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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 $SrTiO_3$ photocatalysts

Shuai Shen [a,b], Yushuai Jia [a,b], Fengtao Fan [a], Zhaochi Feng [a,#], Can Li [a,*]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, Liaoning, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

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ABSTRACT

The kinetics of photogenerated electrons in $SrTiO_3$(La,Cr) pretreated with either H_2 or O_2 were studied using time-resolved infrared spectroscopy. The X-ray photoelectron and Raman spectra showed that the Cr cations in the sample reduced with H_2 were all in Cr^{3+}, whereas those oxidized with O_2 were in mixed of Cr^{3+} and Cr^{6+}. 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 Cr^{3+} was slower than that with Cr^{6+}, implying that trivalent Cr contributed more to retarding recombination of photoinduced electrons and holes, and enhanced photocatalytic H_2 production activity.

1. Introduction

The development of solar energy has attracted much research effort in recent years. Heterogeneous photocatalytic water splitting to H_2 and O_2 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 TiO_2 [6,7], ZnO [8], and $SrTiO_3$ [6,9,10] have been reported to exhibit photocatalytic activity for H_2 or O_2 production in the visible region. In particular, the effects of doping of Cr ions into $SrTiO_3$ on the photocurrents of semiconductor electrodes and photocatalytic H_2 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 H_2 production from aqueous methanol solutions [6]. Photocatalytic activity experiments have also demonstrated that Cr^{3+}-doped $SrTiO_3$ shows higher photocatalytic activity in H_2 evolution than Cr^{6+}-doped $SrTiO_3$ 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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* Corresponding author. Tel: +86-411-84379070; Fax: +86-411-84694447; E-mail: canli@dicp.ac.cn

Corresponding author. Tel: +86-411-84379303; Fax: +86-411-84694447; E-mail: zcfeng@dicp.ac.cn

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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 $SrTiO_3$.

In this work, the kinetics of photogenerated electrons in Cr-doped $SrTiO_3$ was studied using time-resolved IR spectroscopy. Model doped metal oxide photocatalysts were prepared by simple reduction with H_2 or oxidation with O_2; the $SrTiO_3$(La,Cr) samples treated with H_2 contained only Cr^{3+}, and the $SrTiO_3$(La,Cr) samples treated with O_2 contained a mixture of Cr^{3+} and Cr^{6+}. The time-resolved results indicate that the lifetimes of photogenerated electrons on the microsecond timescale for $SrTiO_3$(La,Cr) treated with H_2 are much longer than those for $SrTiO_3$(La,Cr) treated with O_2, suggesting that the photogenerated electrons in the sample containing only Cr^{3+} are more likely to react with surface-adsorbed molecules and are therefore better for H_2 production.

2. Experimental

2.1. Synthesis of materials

$SrTiO_3$(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. $Sr(NO_3)_2$ (3.0157 g; Guangfu Chemical; 99.5%) was added to the reaction mixture to synthesize $SrTiO_3$(La,Cr). Then $La(NO_3)_3·6H_2O$ (0.3248 g; Kermel Chemical; ≥98.5%) and $Cr(NO_3)_3·9H_2O$ (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 Al_2O_3 plate at 900 °C for 2 h in air in a temperature-programmed muffle furnace. The obtained dry samples were then reduced with H_2 or oxidized with O_2 at 400 °C for 2 h. The final products are designated as $SrTiO_3$(La,Cr)-H_2 and $SrTiO_3$(La,Cr)-O_2, 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 $BaSO_4$ 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 spectrometer 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 $SrTiO_3$, $SrTiO_3$(La,Cr)-H_2, and $SrTiO_3$(La,Cr)-O_2. $SrTiO_3$ 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 $SrTiO_3$. 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 Cr^{6+}. The visible-light absorptions are mainly caused by bandgap narrowing by the Cr dopant, whose occupied 3*d* orbital can overlap with the O 2*p* valence band of $SrTiO_3$ [9,19].

The oxidation numbers of the doped Cr were characterized by XPS. Figure 2 shows the Cr 2*p* XPS spectra of $SrTiO_3$(La,Cr)

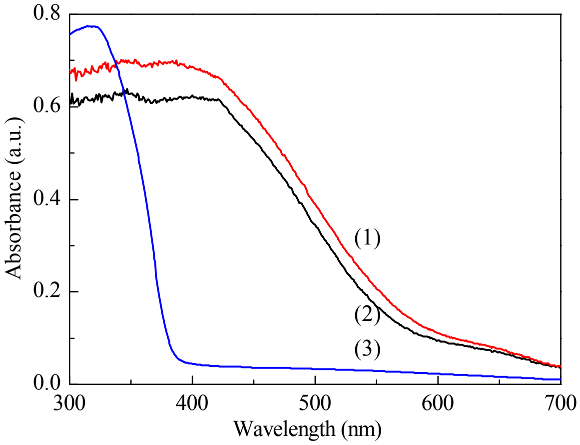

Fig. 1. UV-Vis DR spectra of non-doped $SrTiO_3$(La,Cr)-O_2 (1), $SrTiO_3$(La,Cr)-H_2 (2), and $SrTiO_3$ (3).

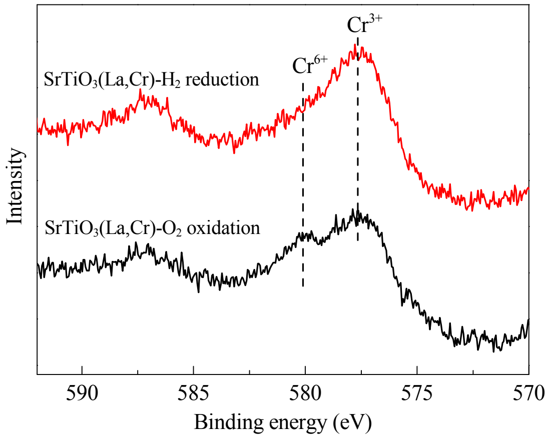

Fig. 2. Cr 2*p* XPS spectra of the samples.