectrochemical water splitting on TiO₂ by Fujishima et al. [4] in 1972 has stimulated a

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considerable amount of research on the photocatalysis technique. Among different types of photocatalysts, nanosized TiO_2 has been widely investigated because of its appropriate redox ability, photostability, non-toxicity, and low cost. However, owing to its large bandgap energy (~ 3.2 eV for anatase), TiO_2 can only use a small portion of the solar spectrum in the UV region ($\sim 5\%$) [5–9]. Moreover, the fast recombination of photogenerated electron-hole pairs limits the photocatalytic activity of nanosized TiO_2 photocatalysts for H_2 evolution [10,11]. Various strategies have been employed to address these issues, such as doping metal or non-metal ions into the TiO_2 crystal lattice, sensitizing TiO_2 by organic dyes, coupling TiO_2 with other semiconductor or metal nanostructures, as well as engineering the nanostructure of TiO_2 by exposing specific crystal facets [12–22].

In the case of anatase TiO_2 , the {001} crystal facets have high surface energy (0.90 J/m^2), which makes them more reactive than the low-energy {101} surfaces (0.44 J/m^2) [21]. As such, the {001} surface of anatase TiO_2 represents the main source of catalytic active sites in various applications [23,24]. However, the conventional synthesis route often results in anatase TiO_2 nanostructures preferentially exposing the {101} facets because of their higher thermodynamic stability. It has been demonstrated that anatase TiO_2 nanocrystals with coexposed {001}/{101} facets can be controllably synthesized through a wet chemical process using a capping or co-capping agent containing HF [25,26]. Upon interband excitation of TiO_2 nanostructures with coexposed {001} and {101} facets, the photoelectrons on the {001} facets will transfer to the adjacent {101} facets simultaneously generating the same amount of photoholes on the {001} facets [27–29]. A high percentage of exposed {001} facets in anatase TiO_2 nanostructures is beneficial for increasing the transport rate of photoholes and oxidizing the sacrificial agent; this enhances the generation of photoelectrons (available for photocatalytic H_2 evolution from water reduction) on the {101} facets [30]. Although TiO_2 nanostructures coexposing {001} and {101} facets show a good diffusion rate of photogenerated charge carriers, their light-harvesting and charge-separation capabilities still need to be improved.

Herein, we introduce lanthanide ions into anatase TiO_2 nanosheets with coexposed {001}/{101} facets through a facile solvothermal method by using HF as the capping agent. It is well known that lanthanide ions possess abundant $4f^n$ orbitals of different energies, which can serve as electron acceptors to extend the charge-separated states in the photocatalysts [31–35]. In this study, a series of lanthanide ions with different electron occupations of $4f$ orbitals are selectively doped into the {101} facets of TiO_2 nanosheets to improve their charge-separation and light-absorption capabilities as shown by UV-vis absorption and steady-state/transient photoluminescence (PL) spectroscopy measurements. Combining these results with those of control experiments, we propose that the photoinduced electrons on the {001} facets of TiO_2 nanosheets can move to the {101} facets with large transfer rate constants ($0.62\text{--}6.45 \times 10^8 \text{ s}^{-1}$) depending on the electron vacancies in the f orbitals of the lanthanide dopants. Upon simulated sunlight irradiation, an optimal sample consisting of Yb^{3+} -doped

TiO_2 nanosheets exhibits a 4.2-fold enhancement in the photocatalytic activity for H_2 evolution compared to the pure TiO_2 nanosheets without cocatalysts. More importantly, when the common Pt cocatalyst is introduced into the Yb^{3+} -doped TiO_2 nanosheets to reduce the H_2 overpotential, the photocatalytic activity enhancement factor further increases to 8.5. In summary, we present a systematic study of the role of charge-separated states in the enhancement of the photocatalytic H_2 evolution activity of lanthanide-doped TiO_2 nanosheets with coexposed {001}/{101} facets.

2. Experimental

2.1. Chemicals and materials

Tetrabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$), absolute ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$), HF, triethanolamine (TEOA), and chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All reagents employed in this study were of analytical grade and used without further purification. Lanthanide halide hexahydrate (Ho, Er, Tm, Yb, and Lu) powders were obtained by dissolving the corresponding rare earth oxide in 36%–38% hydrochloric acid.

2.2. Synthesis of lanthanide-doped TiO_2 nanosheets with coexposed {001}/{101} facets

Typically, a certain amount of lanthanide (Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , or Lu^{3+}) halide was fully dissolved in 8 mL of ethyl alcohol by stirring for 30 min (the lanthanide/ Ti^{4+} ions ratio was 0.5 mol%). Next, 5 mL of tetrabutyl titanate was added dropwise into the above solution under constant stirring for 20 min followed by dropwise addition of 0.6 mL of HF under constant stirring for 10 min. Then, the obtained solution was transferred to a 20-mL Teflon-lined stainless steel autoclave and kept at 180°C for 12 h. After being cooled to room temperature, the precipitate was collected and washed several times with ethanol. Finally, TiO_2 nanosheets with coexposed {001}/{101} facets, doped with different types of lanthanide ions, were obtained by drying at 80°C for 12 h. The TiO_2 nanosheets doped with Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , and Lu^{3+} ions were denoted as Ho^{3+} -, Er^{3+} -, Tm^{3+} -, Yb^{3+} -, and Lu^{3+} -doped TiO_2 nanosheets, respectively. Pure TiO_2 nanosheets with coexposed {001}/{101} facets were also synthesized according to the same procedure, without the addition of lanthanide halides.

2.3. Characterization

The crystallographic structures of all as-synthesized samples were characterized by a Shimadzu XRD-600 (Japan) X-ray diffractometer with $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 0.15406 \text{ nm}$). Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100) were used to inspect the morphologies and structures of the samples. The UV-vis absorption spectra of the as-synthesized samples were recorded by a Lambda 750 spectrophotometer (Perkin-Elmer, USA). The PL decay curves of the

as-synthesized samples were recorded by a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of a hydrogen flash lamp with a wavelength of 290 nm (nF900, Edinburgh Instruments).

2.4. Photocatalytic H_2 evolution

The H_2 evolution reaction via photocatalytic water reduction was carried out in a sealed, 35 mL quartz reactor at 101 kPa and room temperature (25 °C). Typically, 5 mg of the as-synthesized samples were suspended in 10 mL of 15 vol% TEOA aqueous solution. Then, the reactor was sealed by a rubber plug and degassed by argon for 30 min. Subsequently, the quartz reactor loaded with the suspension was placed into a sink connected with a reflux water condenser to maintain the photocatalytic reaction temperature. A 300-W Xe lamp (PLS-SXE300UV) coupled with a solar filter (air mass (AM) 1.5, 100 mW/cm²) was employed as the light source. The composition of the gas product generated in the space above the liquid in the quartz reactor was periodically determined by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD, SP-3420A, Beifen-Ruili Analytical Instrument).

2.5. Photoelectrochemical measurements

The photocurrent responses were measured by an electrochemical analyzer (CHI 600D, CH Instruments Inc.) with a three-electrode system. A NaOH (0.1 M) aqueous solution was used as electrolyte, whereas Pt wire and Ag/AgCl were employed as the counter and reference electrodes, respectively. To prepare the working electrode, pastes of the as-synthesized samples were coated onto an In-doped SnO_2 (ITO) glass with an effective area of 1 cm × 1 cm. Then, Nafion (10 μ L, 1 wt%) was coated onto the working electrodes followed by drying at 60 °C for 12 h.

3. Results and discussion

3.1. Analysis of crystal structure and morphology of the photocatalysts

The crystal structures of the as-synthesized samples were examined by X-ray diffraction (XRD) measurements. Fig. 1(A) shows the XRD patterns of the pure and lanthanide-doped TiO_2 nanosheets. The diffraction peaks around 25.28°, 37.80°, 38.57°, 48.05°, 53.89°, 55.06°, 62.12°, 70.31°, and 75.03° correspond to the (101), (004), (112), (200), (105), (211), (213), (220), and (215) planes, respectively, of the tetragonal anatase TiO_2 phase (JCPDS No. 21-1272). No obvious diffraction peaks of lanthanide species are observed in the XRD patterns of the lanthanide-doped TiO_2 nanosheets, suggesting that the lanthanide ions may have been incorporated into the nanosheets [36,37]. To verify this hypothesis, the XRD patterns of the as-synthesized samples were magnified over three typical areas positioned around the (101), (004), and (200) peaks. After lanthanide doping, the diffraction peak of the TiO_2 (101) planes shifted to lower diffraction angles because of the larger radius of lanthanide ions compared to that of Ti^{4+} ions in TiO_2 . However, no shifts are observed in the peak positions corresponding to the (004) and (200) planes of lanthanide-doped and undoped TiO_2 nanosheets. These observations imply that the lanthanide ions were selectively doped into the lattice spacings between TiO_2 (101) planes because of the larger d -spacing of the TiO_2 (101) plane (0.352 nm) compared to those of the (004) and (200) planes (0.237 and 1.89 nm, respectively).

In Fig. 2, the FE-SEM images of TiO_2 nanosheets are compared to those of TiO_2 nanosheets doped with different types of lanthanide ions. As shown in Fig. 2(A), the pure TiO_2 sample exhibits a sheet-like nanostructure with side lengths of 30–50 nm and thicknesses of 6–10 nm. After introducing lanthanide ions (at a 0.5 mol% lanthanide/ Ti^{4+} ions ratio) during the solvothermal process, the obtained lanthanide-doped samples retain their nanosheet structure (Figs. 2(B)–(F)) but show very slight changes in the nanosheet sizes (side length: 20–60 nm, thickness: 5–8 nm) compared to the pure TiO_2 nanosheets. This suggests a weak influence of the doping with lanthanide ions on

Fig. 1. (A) XRD patterns of as-synthesized TiO_2 nanosheets doped with different lanthanide ions; (B) relationship between diffraction peak positions and lanthanide ion species doped in the TiO_2 nanosheets.

Fig. 2. SEM images of pure (A) and Ho³⁺-doped (B), Er³⁺-doped (C), Tm³⁺-doped (D), Yb³⁺-doped (E), Lu³⁺-doped (F) TiO₂ nanosheets.

the morphology of the TiO₂ samples. In addition, the contents of lanthanide ions doped into the TiO₂ nanosheets were confirmed through energy-dispersive X-ray (EDX) measurements, which yielded values similar to the amounts of lanthanide ions used in the experimental procedure (data not shown).

X-ray photoelectron spectroscopy (XPS) measurements were also carried out on a typical sample of Yb³⁺-doped TiO₂ nanosheets. The analysis confirms the presence of Ti and Yb elements in the sample. In Fig. 3(A), the peaks at binding energies of 458.2 and 463.9 eV can be ascribed to the Ti 2p_{3/2} and Ti 2p_{1/2} levels, respectively, suggesting the presence of Ti⁴⁺ ions in the TiO₂ nanosheets after doping with Yb³⁺ ions. Moreover, a very weak signal is observed in the Yb 4d core-level spectrum (Fig. 3(B)). Two peaks centered at 186.4 and 193.9 eV, corresponding to the Yb 4d_{5/2} and Yb 4d_{3/2} levels, respectively, were obtained after fitting with the XPSPEAK41 software. This confirms the successful doping of Yb³⁺ ions into the TiO₂

Fig. 3. XPS spectra of Yb³⁺-doped TiO₂ nanosheets: Ti 2p (A) and Yb 4d (B) core-level spectra.

Fig. 4. TEM images of pure (A) and Yb³⁺-doped (B) TiO₂ nanosheets; HRTEM images of pure (C) and Yb³⁺-doped (D) TiO₂ nanosheets.

nanosheets.

The microstructures of pure and Yb³⁺-doped TiO₂ nanosheets were compared by TEM (Fig. 4). Both the TiO₂ nanosheets show ultrathin thicknesses and weak aggregation (Figs. 4(A) and (B)). Further investigation, based on the high-resolution TEM (HRTEM) images shown in Fig. 4(C) and (D), highlights the co-exposure of {001} and {101} facets in the TiO₂ nanosheets. The distance between the lattice fringes appearing on the side faces of the TiO₂ nanosheets is ~0.352 nm, corresponding to the {101} facets of anatase TiO₂ [38]. A *d*-spacing of ~0.235 nm can be observed on the top face of the TiO₂ nanosheets, corresponding to the anatase TiO₂ {001} facets [39]. Notably, an obvious lattice distortion is observed on the {101} facets of doped TiO₂ nanosheets (Fig. 4(D)), compared to their pure counterparts. This observation further confirms the selective doping of lanthanide ions into the {101} facets of the TiO₂ nanosheets. According to the TEM results, the percentage of exposed {001} facets on the TiO₂ nanosheets can be estimated to be ~70.99%, which is similar to the corresponding values obtained for the TiO₂ nanosheets doped with different types of lanthanide ions (Table 1).

3.2. Optical properties of the photocatalysts

The optical properties of the as-synthesized samples, including pure and lanthanide-doped TiO₂ nanosheets, were studied by UV-vis absorption spectroscopy, and the corre-

Table 1

Fractions of {001}/{101} facets in TiO₂ nanosheets doped with different lanthanide ions.

Sample	{101} percentage (%)	{001} percentage (%)
Pure TiO ₂	29.01	70.99
Ho ³⁺ -TiO ₂	31.05	68.95
Er ³⁺ -TiO ₂	30.51	69.49
Tm ³⁺ -TiO ₂	29.75	70.25
Yb ³⁺ -TiO ₂	29.25	70.75
Lu ³⁺ -TiO ₂	29.05	70.95

Fig. 5. (A) UV-vis absorption spectra of pure (a) and Ho³⁺-doped (b), Er³⁺-doped (c), Tm³⁺-doped (d), Yb³⁺-doped (e), Lu³⁺-doped (f) TiO₂ nanosheets; (B) bandgap of TiO₂ nanosheets doped with different lanthanide ions (W/O denotes undoped TiO₂).

sponding results are shown in Fig. 5(A). The absorption edge of pure TiO₂ nanosheets is located at ~398 nm, corresponding to a bandgap energy of 3.11 eV. This value is slightly lower than the bandgap energy of anatase TiO₂ nanoparticles, which can be ascribed to the selective exposure of {001} and {101} facets on the TiO₂ nanosheets obtained in this study [22–24]. Upon doping with lanthanide ions, the absorption edges of the TiO₂ nanosheets show a slight red shift toward the visible region (Fig. 5(A)), indicating an extended light-harvesting region due to the formation of impurity levels in the interband region of TiO₂ nanosheets. The bandgaps of the pure and lanthanide-doped TiO₂ nanosheets were obtained using the following equation [40]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

where $h\nu$, E_g , and A are the photon energy, the bandgap, and a constant, respectively, and $n = 4$ for indirect transition semiconductors such as TiO₂ [41]. As shown in Fig. 5(B), the bandgap energies of Ho³⁺-, Er³⁺-, Tm³⁺-, Yb³⁺-, and Lu³⁺-doped TiO₂ nanosheets are 3.05, 3.04, 3.03, 2.99, and 3.01 eV, respectively. These results further confirm that the lanthanide ions were doped into the TiO₂ nanosheets, extending the light absorption from the UV to the visible region, which can improve their photocatalytic activity for H₂ evolution. It should be noted that the ultra-low content of lanthanide ions used in this study implies that weak electronic interactions are present in the lanthanide-doped TiO₂ nanosheets. Thus, the TiO₂ nanosheets doped with different lanthanide ions are expected to exhibit similar optical response properties.

3.3. Photocatalytic H₂ evolution

3.3.1. Influence of lanthanide doping on photocatalytic H₂ evolution

The photocatalytic H₂ evolution activities of the as-synthesized samples were investigated under simulated sunlight irradiation (using a 300-W Xe lamp coupled with an AM 1.5 filter with a light density of 100 mW/cm²) in the presence of TEOA as a sacrificial reagent. As observed in Fig. 6(A), the pure TiO₂ nanosheets with coexposed {001}/{101} facets yield a H₂ evolution amount of 0.31 μmol after simulated sunlight irradiation for 1 h. This low photoactivity can be attributed to the limited light absorption and fast charge recombina-

tion process in the TiO₂ nanosheets. However, upon introducing the lanthanide ions in the TiO₂ nanosheets, the H₂ evolution amounts show a clear increase. This suggests that doping with lanthanide ions can effectively promote the photocatalytic H₂ evolution activity of TiO₂ nanosheets coexposing {001} and {101} facets. The photocatalytic activity changes in the following order: TiO₂ < Lu³⁺-doped TiO₂ < Ho³⁺-doped TiO₂ < Er³⁺-doped TiO₂ < Tm³⁺-doped TiO₂ < Yb³⁺-doped TiO₂. It is clear that the Yb³⁺-doped TiO₂ nanosheets exhibit optimal photoactivity for H₂ evolution. Then, we optimized the content of Yb³⁺ ions doped in the TiO₂ nanosheets with coexposed {001}/{101} facets on the basis of the corresponding photocatalytic H₂ evolution (Fig. 6(B)). The photocatalytic activity of Yb³⁺-doped TiO₂ nanosheets depends on the Yb³⁺ content. The optimal content (with respect to the content of Ti⁴⁺ ions in the sample) is 0.5 mol%; when the content is higher than 0.5 mol%, the photocatalytic H₂ evolution activity of the nanosheets shows a gradual decrease. This is ascribed to the formation of charge carrier recombination centers in the interband region of TiO₂ due to the increased content of doped Yb³⁺ ions. Therefore, the 0.5 mol% Yb³⁺-doped TiO₂ nanosheets were selected for further analysis.

Fig. 6(C) shows the time-dependent H₂ evolution behavior of pure and Yb³⁺-doped TiO₂ nanosheets. The figure reveals that the H₂ evolution amounts of both photocatalysts linearly increase with the irradiation time; moreover, the H₂ amount generated by Yb³⁺-doped TiO₂ nanosheets is ~4.25 times higher than that produced by pure TiO₂ nanosheets. We thus conclude that the enhanced photocatalytic activity of lanthanide-doped TiO₂ nanosheets can be ascribed to the extended light absorption range and to the longer of photoinduced charge-separated pairs.

3.3.2. Cocatalyst optimization

To further investigate the photocatalytic H₂ evolution activity of the lanthanide-doped TiO₂ nanosheets, we introduced the common Pt nanoparticle cocatalysts into the optimal Yb³⁺-doped TiO₂ nanosheets, in order to reduce the H₂ overpotential. Different amounts of Pt nanoparticles were loaded onto the Yb³⁺-doped TiO₂ nanosheets through an in-situ photoreduction process. Fig. 6(D) displays the H₂ evolution amount of Yb³⁺-doped TiO₂ nanosheets loaded with different contents of Pt nanoparticles after simulated sunlight irradiation for 1 h. The H₂ evolution amount shows an initial increase when Pt content increases from 0.05 to 0.3 wt% followed by a rapid decrease for Pt contents higher than 0.3 wt%. This decrease is mainly due to the formation of recombination centers of photoinduced charge carriers on the excess Pt nanoparticles incorporated in the photocatalysts. Thus, we estimated the optimal content of Pt cocatalysts for the Yb³⁺-doped TiO₂ nanosheets as 0.3 wt%. Fig. 6(E) displays the time-dependent H₂ evolution of pure and Yb³⁺-doped TiO₂ nanosheets after loading 0.3 wt% Pt nanoparticles. In this case, the results show that the H₂ evolution amount of the Yb³⁺-doped TiO₂ nanosheets is ~8.50 times higher than that of their pure TiO₂ counterparts. This value is twice that (~4.25) obtained for the same system without Pt cocatalysts. This implies that the pho-

Fig. 6. (A) Photocatalytic H₂ evolution amounts after simulated sunlight irradiation for 1 h over pure and lanthanide-doped TiO₂ nanosheets (W/O denotes undoped TiO₂ nanosheets); (B) photocatalytic H₂ evolution amounts after simulated sunlight irradiation for 1 h over TiO₂ nanosheets doped with different contents of Yb³⁺ ions; (C) photocatalytic H₂ evolution plots of pure (a) and Yb³⁺-doped (b) TiO₂ nanosheets; (D) photocatalytic H₂ evolution amounts of Yb³⁺-doped TiO₂ nanosheets loaded with different contents of Pt nanoparticles after simulated sunlight irradiation for 1 h; (E) photocatalytic H₂ evolution plots of pure (a) and Yb³⁺-doped (b) TiO₂ nanosheets loaded with 0.3 wt% Pt.

toinduced charge-separation process may be the key factor for the enhancement of the H₂ evolution activity of lanthanide-doped TiO₂ nanosheets with coexposed {001}/{101} facets.

3.4. Mechanism of enhanced photocatalytic activity

In the case of interband-excited TiO₂ nanosheets with coexposed {001} and {101} facets, the photocatalytic H₂ evolution process involves the transfer of photoinduced electrons from the {001} to the {101} facets [42–45]. However, after selectively doping lanthanide ions into the {101} facet of TiO₂ nanosheets, the doped nanosheets possess not only an extended light absorption region, but also improved photoinduced charge-separation capabilities, and therefore exhibit an enhanced photocatalytic activity for H₂ evolution. In our study, the low doping content of lanthanide ions in the TiO₂ nanosheets induces only weak red shifts of the absorption edges of the nanosheets (Fig. 5(B)). Thus, we deduce that the enhanced photocatalytic activity of the present lanthanide-doped TiO₂ nanosheets should be mainly ascribed to the longer charge-separated states because of the formation of

discrete “electrons sinks” on the {101} facets of the nanosheets. To clarify this aspect, we investigated the photoinduced kinetic processes involving charge carriers in both pure and lanthanide-doped TiO₂ nanosheets using steady-state and transient PL spectroscopy. As shown in Fig. 7(A), the pure TiO₂ nanosheets display a distinct PL peak centered around 375 nm. However, after doping with lanthanide ions, the PL intensities of the doped TiO₂ nanosheets show a marked decrease. This implies a suppressed recombination of photoinduced charge carriers in the lanthanide-doped TiO₂ nanosheets. Further analysis of the time-resolved transient PL spectroscopy measurements (Fig. 7(B)) shows that the decay curves of all samples can be fitted by a biexponential kinetic model, which reflects the intrinsic (shorter time constant) and defect (longer time constant) emission processes of TiO₂ [9,10]. The introduction of lanthanide ions into the TiO₂ nanosheets results in a change in the decay time constants of the doped nanosheets compared to those of their pure TiO₂ counterparts. The emission decay behaviors of pure and lanthanide-doped TiO₂ nanosheets can be further compared through the average lifetimes (τ_A), calculated according to the following equation [46–50]:

Fig. 7. (A) Steady-state PL spectra of as-synthesized samples under 290 nm excitation: (a) TiO₂ nanosheets, (b) Ho³⁺-doped TiO₂ nanosheets, (c) Yb³⁺-doped TiO₂ nanosheets, and (d) Lu³⁺-doped TiO₂ nanosheets; (B) time-resolved transient PL decay of the above samples; (C) schematic diagram of the proposed mechanism for the photoinduced charge carrier transfer in lanthanide-doped TiO₂ nanosheets.

$$\tau_A = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}$$

The τ_A of the pure TiO₂ nanosheets (0.987 ns) is larger than the corresponding values obtained for the Ho³⁺-doped (0.603 ns), Yb³⁺-doped (0.632 ns), and Lu³⁺-doped (0.930 ns) TiO₂ nanosheets. These results prove that the quenched emission of the TiO₂ nanosheets after doping with lanthanide ions is due to the emergence of a new nonradiative pathway in the doped nanosheets.

According to the above observations, we propose that the photoinduced electrons in the conduction band (CB) of TiO₂ can be trapped by the doped lanthanide ions before they combine with the photoinduced holes in the valence band (VB) of TiO₂ (Fig. 7(C)), thereby leading to longer-lived charge-separated states in the lanthanide-doped TiO₂ nanosheets. In other words, the doped lanthanide ions can serve as acceptors of the photoinduced electrons in the CB of TiO₂. The τ_A value of the lanthanide-doped TiO₂ nanosheets increases with the electron population of the 4f orbitals of the lanthanide ions (Fig. 7(B)). This implies that the photoinduced electrons in the TiO₂ VB can be trapped more easily by lanthanide ions with low electron population. That is, decreasing the electron population on the

4f orbital of the doped lanthanide ions enhances the “electron sink” effect on the photoinduced electrons of TiO₂, leading to an enhanced separation of photoinduced charge carriers in the doped TiO₂ nanosheets. For example, the full occupation (14 electrons) of the 4f orbital of Lu³⁺ ions would result in a weak electron sink effect to trap the photoinduced electrons transferred from {001} to {101} facets in the Lu³⁺-doped TiO₂ nanosheets due to the lack of empty orbitals. The similar average time constants of pure and Lu³⁺-doped TiO₂ nanosheets support this view. The transfer rate of photoinduced charge carriers in the lanthanide-doped TiO₂ nanosheets can be estimated through the electron-transfer rate constants k_{et} , expressed as follows [46–50]:

$$k_{et}(\text{TiO}_2 \rightarrow \text{Doped TiO}_2) = \frac{1}{\langle \tau_A \rangle_{(\text{Doped TiO}_2)}} - \frac{1}{\langle \tau_A \rangle_{(\text{TiO}_2)}}$$

The k_{et} values calculated for the Ho³⁺-, Yb³⁺-, and Lu³⁺-doped TiO₂ systems are 6.45×10^8 , 5.69×10^8 , and $0.62 \times 10^8 \text{ s}^{-1}$, respectively.

However, among the lanthanide-doped TiO₂ nanosheets examined in this study, the Yb³⁺-doped TiO₂ nanosheets exhibited the highest photocatalytic activity. This result is not consistent with the above mechanism, which implies that another

Fig. 8. (A) Mott-Schottky plots of pure and lanthanide-doped TiO_2 nanosheets; (B) photocurrent density recorded at the applied potential of -0.1 V vs. Ag/AgCl under chopped simulated sunlight irradiation, using pure (a) and Ho^{3+} - (b), Er^{3+} - (c), Tm^{3+} - (d), Yb^{3+} - (e), Lu^{3+} -doped (f) TiO_2 nanosheets as photocathodes.

factor affects the photocatalytic activity of the lanthanide-doped TiO_2 nanosheets. As shown in Fig. 7(C), the Yb^{3+} ion has the lowest number of energy levels among the lanthanide ions considered in our study. This suggests a lower probability of electron-hole recombination in the case of the Yb^{3+} ions (corresponding to the relaxation process of electrons from high- to low-energy states, with the emission of photons or heat, see Fig. 7(C)). In this way, the more effectively trapped electrons on the Yb^{3+} ions would be used to initiate the proton reduction leading to H_2 evolution on the {101} facets of Yb^{3+} -doped TiO_2 nanosheets.

To confirm the above interpretation, we obtained the electrochemical flat-band potentials (E_{fb}) of the as-synthesized samples using Mott-Schottky plots [50,51]. As shown in Fig. 8(A), the intercept of the tangent to the pure TiO_2 plot gives an E_{fb} value of -0.44 V vs. saturated calomel electrode (SCE). Upon doping lanthanide ions into the TiO_2 nanosheets, the E_{fb} values show a slight increase, within the range of 0.07–0.11 V. The increased E_{fb} values suggest a decrease in the reduction potential of the photoinduced electrons generated on the TiO_2 nanosheets due to the doping with lanthanide ions. This further confirms that the doped lanthanide ions can accept the photoinduced electrons generated on the CB of TiO_2 nanosheets, completing the photocatalytic reduction reaction (Fig. 7(C)). The photocurrent densities of the as-synthesized samples were also measured, in order to obtain further insight into the photoinduced charge-separation process. As shown in Fig. 8(B), the TiO_2 nanosheets with coexposed {001}/{101} facets exhibit a low photocurrent density ($\sim 0.5 \mu\text{A/cm}^2$) because of their large exciton binding energy. However, the photocurrent densities of the lanthanide-doped TiO_2 nanosheets are significantly higher than those of their pure counterparts. Among the doped TiO_2 nanosheets, the Yb^{3+} -doped ones exhibit the highest photocurrent density, suggesting a greatly enhanced separation effi-

ciency of photoinduced charge carriers in this sample. This observation is in good agreement with the results of the photocatalytic H_2 evolution tests discussed above.

The photoinduced charge carrier kinetics in lanthanide-doped TiO_2 nanosheets with coexposed {001}/{101} facets is schematically illustrated in Fig. 9(A). Upon simulated sunlight irradiation, the photoinduced electrons on the {001} facets of the TiO_2 nanosheets transfer to the {101} facets, with simultaneous generation of the same amount of photoinduced holes on the {001} facets. As such, the photocatalytic oxidation reaction should occur on the {001} facets of the TiO_2 nanosheets, while the {101} facets are responsible for the photocatalytic reduction. After the selective doping of lanthanide ions into the {101} facets of the TiO_2 nanosheets, the photoinduced electrons can be trapped by the doped lanthanide ions, extending the charge-separated states. Thus, the photocatalytic reduction activity of the lanthanide-doped TiO_2 nanosheets is enhanced on the {101} facets. Figs. 9(B) and (C) shows the photocatalytic reduction of Ag nanoparticles onto pure and Yb^{3+} -doped TiO_2 nanosheets, respectively. As shown in the fig-

Fig. 9. (A) Schematic illustration of the photoinduced charge carrier kinetics in lanthanide-doped TiO_2 nanosheets with coexposed {001}/{101} facets; SEM images of pure (B) and Yb^{3+} -doped (C) TiO_2 nanosheets after photocatalytic deposition of Ag nanoparticles.

ures, the Ag nanoparticles are loaded on the side surface/{101} facets of the TiO₂ nanosheets, indicating that the photocatalytic reduction process only occurs on the {101} facets. Notably, the Ag nanoparticles deposited on the Yb³⁺-doped TiO₂ nanosheets are smaller and more dispersed than those loaded on the pure TiO₂ nanosheets. This result clearly demonstrates the enhanced photocatalytic reduction activity of the TiO₂ nanosheets examined in this study because of the longer lifetimes of the charge-separated states achieved by doping with lanthanide ions.

4. Conclusions

In summary, a series of lanthanide ions with different electron occupations of *f* orbitals have been selectively doped into the {101} facets of TiO₂ nanosheets with coexposed {001}/{101} facets using a one-step solvothermal method. Upon simulated sunlight irradiation, the lanthanide-doped TiO₂ nanosheets show much higher photocatalytic H₂ evolution activities compared with those of the pure TiO₂ nanosheets. The enhanced photocatalytic activity is mainly attributed to the considerably extended the photoinduced charge-separated states due to the trapping of the photoinduced electrons by the doped lanthanide ions on the {101} facets of the TiO₂ nanosheets. Interestingly, among the lanthanide-doped TiO₂ nanosheets examined in this study, the Yb³⁺-doped ones exhibit the optimal photocatalytic activity for H₂ evolution. The H₂ evolution amount of Yb³⁺-doped TiO₂ nanosheets in the presence of Pt cocatalysts is ~8.5 times higher than that of the pure TiO₂ nanosheets. This can be ascribed to the poor relaxation process of the captured electrons between the energy levels of

the Yb³⁺ ions, leading to a highly efficient proton reduction on the {101} facets of the Yb³⁺-doped TiO₂ nanosheets. The present lanthanide doping strategy is expected to have a significant impact toward the enhancement of the photoactivity of semiconductor-based nanomaterials with applications in photocatalysis, photoelectrochemistry, and solar cells.

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Graphical Abstract

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Prolonging charge-separation states by doping lanthanide-ions into {001}/{101} facets-coexposed TiO₂ nanosheets for enhancing photocatalytic H₂ evolution

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The lanthanide ions were selectively doped into the {101} facets of the TiO₂ nanosheets with coexposed {001}/{101} facets by using a one-step solvothermal method. These samples exhibited a remarkable enhancement of photocatalytic activity for H₂ evolution due to the prolonged charge-separation states, as evidenced by the kinetics analyses.

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利用镧系离子掺杂延长{001}/{101}晶面共暴露的TiO₂纳米片 电荷分离态以增强其光催化产氢性能

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摘要: 随着工业化的快速发展, 化石燃料等不可再生能源的快速消耗, 人类将面临不可预测的能源危机. 寻找有效的方法来解决能源短缺问题已成为当今的重要研究课题. 氢能是一种可以替代化石燃料的清洁可再生能源. 利用半导体光催化分解水制氢技术可以将太阳能转化为氢能. 目前, 在已开发的半导体光催化材料中, TiO₂因具有无毒、稳定、廉价等优点而备受光催化领域关注. 但是, 在实际应用方面, TiO₂的光催化效率受限于其低的光子利用率和较高的光生电子-空穴复合率. 许多研究表明, TiO₂不同晶面的协同作用有利于光生载流子的迁移分离, 并且适量的掺杂能够捕获光生电子, 从而抑制其复合. 而镧系元素因其特殊4f电子结构受到广泛的关注. 采用物理或化学方法将镧系离子引入TiO₂晶格中, 可以影响光生电子和空穴的动力学过程, 延长光生载流子的分离状态, 从而提高光催化活性.

本文通过简单溶剂热法成功合成了镧系离子掺杂{001}/{101}面共暴露的TiO₂纳米片. X-射线粉末衍射(XRD)、X-射线光电子能谱(XPS)和高分辨透射电子显微镜(HRTEM)的表征结果证明了镧系离子选择性掺杂在TiO₂纳米片{101}面上. 结合紫外可见吸收光谱、稳态荧光、瞬态荧光衰减曲线、光电流及莫特-肖特基曲线等手段对镧系离子掺杂TiO₂光催化剂

进行了表征, 结果表明, 镧系离子掺杂 TiO_2 纳米片增强了对光的吸收, 同时延长光生载流子的分离状态, 阻碍光生电子和空穴的复合. 考察其光催化分解水制氢的性能. 研究表明, 在相同掺杂量($0.5 \text{ mol}\% \text{RE}^{3+} = \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$)的 TiO_2 纳米片中, Yb^{3+} - TiO_2 纳米片光催化剂具有优异的产氢活性, 在模拟太阳光照射1 h后产氢量是纯 TiO_2 的4.25倍. 同时讨论了不同浓度助催化剂Pt作用下的 Yb^{3+} - TiO_2 纳米片产氢效果, 当Pt含量为0.3 wt%时, 光解水产氢活性最佳, Pt/ Yb^{3+} - TiO_2 纳米片的产氢量是 Yb^{3+} - TiO_2 的2倍, 纯 TiO_2 的8.5倍. 光催化分解水产氢活性的显著提高可以归因于光生电子-空穴对在 TiO_2 纳米片{001}/{101}面的快速分离, 以及镧系离子4f电子轨道对电子的捕获和杂质能级的产生减小了禁带宽度, 这不仅延长了光生载流子的分离状态, 增加了 H^+ 还原成 H_2 的机会, 而且还可以拓展可见光的吸收范围. 可见, 利用镧系离子掺杂 TiO_2 和共暴露{001}/{101}面协同作用是一种实现 TiO_2 基光催化活性提高的有效方法之一. 镧系离子掺杂的策略对提高半导体纳米材料的光催化活性有显著的影响, 可能在光催化、光电化学和太阳能电池领域有更广泛的应用.

关键词: 光催化; 产氢; 镧系离子掺杂; TiO_2 ; 共暴露面; {001}面; 纳米片

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