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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Time-resolved infrared spectroscopic investigation of roles of valence states of Cr in (La,Cr)-doped SrTiO₃ photocatalysts

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ABSTRACT

The kinetics of photogenerated electrons in SrTiO₃(La,Cr) pretreated with either H₂ or O₂ were studied using time-resolved infrared spectroscopy. The X-ray photoelectron and Raman spectra showed that the Cr cations in the sample reduced with H₂ were all in Cr³⁺, whereas those oxidized with O₂ were in mixed of Cr³⁺ and Cr⁶⁺. Electrons excited with 355 and 532 nm light pulses showed the absorption of mid-IR light, and this was traced as a function of the time delay in a microsecond domain. The time-resolved results revealed that the decay rate of the photoinduced electrons with Cr³⁺ was slower than that with Cr⁶⁺, implying that trivalent Cr contributed more to retarding recombination of photoinduced electrons and holes, and enhanced photocatalytic H₂ production activity.

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1. Introduction

The development of solar energy has attracted much research effort in recent years. Heterogeneous photocatalytic water splitting to H₂ and O₂ with semiconductors is a promising strategy for the effective use of solar energy [1–3]. Although many photocatalysts show high quantum efficiencies in the ultraviolet (UV) region, approximately 43% of the whole solar spectrum is visible light, whereas merely ~4% is UV light. The use of these photocatalysts in practical solar light energy conversion is therefore significantly hindered by their limited absorption of visible light. However, doping of foreign elements into UV-responsive semiconductors shows great promise for extension of the light absorption of semiconductors into the visible region [4,5].

Many doped photocatalysts such as doped TiO₂ [6,7], ZnO

[8], and SrTiO₃ [6,9,10] have been reported to exhibit photocatalytic activity for H₂ or O₂ production in the visible region. In particular, the effects of doping of Cr ions into SrTiO₃ on the photocurrents of semiconductor electrodes and photocatalytic H₂ production have been widely studied [11–13]. It was found that Cr doping was an effective way of shifting the light absorption of titanates into the visible region for H₂ production from aqueous methanol solutions [6]. Photocatalytic activity experiments have also demonstrated that Cr³⁺-doped SrTiO₃ shows higher photocatalytic activity in H₂ evolution than Cr⁶⁺-doped SrTiO₃ does under visible-light irradiation [9,13–15]. The mechanism by which the valence state of Cr affects photoinduced electrons is still not clear, and clarifying this is challenging because the behavior of photogenerated charge carriers in a photocatalytic reaction is complex. In addition to transfer of charge carriers from the bulk to surface reaction sites, charge

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carriers can be captured or recombined with each other, and this occurs across a very broad time range, from picoseconds to milliseconds. Because photoinduced electrons show a broad absorption in the mid-infrared (IR) region, and there is less absorption by photoinduced holes in the mid-IR region, time-resolved IR spectroscopy with nanosecond resolution can serve as a convenient tool for investigating the kinetics of electrons in the conduction band [16,17]; this can be used to explore the effect of the valence state of Cr on photocatalysis by Cr-doped SrTiO₃.

In this work, the kinetics of photogenerated electrons in Cr-doped SrTiO₃ was studied using time-resolved IR spectroscopy. Model doped metal oxide photocatalysts were prepared by simple reduction with H₂ or oxidation with O₂; the SrTiO₃(La,Cr) samples treated with H₂ contained only Cr³⁺, and the SrTiO₃(La,Cr) samples treated with O₂ contained a mixture of Cr³⁺ and Cr⁶⁺. The time-resolved results indicate that the lifetimes of photogenerated electrons on the microsecond timescale for SrTiO₃(La,Cr) treated with H₂ are much longer than those for SrTiO₃(La,Cr) treated with O₂, suggesting that the photogenerated electrons in the sample containing only Cr³⁺ are more likely to react with surface-adsorbed molecules and are therefore better for H₂ production.

2. Experimental

2.1. Synthesis of materials

SrTiO₃(La,Cr) was prepared by the polymerized complex method [15]. In a typical procedure, titanium tetraisopropoxide (4.0507 g; J&K Chemical; ≥98%) was dissolved in ethylene glycol (33.5 mL; Sinopharm Chemical; ≥99.0%), followed by addition of citric acid (31.521 g; Kermel Chemical; ≥99.5%). The reaction mixture was vigorously stirred at 50 °C until it became transparent. Sr(NO₃)₂ (3.0157 g; Guangfu Chemical; 99.5%) was added to the reaction mixture to synthesize SrTiO₃(La,Cr). Then La(NO₃)₃·6H₂O (0.3248 g; Kermel Chemical; ≥98.5%) and Cr(NO₃)₃·9H₂O (0.3001 g; J&K Chemical; 99%) were added, and the mixture was stirred at 50 °C for 4 h to give complete dissolution. The solution was polyesterified at 130 °C for 20 h, followed by pyrolysis at 350 °C for 2 h. The resulting black solid product was then ground into a powder and calcined on an Al₂O₃ plate at 900 °C for 2 h in air in a temperature-programmed muffle furnace. The obtained dry samples were then reduced with H₂ or oxidized with O₂ at 400 °C for 2 h. The final products are designated as SrTiO₃(La,Cr)-H₂ and SrTiO₃(La,Cr)-O₂, respectively.

2.2. Characterizations of materials

UV-visible (UV-Vis) diffuse reflectance (DR) spectra were recorded using a UV-Vis spectrophotometer (JASCO V-550) equipped with an integrating BaSO₄ sphere. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Escalab 250 equipped with a monochromatic Al K_α X-ray source. Time-resolved (millisecond) Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet 870 FT-IR spec-

trometer equipped with a mercury cadmium telluride detector, using 355 and 532 nm laser pulses of duration 6–8 ns. The decay curves were recorded at room temperature by accumulating 60 traces repeated at 1 Hz.

3. Results and discussion

3.1. Material characterization

Figure 1 shows the UV-Vis DR spectra of SrTiO₃, SrTiO₃(La,Cr)-H₂, and SrTiO₃(La,Cr)-O₂. SrTiO₃ shows absorption bands only in the UV region, with absorption edges at ca. 380 nm. After La and Cr codoping, the absorption edges are extended to the visible region. This suggests that the presence of doped transition-metal ions changes the absorption in the visible-light region for SrTiO₃. It has been reported that La usually replaces the Sr sites and Cr replaces the Ti sites in La- and Cr-codoped titanates [14,18]. As a result of charge compensation, the presence of La largely suppresses the formation of Cr⁶⁺. The visible-light absorptions are mainly caused by bandgap narrowing by the Cr dopant, whose occupied 3d orbital can overlap with the O 2p valence band of SrTiO₃ [9,19].

The oxidation numbers of the doped Cr were characterized by XPS. Figure 2 shows the Cr 2p XPS spectra of SrTiO₃(La,Cr)

Fig. 1. UV-Vis DR spectra of non-doped SrTiO₃ (1), SrTiO₃(La,Cr)-H₂ (2), and SrTiO₃ (3).

Fig. 2. Cr 2p XPS spectra of the samples.

pretreated with either H₂ or O₂. SrTiO₃(La,Cr)-O₂ has a large peak at 576.7 eV, assigned to Cr³⁺, and a shoulder peak at 579.2 eV, assigned to Cr⁶⁺. After H₂ reduction to SrTiO₃(La,Cr)-H₂, only the peak from Cr³⁺ is observed. The disappearance of the shoulder signal suggests that the Cr⁶⁺ ions are all reduced to Cr³⁺ ions on H₂ reduction. The XPS results indicate that the valence state of Cr in the samples could be easily controlled by pretreatment with H₂ or O₂.

Figure 3 shows the Raman spectra of the samples excited with 532 nm laser light. It has been reported that Raman bands are generally observed at around 800 cm⁻¹ for perovskite-structured materials; this is a result of the ordered distribution of metal cations at the B sites, because the bands only appear in complex AB_xB'_{1-x}O₃ perovskites, not in simple ABO₃ perovskites [20]. The presence of a band at 792 cm⁻¹ for SrTiO₃(La,Cr)-H₂ and SrTiO₃(La,Cr)-O₂ indicates that Cr is substituted for Ti⁴⁺ sites in the crystal lattice of the SrTiO₃ host. Moreover, in comparison with the Raman spectra of SrTiO₃-O₂ and SrTiO₃(La,Cr)-H₂, the SrTiO₃(La,Cr)-O₂ sample has an additional vibrational band at 864 cm⁻¹, which is caused by the presence of Cr⁶⁺ ions [21,22].

3.2. Decay kinetics of photogenerated electrons in SrTiO₃(La,Cr)

The decay of photogenerated electrons as a result of recombination and carrier reactions can be traced by monitoring the IR absorption. Figure 4(a) shows the photoinduced decay kinetics of the electrons on SrTiO₃(La,Cr)-H₂ and SrTiO₃(La,Cr)-O₂ irradiated with 355 nm light. Because the catalyst was placed in a vacuum in the absence of an appropriate substrate for adsorption, the electron decay is ascribed to recombination in the bulk rather than photocatalytic reactions at the surface. If the electrons are assumed to consist of two first-order decaying species with lifetimes of τ_1 and τ_2 , the decay curves can be well fitted by the corresponding two-exponential formula:

$$y = A1\exp(-x/\tau_1) + A2\exp(-x/\tau_2)$$

where $A1$ and $A2$ represent the components with lifetimes of τ_1 and τ_2 , respectively. The lifetimes and relative amplitudes from the non-linear least-square fits are listed in Table 1.

The electron-hole recombination kinetics show that the lifetimes of long-lived photogenerated electrons on the microsec-

Fig. 3. Raman spectra of the catalysts. Excitation wavelength: 532 nm.

Fig. 4. FT-IR absorbance as a function of time delay of reduced and oxidized SrTiO₃(La,Cr) samples irradiated with 355 (a) and 532 nm (b) light pulses.

ond timescale for SrTiO₃(La,Cr)-H₂ are much longer than those for SrTiO₃(La,Cr)-O₂. For SrTiO₃(La,Cr)-O₂, $A1 \gg A2$, so electron decay mainly occurs for the fast component ($\tau = 0.57 \mu\text{s}$); this is attributed to the capture of electrons by Cr⁶⁺. The Cr⁶⁺ level in SrTiO₃ is usually below the Ti 3d level and is also lower than the potential level for H₂ evolution, so Cr⁶⁺ can only act as a trapping center for photoinduced electrons and cannot contribute to photocatalytic H₂ production. The electron decay of the slow component ($\tau = 9.17 \mu\text{s}$) is attributed to the recombination of electrons with holes in the valence band [23]. For SrTiO₃(La,Cr)-H₂, $A1$ and $A2$ are almost the same order of magnitude. The fast component ($\tau = 5.69 \mu\text{s}$) is the same as the slow component for SrTiO₃(La,Cr)-O₂. The slow component ($\tau = 114 \mu\text{s}$) is mainly the result of electrons trapped in defects or surface adsorbates [16,23,24]. In general, long-lived electrons are most likely to be responsible for the enhancement of photocatalytic activity [17,25]. Based on the above discussion, it is

Table 1

Lifetimes and relative amplitudes from two-exponential fits of decay curves.

Sample	$A1$	$\tau_1 (\mu\text{s})$	$A2$	$\tau_2 (\mu\text{s})$	$A3$	$\tau_3 (\mu\text{s})$
SrTiO ₃ (La,Cr)-O ₂	5.37	0.57	0.26	9.17	—	—
SrTiO ₃ (La,Cr)-H ₂	—	—	0.59	5.69	0.15	114

reasonable to suggest that compared with Cr^{6+} , Cr^{3+} is more beneficial for charge transfer and separation.

The decay curves observed with 532 nm pulses are presented in Fig. 4(b). It can be seen that the recombination kinetics was insensitive to the pump-light wavelength. With 355 nm irradiation, electrons are excited to the conduction band, with holes created in the valence band. With 532 nm irradiation, electrons are also excited to the conduction band, but the holes are created in the Cr^{3+} -derived occupied states in the bandgap. This is probably because the holes created in the valence band can transfer to the Cr^{3+} -derived states when the sample is excited at 355 nm. It is suggested that the occupied states of Cr^{3+} form a donor band in $\text{SrTiO}_3(\text{La,Cr})$ catalysts and holes migrate to the donor band until they are recombined. Electrons in the conduction band are thought to be more mobile than the holes in the valence and donor bands. The recombination rate is therefore determined by the frequency of holes visiting recombination centers. Similar recombination kinetics has been observed in TiO_2 doped with Cr and Sb [26].

3.3. Mechanism of photoinduced electron decay on $\text{SrTiO}_3(\text{La,Cr})$

Figure 5 shows the mechanism of photoinduced electron decay in $\text{SrTiO}_3(\text{La,Cr})$. As mentioned above, XPS and DRS analyses revealed that the Cr species doped into SrTiO_3 oxidized with O_2 were a mixture of Cr^{3+} and Cr^{6+} ions, and the Cr species doped into SrTiO_3 reduced with H_2 were only Cr^{3+} ions. When the photocatalyst was excited by visible light with a photon energy equal to or higher than the bandgap of $\text{SrTiO}_3(\text{La,Cr})$, the electrons in the valence band could be excited to the conduction band. The majority of the electrons will quickly be trapped by the Cr^{6+} ions, within 0.57 μs , and only a small proportion of the photoinduced electrons will recombine with the valence-band holes. The empty Cr^{6+} potential is lower than that required for H_2 evolution, so H_2 is unable to evolve over SrTiO_3 with Cr^{6+} . In contrast, there are no Cr^{6+} ions in $\text{SrTiO}_3(\text{La,Cr})\text{-H}_2$ and the excited-state conduction-band electrons mainly recombine with valence-band holes, within 5.69 μs . In addition, as a result of doping with foreign elements, some conduction-band electrons can be trapped in shallow

Fig. 5. Kinetics of electrons on $\text{SrTiO}_3(\text{La,Cr})$ pretreated with H_2 or O_2 under visible-light irradiation.

traps below the conduction band, and this might be the reason for the generation of long-lived electrons with lifetimes of 114 μs .

4. Conclusions

$\text{SrTiO}_3(\text{La,Cr})$ containing Cr cations with different valence states was obtained by simple treatment with H_2 or O_2 . Time-resolved IR results suggest that compared with $\text{SrTiO}_3(\text{La,Cr})$ containing Cr^{6+} , a larger amount of long-lived electrons and longer electron lifetimes are obtained with $\text{SrTiO}_3(\text{La,Cr})$ containing Cr^{3+} . This is probably the reason for the higher photocatalytic activity in H_2 production of $\text{SrTiO}_3(\text{La,Cr})$ containing Cr^{3+} under visible-light irradiation.

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Graphical Abstract

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The Cr valence state plays an important role in H_2 production under irradiation in the visible light region. Electrons are quickly trapped by Cr^{6+} ions and cannot contribute to H_2 production.

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时间分辨红外光谱研究Cr价态在La, Cr共掺杂SrTiO₃光催化剂中的作用

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摘要: 使用时间分辨红外光谱研究了经H₂和O₂处理的La和Cr共掺杂SrTiO₃的光生电子动力学. X射线光电子能谱和Raman光谱结果表明, H₂处理后样品中的Cr均是+3价, 而O₂处理后Cr为+3和+6价. 使用355和532 nm激光激发样品所得时间分辨红外光谱表明, 相比在Cr⁶⁺存在时, 光生电子衰减速率在Cr³⁺存在的情况下要慢, 这说明Cr³⁺更有利于抑制光生电子空穴的复合, 从而增加光催化产氢的活性.

关键词: 时间分辨光谱; 铬掺杂; 钛酸锶; 光催化

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