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La and Cr Co-doped SrTiO₃ as an H₂ evolution photocatalyst for construction of a Z-scheme overall water splitting system

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ABSTRACT

The photocatalytic activity of a semiconductor-based photocatalyst largely depends on the semiconductor's intrinsic crystal and electronic properties. We have prepared two types of La and Cr co-doped SrTiO₃ photocatalysts (SrTiO₃(La,Cr)) using the polymerized complex method (PCM) and sol-gel hydrothermal method (SHM). Under $\lambda > 420$ -nm visible light irradiation, only the Pt-loaded SrTiO₃(La,Cr) prepared by the SHM showed efficient photocatalytic activities for both H₂ evolution in the presence of an I⁻ sacrificial reagent and for Z-scheme overall water splitting when it was coupled with the Pt-loaded WO₃ in the presence of I⁻ and IO₃⁻ as the shuttle redox mediator. The superior photocatalytic activity of SrTiO₃(La,Cr) prepared by the SHM has been ascribed to its more negative conduction-band position, higher carrier concentration, and higher carrier mobility, demonstrating that the design and synthesis of an H₂-evolution photocatalyst with appropriate electronic properties is crucial for achieving Z-scheme overall water splitting.

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1. Introduction

Conversion of solar energy to chemical energy in the form of hydrogen by photocatalytic splitting of water is a viable means of producing renewable energy [1,2]. Photocatalytic water-splitting is a four-electron transfer and energetically uphill reaction that requires at least 1.23 eV of energy input [3]. In the most widely studied semiconductor-based photocatalysis of a water-splitting approach, the overall photocatalytic water-splitting efficiency largely depends on the efficiencies of the key energy conversion and utilization courses, i.e., light absorption to generate excited electrons and holes, charge separation and migration, and surface catalytic reactions with water [4].

The majority of these processes are related to the intrinsic crystal and electronic properties of the semiconductor photocatalyst [5]. Various kinds of semiconductor materials and structural engineering strategies have been explored for overall water-splitting reactions. Many semiconductor photocatalysts have been reported to be effective for water oxidation, proton reduction, and even overall water-splitting reactions [1,6–9]. However, the overall water-splitting efficiency is still quite low.

Improvement of the charge-separation efficiency and the resulting carrier mobility to the surface reaction sites is a vitally important concern in the development of semiconductor-based composite photocatalytic water-splitting systems. To

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this end, various strategies have been explored. For composite photocatalyst systems, co-catalysts and junctions between different functional components have been found to be crucial for improving the efficiency of charge separation [10–13]. Lee's group reported that the formation of *p-n* junctions between *n*- and *p*-type semiconductors could efficiently separate photo-generated charges by the internal electric field [14,15]. We have also reported that surface phase junctions [16,17], heterojunctions [18], and solid-solution junctions [19] can improve charge-separation efficiency, hence enhancing photocatalytic activities. However, although the photocatalytic activity could usually be improved by the use of junction and co-catalyst approaches, further improvement of the photocatalytic activity was found to be extremely difficult. In this case, it is necessary to improve the intrinsic properties of the semiconductor photocatalyst itself [20–22]. We believe that the functions of the co-catalysts and junctions can only be fully exploited if the semiconductor photocatalyst itself favors charge separation and carrier migration. Co-catalysts and junctions cannot improve the photocatalytic activity much for a semiconductor photocatalyst with poor charge separation and migration efficiency. In view of this, engineering of the semiconductor photocatalyst itself to possess suitable crystal- and electronic-structure that matches that of the coupled co-catalysts should be a vitally important priority in research into co-catalyst- and junction-based composite photocatalyst approaches for water splitting.

Herein, we have prepared La and Cr co-doped SrTiO₃ photocatalysts [SrTiO₃(La,Cr)] using the polymerized complex method (PCM) and sol-gel hydrothermal method (SHM), denoted SrTiO₃(La,Cr)-PCM and SrTiO₃(La,Cr)-SHM, respectively. Under visible light irradiation ($\lambda > 420$ nm), the Pt-loaded SrTiO₃(La,Cr)-SHM sample [Pt/SrTiO₃(La,Cr)-SHM] showed efficient photocatalytic activities for hydrogen evolution in the presence of an I[−] sacrificial reagent. More importantly, we can achieve overall water-splitting by construction of a Z-scheme system [23–32] with Pt/SrTiO₃(La,Cr)-SHM as a hydrogen evolution photocatalyst, Pt-loaded WO₃ (PtO_x/WO₃) as an oxygen evolution photocatalyst, and an I[−] and IO₃[−] couple (I[−]/IO₃[−]) as the shuttle redox mediator. In comparison, under the same experimental conditions, the Pt-loaded SrTiO₃(La,Cr)-PCM sample [Pt/SrTiO₃(La,Cr)-PCM] showed rather low photocatalytic activity in the hydrogen evolution half-reaction and no photocatalytic activity for overall water-splitting when it was used as the hydrogen evolution photocatalyst in the Z-scheme system. The negative shift of the conduction band and the relatively higher carrier concentration and mobility were found to be responsible for the high photocatalytic activities of the sample prepared using the SHM. This work demonstrates that use of the proper synthetic methods to obtain semiconductor photocatalysts with appropriate electronic structures is crucial for the construction of the Z-scheme system for overall water-splitting.

2. Experimental

2.1. Preparation of catalysts

Titanium tetra-isopropoxide (> 98%) and Cr(NO₃)₃·9H₂O (99%) were purchased from Beijing J&K Scientific Ltd., China; Sr(NO₃)₂ (99.5%) was purchased from Tianjin Guangfu Chemical Co., China; La(NO₃)₃·6H₂O (99.99%) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., China; citric acid (≥ 99.5%) was purchased from Tianjin Kermel Chemical Co., China; and ethylene glycol (≥ 99.0%) and WO₃ were purchased from SinoPharm Chemical Reagent Co., Ltd., China. All chemicals were used as received without further purification.

Two types of SrTiO₃(La,Cr) samples; namely, SrTiO₃(La,Cr)-PCM and SrTiO₃(La,Cr)-SHM, were prepared by the PCM [18] and SHM methods as depicted in Fig. S1. Typically, for the synthesis of the SrTiO₃(La,Cr)-PCM sample, titanium tetra-isopropoxide (4.05 g) was dissolved in an ethylene glycol (33.50 mL) solution containing citric acid (31.52 g). The reaction mixture was stirred vigorously at 50 °C until it became clear, and the metal precursors Sr(NO₃)₂ (3.02 g), La(NO₃)₃·6H₂O (0.33 g), and Cr(NO₃)₃·9H₂O (0.30 g) were added. The mixture was stirred continuously at 50 °C for another 4 h to yield a completely dissolved reaction mixture. The reaction mixture was polyesterified at 130 °C for 20 h in an evaporation pan, followed by pyrolysis at 350 °C for 2 h. The resulting black solid product was then ground into fine powder and calcined at 900 °C for 2 h in a temperature-programmed muffle furnace in the flow of air. After cooling to room temperature, the calcined samples were kept in vials and stored in a desiccator.

The SrTiO₃(La,Cr)-SHM sample was synthesized by following the procedure reported in the literature, except that Sr(NO₃)₂ was used as the Sr precursor instead of Sr(Ac)₂·0.5H₂O [33]. Typically, titanium tetra-isopropoxide (5.40 g) was dissolved in an ethylene glycol (55 mL) solution, and the metal precursors Sr(NO₃)₂ (4.02 g), La(NO₃)₃·6H₂O (0.43 g), and Cr(NO₃)₃·9H₂O (0.40 g) were added and stirred continuously at 38 °C for 2–4 h to yield a completely dissolved reaction mixture. The resulting solution was dried at 80 °C for 10 d to obtain a dry gel and then ground into a fine powder in a mortar. The resulting light-blue fine powder was added into an aqueous solution containing 75 mL NaOH (5 mol L^{−1}). After additional stirring for approximately 1 h, the mixture was put into a 100-mL Teflon-lined stainless-steel autoclave, which was sealed and kept at 180 °C for 36 h. Cooling to room temperature yielded crystalline powder, which was filtered out and washed with deionized water until the pH was approximately 7. The sample was further dried in an oven at 80 °C overnight in air. The final product was also kept in a vial and stored in a desiccator.

Pt co-catalyst was loaded on the surface of the SrTiO₃(La,Cr) samples by the photodeposition method [24]. Photodeposition reactions were carried out in an inner irradiation reaction vessel connected to a closed circulation system. The powdered photocatalysts (1 g) were dispersed in a 1-vol% aqueous methanol solution (500 mL) containing the Pt precursor H₂PtCl₆. The photodeposition reactions were carried out by irradiation of the reaction mixture using a 450-W high-pressure mercury lamp for 8–10 h. Such Pt-loaded samples were centrifuged, washed with deionized water, and dried

in a vacuum oven at 80 °C overnight. The loading of Pt on the surface of WO₃ followed the impregnation method described previously [24,30]; that is, Pt was impregnated on the surface of commercial WO₃ in an H₂PtCl₆ aqueous solution followed by drying and calcination in air at 550 °C to give Pt-loaded PtO_x/WO₃.

2.2. Characterization

The crystallinities of the synthesized samples were studied by X-ray diffraction (XRD) on a Rigaku (Japan) D/Max-2500/PC powder diffractometer equipped with a Cu K α (λ = 1.54056 Å) radiation source. The XRD patterns were measured at an operating voltage of 40 kV and a current of 300 mA. The scanning rate was kept at 0.12° min⁻¹, with a step size of 0.01° in the 2 θ range 10°–105°. The morphologies of the samples were examined by scanning electron microscopy (SEM) with a Quanta 200FEG scanning electron microscope. The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a Tecnai G² F30 S-Twin (FEI Corp., USA) with an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Escalab 250 Xi instrument with a monochromatic Al K α X-ray source. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded on a JASCO V-550 UV-vis spectrophotometer equipped with an integrating BaSO₄ sphere. The Brunauer-Emmett-Teller (BET) surface areas of the samples were calculated based on the nitrogen-adsorption isotherms measured on a Micromeritics ASAP 2000 adsorption analyzer. The results showed that the BET surface areas of SrTiO₃(La,Cr)-SHM and SrTiO₃(La,Cr)-PCM were approximately 20.6 and 9.6 m² g⁻¹, respectively. The amounts of the doped Cr and La in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an ICPS-8100 spectrometer. Per ICP-MS analysis, the doping concentrations of La and Cr were 5.34 and 4.81 mol% in SrTiO₃(La,Cr)-SHM, respectively, and 5.42 and 4.96 mol% in SrTiO₃(La,Cr)-PCM (Table S1), respectively. This gives a ratio of La/Cr of 1.09 for SrTiO₃(La,Cr)-PCM and 1.11 for SrTiO₃(La,Cr)-SHM, indicating that the doping levels of La and Cr are similar in these two samples.

The flat-band potentials of the samples were determined by extrapolation of the Mott-Schottky plots measured on a standard three-electrode-cell electrochemical workstation (CHI660A, Shanghai Chenhua Instruments, China). In this system, a Pt plate was used as the counter electrode, a saturated calomel electrode (SCE) was employed as the reference electrode, and the thin films of the photocatalyst samples fabricated by the electrophoretic deposition method were used as the working electrode. The electrolyte was a Na₂SO₄ solution (0.5 mol L⁻¹). The carrier mobility, concentration, and resistivity of the SrTiO₃(La,Cr) samples were measured using a four-point probe and a Hall-effect measurement system (HL5550 LN2) under a magnetic field of 0.51 T at room temperature. The adsorption properties of the samples toward I⁻ and IO₃⁻ anions were analyzed at room temperature by ion chromatography (Dionex, ICS1100). The mobile phase was an aqueous solution

containing 4.5 mmol L⁻¹ Na₂CO₃ and 1.4 mmol L⁻¹ NaHCO₃. The powder samples (0.1 g) were dispersed in an aqueous solution (10 mL) containing I⁻ or IO₃⁻ (2.00 mmol L⁻¹) and stirred for 10 h at room temperature in the dark to establish adsorption-desorption equilibrium, followed by filtration to obtain the ion-adsorbed sample. The filtrate was diluted 10 times with H₂O prior to chromatography. The amounts of the ion adsorbed on the samples were evaluated by comparison of the ion concentration in the solution phase before and after the adsorption experiment. The error bars for such a measurement were estimated to be approximately 5 ppm. Water contact angle data were measured using a JC 2000 C1 instrument under atmospheric conditions at room temperature. Thin films of the samples were prepared by the electrophoretic deposition method on an indium-doped tin oxide (ITO) substrate. The distilled water (approximately 1 μ L) was then vertically dropped onto the thin films using a microsyringe. The water droplet images on the thin-film surfaces were taken with a camera, from which the contact angles were calculated.

2.3. Photocatalytic activity measurements

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed-gas circulation and evacuation system. In a typical hydrogen production half-reaction, the SrTiO₃(La,Cr) sample (100 mg) was suspended in a 200-mL NaI aqueous solution (2 mmol L⁻¹) and thoroughly degassed by evacuation. For the overall water-splitting reaction, Pt-loaded SrTiO₃(La,Cr) samples (100 mg) and Pt-loaded WO₃ samples (200 mg) were suspended in a 200-mL aqueous solution containing NaI (2 mmol L⁻¹) and thoroughly degassed by evacuation. The photoirradiation light source was a 300-W Xe lamp (Ushio-CERMAX LX300) equipped with an optical cutoff filter (Kenko, L-42; λ > 420 nm) and a water filter to prevent the passage of the ultraviolet and infrared light, respectively. The temperature of the reaction mixture was maintained at 15 °C by a continuous flow of cooling water. The amounts of the evolved H₂ and O₂ gases were determined by online gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier). For the hydrogen evolution reactions in an aqueous methanol solution, photocatalysts (1.0 g) were dispersed in a 1-vol% aqueous methanol solution (500 mL) and irradiated with a 450-W mercury lamp (USHIO UM452). The Pt (0.5 wt%) co-catalyst was loaded onto the SrTiO₃(La,Cr) samples by *in situ* photodeposition.

3. Results and discussion

Fig. 1(A) shows the photocatalytic H₂ evolution activities of the Pt-loaded SrTiO₃(La,Cr)-SHM and SrTiO₃(La,Cr)-PCM samples. The reactions were carried out under the same experimental conditions with the same amount of NaI as the electron-donating sacrificial reagent under visible light irradiation (λ > 420 nm). It can be seen that the SrTiO₃(La,Cr)-SHM sample shows efficient activities for H₂ evolution, while the SrTiO₃(La,Cr)-PCM sample does not. After approximately 4 h, the reaction reaches the steady state, which is due to the gen-

Fig. 1. Time course of H₂ evolution over SrTiO₃(La,Cr)-SHM (a), and SrTiO₃(La,Cr)-PCM (b) with NaI (A) and methanol (B) as sacrificial reagents, respectively.

erated IO₃[−] competing with the proton-reduction reaction. Fig. 1(B) shows the photocatalytic activities of these two samples under high-pressure Hg lamp UV-light irradiation in the presence of methanol as the sacrificial reagent. It can be seen that the SrTiO₃(La,Cr)-PCM sample shows photocatalytic activity of H₂ evolution under UV-light irradiation. Although it is still much lower than that of the SrTiO₃(La,Cr)-SHM sample, this is a strong indication that the conduction band of the SrTiO₃(La,Cr)-PCM sample is high enough to reduce H⁺ to H₂. The low photocatalytic activity of SrTiO₃(La,Cr)-PCM for H₂ evolution might be due to its other intrinsic properties.

The Pt-loaded SrTiO₃(La,Cr)-PCM and SrTiO₃(La,Cr)-SHM samples were also used as the H₂ evolution photocatalyst for the construction of the overall water-splitting Z-scheme system. In both cases, the counter component of the water oxidation photocatalyst was Pt-loaded WO₃, and the shuttle redox mediator was I[−]/IO₃[−]. The photocatalytic performances of these two systems were evaluated for two-step photoexcitation overall water-splitting under visible-light ($\lambda > 420$ nm) irradiation. No H₂ or O₂ evolution was observed for the Pt/SrTiO₃(La,Cr)-PCM | I[−]/IO₃[−] | PtO_x/WO₃ system (where “|” refers to the solid-solution interfaces between the samples and the I[−]/IO₃[−] aqueous solution). However, the Pt/SrTiO₃(La,Cr)-SHM | I[−]/IO₃[−] | PtO_x/WO₃ Z-scheme system is efficient in overall water-splitting since the simultaneous evolution of H₂ and O₂ was observed. As shown in Fig. 2, in the first run of the 10-h photocatalytic reaction course, the H₂/O₂ ratio of the evolved gas products was approximately 3.7, which is larger than the expected stoichiometric water-splitting ratio of 2/1. This is not surprising because H₂ evolution should be the dominant reaction at the initial stage. We should note that only I[−], which is a good hole scavenger that favors the H₂-evolution reaction on the Pt/SrTiO₃(La,Cr)-SHM side, was used at the beginning of the reactions in our experiment. With the H₂ evolution reaction proceeding on the Pt/SrTiO₃(La,Cr)-SHM side, I[−] anions were gradually oxidized to IO₃[−], which is a good electron acceptor favoring the O₂-evolution reaction. Generation of IO₃[−] further triggers O₂ evolution on the PtO_x/WO₃ side, creating the functional shuttle redox mediator I[−]/IO₃[−] that facilitates the evolution of both H₂ and O₂. To test the system's stability, we

also performed another two runs of 10-h reactions after thoroughly degassing the entire system to remove the gases evolved in the previous run. Under the same experimental conditions, the average reaction rates of H₂ and O₂ evolution were approximately 9.1 and 2.4 μmol h^{−1} for run 1, 9.9 and 3.7 μmol h^{−1} for run 2, and 10.4 and 4.9 μmol h^{−1} for run 3. That there was no significant decline in activity implies that the photocatalytic system was stable. Furthermore, the evolved gas ratio of H₂/O₂ changed from 3.7 for run 1 to approximately 2.6 for run 2 and approximately 2.1 for run 3, indicating that the stoichiometric water-splitting could be achieved after 20 h of reaction time due to the efficient shuttling of the charge carriers by the shuttle redox mediator I[−]/IO₃[−]. The remarkable difference in the photocatalytic water-splitting activity between the two constructed Z-scheme systems might have arisen from the differences in the Pt/SrTiO₃(La,Cr) samples prepared by the different methods. In order to find out the key factors enabling overall water-splitting in the Pt/SrTiO₃(La,Cr)-SHM | I[−]/IO₃[−] | PtO_x/WO₃ system, the crystal and electronic structures of the two synthesized Pt/SrTiO₃(La,Cr) materials were subjected to detailed investigation and comparison.

Fig. 2. Time courses of H₂ and O₂ evolution in photocatalytic overall water splitting reactions by the constructed Z-scheme system of Pt/SrTiO₃(La,Cr)-SHM | I[−]/IO₃[−] | PtO_x/WO₃ under visible light irradiation.

Fig. 3. XRD patterns of $\text{SrTiO}_3(\text{La,Cr})$ -SHM (a), and $\text{SrTiO}_3(\text{La,Cr})$ -PCM (b).

The XRD patterns of the $\text{SrTiO}_3(\text{La,Cr})$ -PCM and $\text{SrTiO}_3(\text{La,Cr})$ -SHM samples are shown in Fig. 3. Both samples showed five major diffraction peaks, with 2θ positions at approximately 32.3° , 39.9° , 46.5° , 57.7° , and 67.7° , which can be assigned to the (110), (111), (200), (211), and (220) planes of cubic-structured SrTiO_3 (JCPDS Card No. 84-0443), respectively. Small amounts of La- and Cr-doping (Table S1) achieved by

different doping methods (PCM and SHM) did not result in obvious differences in XRD patterns. Careful comparison by magnification of these diffraction peaks, as shown in the inset of Fig. 3 using the (110) peak as an example, revealed that all of the principal peaks in these two samples are in the same corresponding 2θ positions within experimental error. It was noted that the full width at half-maximum of the (110) XRD peak of $\text{SrTiO}_3(\text{La,Cr})$ -PCM was relatively narrow compared to that of $\text{SrTiO}_3(\text{La,Cr})$ -SHM. In addition, a higher intensity was observed for the diffraction peaks in the XRD pattern of $\text{SrTiO}_3(\text{La,Cr})$ -PCM. These results indicate that the $\text{SrTiO}_3(\text{La,Cr})$ -PCM sample had the larger crystallite size and higher crystallinity.

The TEM images (Fig. 4) show that both samples are constituted of a type of small nanoparticle of sizes ranging from approximately 10–50 nm. The major difference is that the nanoparticles in $\text{SrTiO}_3(\text{La,Cr})$ -SHM are well dispersed, while those in $\text{SrTiO}_3(\text{La,Cr})$ -PCM are sintered into agglomerated aggregates after high-temperature calcination. The dark contrasts in the TEM images are due to the thickness differences of the samples in that particular area. HRTEM images of both samples (Fig. 4(b) and 4(d)) show well-resolved lattice-structure patterns with spacing parameters of approximately 3.90 and 2.80 Å, which correspond to the (100) and (110) lattice fringes of SrTiO_3 , respectively. According to the results of N_2 adsorption-desorption isotherm analysis, the BET

Fig. 4. TEM images of $\text{SrTiO}_3(\text{La,Cr})$ -SHM (a) and $\text{SrTiO}_3(\text{La,Cr})$ -PCM (c), and HRTEM images of $\text{SrTiO}_3(\text{La,Cr})$ -SHM (b) and $\text{SrTiO}_3(\text{La,Cr})$ -PCM (d).

Fig. 5. SEM images of SrTiO₃(La,Cr)-SHM (a) and SrTiO₃(La,Cr)-PCM (b), and 0.5 wt% Pt loaded samples of SrTiO₃(La,Cr)-SHM (c) and SrTiO₃(La,Cr)-PCM (d).

surface areas of SrTiO₃(La,Cr)-SHM and SrTiO₃(La,Cr)-PCM were approximately 20.6 and 9.6 m² g⁻¹, respectively. The smaller surface area of the latter might be due to the aggregation of nanoparticles. The difference in the BET surface areas might have some impact on the photocatalytic performance of the samples. Fig. 5 shows the SEM images of the samples before and after Pt-loading. Before Pt-loading, both samples have relatively smooth surfaces. Consistent with the observations by TEM, the SrTiO₃(La,Cr)-SHM sample (Fig. 5(a)) is constituted of better dispersed nanoparticles, while the SrTiO₃(La,Cr)-PCM sample (Fig. 5(b)) is sintered into irresolvable aggregates. Fig. 5(c) and (d) show the SEM images of these two samples after 0.5-wt% Pt-loading by the photodeposition method. The size of the Pt nanoparticles deposited on the surface of these two samples was approximately 1–3 nm, with better dispersion on

the surface of the SrTiO₃(La,Cr)-PCM sample. Overall, the SrTiO₃(La,Cr)-SHM sample has smaller particle sizes, better particle dispersion, and a higher surface area than the SrTiO₃(La,Cr)-PCM sample. These differences might contribute to the enhancement of the photocatalytic activity of SrTiO₃(La,Cr)-SHM. However, it seems unlikely that they are the decisive factors leading to such a significant difference, such that one sample has efficient photocatalytic activities for both H₂ evolution and overall water-splitting in a Z-scheme system, while the other does not.

The band structures of the samples were analyzed by combining the UV-vis DRS and the Mott-Schottky plots. Fig. 6(A) shows the UV-vis DRS of the samples. The absorption edges of SrTiO₃(La,Cr)-SHM and SrTiO₃(La,Cr)-PCM lie at approximately 500 and 570 nm, respectively. The SrTiO₃(La,Cr)-SHM sample

Fig. 6. UV-vis DRS (A) and plots of the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) (B) of SrTiO₃(La,Cr)-SHM (a) and SrTiO₃(La,Cr)-PCM (b).

is yellow-colored, while the $\text{SrTiO}_3(\text{La,Cr})$ -PCM one is brown, which is consistent with the results of UV-vis DRS. The band-gap energies of these two samples were determined by extrapolation of the plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) (Fig. 6(B)) and calculated by the following formula: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α , ν , E_g , and A are absorption coefficient, light frequency, band gap, and a constant, respectively [34]. The index n depends on the transition characters of a semiconductor, i.e., direct transition ($n = 1$) or indirect transition ($n = 4$). The best fits of $(\alpha h\nu)^2$ versus E_g were obtained only when $n = 1$, suggesting that both of these two La and Cr co-doped samples are direct semiconductors. The band-gap energies were estimated by the interception of the tangent to the X-axis. The calculated band gaps of $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM were 2.52 and 2.19 eV, respectively.

The flat-band potentials (E_{fb}) of $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM samples were determined by the Mott-Schottky measurements conducted in a 0.5-mol L⁻¹ Na_2SO_4 solution (Fig. 7). The E_{fb} values were obtained by the extrapolation of the Mott-Schottky plots (C^{-2} versus E , electrode potential) using the following equation: $C_{sc}^{-2} = 2(E - E_{fb} - \kappa T/e)/e\epsilon\epsilon_0 N_D$ [35]. The E_{fb} values of $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM are -1.64 and -1.48 V (versus SCE, pH = 7), respectively. In other words, the E_{fb} value of $\text{SrTiO}_3(\text{La,Cr})$ -SHM is 0.16 V more negative than that of $\text{SrTiO}_3(\text{La,Cr})$ -PCM. Based on the data derived from UV-vis DRS and the Mott-Schottky plots, the band structures of these two samples are depicted as shown in Scheme 1. Both of these samples have visible light-absorption characteristics with sufficiently negative conduction-band positions for H^+ -reduction and sufficiently positive valence-band positions for H_2O -oxidation, except that the band gap of the $\text{SrTiO}_3(\text{La,Cr})$ -SHM sample is slightly broadened, with more negative conduction-band positions and more positive valence-band positions. We also measured the Hall effects, and the results of the electric properties are summarized in Table 1. Both of these two $\text{SrTiO}_3(\text{La,Cr})$ samples exhibited n -type conductivity. However, the $\text{SrTiO}_3(\text{La,Cr})$ -SHM sample showed much higher carrier mobility and concentration, as well as much lower resistivity, than the $\text{SrTiO}_3(\text{La,Cr})$ -PCM sample.

To further exclude the possibility that the photocatalytic ac-

Fig. 7. Mott-Schottky plots of $\text{SrTiO}_3(\text{La,Cr})$ -SHM (a) and $\text{SrTiO}_3(\text{La,Cr})$ -PCM (b).

Scheme 1. Schematic energy diagrams of $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM samples.

Table 1

The results of the Hall measurements.

Sample	Mobility (cm ² /V s)	Carrier concentration (cm ⁻³)	Resistivity (ohm cm)
$\text{SrTiO}_3(\text{La,Cr})$ -PCM	15	-1.438×10^{10}	1.144×10^6
$\text{SrTiO}_3(\text{La,Cr})$ -SHM	41	-6.146×10^{10}	1.515×10^5

tivity difference between $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM is due to the formation of different levels of defects or different types of Pt co-catalysts, XPS analyses were carried out. It is well known that formation of Cr^{6+} should be avoided during Cr-doping since the Cr^{6+} 3d orbital level is usually located below the Ti 3d conduction-band level acting as an electron trap site. However, the XPS spectra (Fig. S2(A)) mainly showed Cr 2p_{3/2} peaks at 576.5 eV due to the trivalent Cr, demonstrating that the formation of Cr^{6+} recombination sites was suppressed in either of these samples. The deconvoluted XPS spectra of the samples after 0.5-wt% Pt-loading are shown in Fig. S2(B). The standard Pt 4d_{5/2} peak is at approximately 314.6 eV for bulk metallic Pt and at approximately 318.0 eV for Pt²⁺ [36]. After deconvolution, the maxima of the Pt 4d_{5/2} peaks for Pt⁰ and Pt²⁺ were at approximately 314.5 and 318.9 eV for Pt/ $\text{SrTiO}_3(\text{La,Cr})$ -SHM and at 314.9 and 318.7 eV for Pt/ $\text{SrTiO}_3(\text{La,Cr})$ -PCM, respectively. This implies that Pt is mainly in the form of reduced metallic Pt⁰ in both samples, whereas a very small proportion of Pt is in the form of Pt²⁺. Attempts to quantify the ratio of Pt⁰ and Pt²⁺ failed due to the low signal-to-noise ratio resulting from the low Pt loading. XPS spectra reveal that the majority of the Pt is reduced to Pt⁰ in both samples, and it is unlikely that the dramatic difference in their photocatalytic activity is due to differences in the Pt co-catalysts.

Finally, the effects of the surface properties were also considered. We considered that the adsorption of I⁻ and IO₃⁻ anions on the surface of photocatalysts may also affect their photocatalytic activity [24,30]. Therefore, the adsorptivities of I⁻ and IO₃⁻ on $\text{SrTiO}_3(\text{La,Cr})$ -SHM and $\text{SrTiO}_3(\text{La,Cr})$ -PCM photocatalysts were also measured by ion chromatography, and the results are summarized in Table S2. No significant differences in adsorptivity were observed, indicating that the different photocatalytic behaviors of these two samples do not originate from their capacity for I⁻ and IO₃⁻ adsorption. It has also been

reported that the photocatalytic activity may be related to the hydrophilicity and hydrophobicity of photocatalysts. However, water-contact-angle measurements on the films of these two samples (Fig. S3) showed that the average water contact angle is 17.7° for $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ and 11.2° for $\text{SrTiO}_3(\text{La,Cr})\text{-PCM}$, indicating that both samples have good hydrophilicity. The different photocatalytic activities of these two samples are not due to hydrophilicity differences.

In summary, all of the current experimental and spectroscopic studies demonstrate that the drastically different behaviors of the $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ and $\text{SrTiO}_3(\text{La,Cr})\text{-PCM}$ samples during H_2 evolution and the overall water-splitting activities are obviously due to the different electronic structures resulting from the different synthesis methods. The $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ sample gives slightly more negative conduction-band positions, higher carrier mobility, and higher carrier concentration than the $\text{SrTiO}_3(\text{La,Cr})\text{-PCM}$ sample. The more negative conduction-band positions means that the $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ sample may have photogenerated electrons with more reducing power, which facilitates the electron transfer and separation from the $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ to Pt; the higher carrier mobility and concentration may further enhance the separation and migration of the photogenerated charges to the surface to participate in the reduction of water to H_2 and oxidation of I^- to IO_3^- . The synergism of these two effects might be responsible for the efficient photocatalytic activity of $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$. Although the $\text{SrTiO}_3(\text{La,Cr})\text{-PCM}$ sample has better visible-light absorption and proper energy-band positions for water reduction and I^- oxidation, its poor carrier concentration and mobility restrict its efficiency at charge separation and carrier migration, thereby leading to inefficient photocatalytic activity. Other factors, such as particle size, surface area, and hydrophilicity, might have some impact on the photocatalytic activities, but it is unlikely that they are decisive factors causing such significant differences.

4. Conclusions

We prepared two types of La and Cr co-doped SrTiO_3 photocatalysts by the PCM and SHM methods. For H_2 evolution half-reactions in the presence of NaI or methanol as hole-scavenging sacrificial reagents, the Pt-loaded $\text{SrTiO}_3(\text{La,Cr})\text{-SHM}$ sample exhibited efficient photocatalytic activity, while the Pt-loaded $\text{SrTiO}_3(\text{La,Cr})\text{-PCM}$ sample showed negligible photocatalytic activity. Furthermore, when these two samples were used as H_2 -evolution photocatalysts in visible-light-driven two-step excitation Z-scheme systems, overall water-splitting activity was only observed on the $\text{Pt/SrTiO}_3(\text{La,Cr})\text{-SHM} \mid \text{I}^-/\text{IO}_3^- \mid \text{PtO}_x/\text{WO}_3$ system. Detailed investigation of these two $\text{SrTiO}_3(\text{La,Cr})$ -based photocatalysts revealed that the superior photocatalytic activity of $\text{Pt/SrTiO}_3(\text{La,Cr})\text{-SHM}$ is due to the synergistic effect of more negative conduction-band edges and the relatively higher carrier concentration and mobility, which resulted from their different methods of synthesis. This work demonstrates that the design and synthesis of semiconductor photocatalysts with appropriate electronic structures is crucial for achieving effi-

cient overall water-splitting.

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Graphical Abstract

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La and Cr Co-doped SrTiO₃ as an H₂ evolution photocatalyst for construction of a Z-scheme overall water splitting system

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La and Cr co-doped SrTiO₃ prepared by the sol-gel hydrothermal method as an H₂-evolution photocatalyst for construction of a Z-scheme overall water-splitting system.

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基于镧和铬共掺杂钛酸锶产氢光催化剂构建Z机制全分解水体系

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摘要: 光催化剂的晶体结构、电子结构、表面结构等都会对自身性质产生决定性的作用, 因此认识和理解光催化材料自身结构和光催化性能之间的内在联系有助于设计合成更高效的光催化剂以及光催化复合体系. 本文通过聚合络合法和溶胶凝胶水热法分别制备了镧和铬共掺杂的SrTiO₃光催化剂, 标记为SrTiO₃(La,Cr)-PCM和SrTiO₃(La,Cr)-SHM. 在碘化钠或甲醇作为牺牲试剂的产氢反应中, 负载Pt的SrTiO₃(La,Cr)-SHM 样品显示了光催化活性, 而负载Pt的SrTiO₃(La,Cr)-PCM样品活性很低, 甚至无活性. 我们将这两种材料分别作为产氢光催化剂与三氧化钨耦合构建Z机制全分解水体系. 研究发现, 只有Pt/SrTiO₃(La,Cr)-SHM|I⁻/IO₃⁻|PtO_x/WO₃体系观察到了氢气和氧气的产生. 在第一个10 h的循环反应中, 产生的H₂/O₂ 摩尔比为3.7, 明显高于水分解H₂/O₂为2的化学计量比. 这是因为在反应起始时加入的是NaI, 质子还原产氢反应占据了主导. 随着氢气的不断产生, 部分I⁻被氧化成了IO₃⁻, 而IO₃⁻的存在就可以驱动氧气的产生, 由于溶液中I⁻/IO₃⁻氧化还原电的共存就可以持续驱动氢气和氧气的同时生成. 为了测试体系的稳定性, 我们将前面产生的气体完全抽空后又进行第二次10 h的循环反应, 总共进行三次循环反应. 在第一次循环过程中氢气、氧气生成速率分别为9.1和2.4 μmol h⁻¹, 第二次循环其速率分别为9.9 和3.7 μmol h⁻¹, 第三次循环速率分别达到10.4和4.9 μmol h⁻¹. 此外, 通过三次循环后H₂/O₂摩尔比为2.1, 接近水分解的化学计量比.

结合紫外可见漫反射光谱和Mott-Schottky曲线可以确定两种样品的能带位置. 从能带位置示意图可知, 两种样品都具有足够负的导带电势还原质子产氢以及足够正的价带电势氧化水产氧. 需要指出的是, SrTiO₃(La,Cr)-SHM样品的导带电

势比 $\text{SrTiO}_3(\text{La,Cr})$ -PCM样品的导带电势更负,这意味着前者的导带电势更有利于还原质子产氢. 霍尔效应测试的结果表明,两种样品均显示出 n 型半导体的特征,此外 $\text{SrTiO}_3(\text{La,Cr})$ -SHM样品显示出比 $\text{SrTiO}_3(\text{La,Cr})$ -PCM样品更快的载流子迁移率以及更高的载流子浓度. 因此,两种样品不同的导带位置以及不同的载流子迁移率和载流子浓度很可能是造成两者光催化性能具有显著差异的主要原因.

关键词: 钛酸锶; 光催化; 分解水; Z机制; 产氢

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