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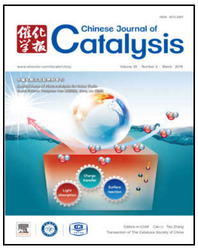

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La and Cr Co-doped $SrTiO_3$ as an H_2 evolution photocatalyst for construction of a Z-scheme overall water splitting system

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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 $SrTiO_3$ photocatalysts ($SrTiO_3$(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 $SrTiO_3$(La,Cr) prepared by the SHM showed efficient photocatalytic activities for both H_2 evolution in the presence of an I^- sacrificial reagent and for Z-scheme overall water splitting when it was coupled with the Pt-loaded WO_3 in the presence of I^- and IO_3^- as the shuttle redox mediator. The superior photocatalytic activity of $SrTiO_3$(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 H_2-evolution photocatalyst with appropriate electronic properties is crucial for achieving Z-scheme overall water splitting.

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 photogenerated 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 $SrTiO_3$ photocatalysts [$SrTiO_3$(La,Cr)] using the polymerized complex method (PCM) and sol-gel hydrothermal method (SHM), denoted $SrTiO_3$(La,Cr)-PCM and $SrTiO_3$(La,Cr)-SHM, respectively. Under visible light irradiation (λ > 420 nm), the Pt-loaded $SrTiO_3$(La,Cr)-SHM sample [Pt/$SrTiO_3$(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/$SrTiO_3$(La,Cr)-SHM as a hydrogen evolution photocatalyst, Pt-loaded WO_3 (PtO_x/WO_3) as an oxygen evolution photocatalyst, and an I^- and IO_3^- couple (I^-/IO_3^-) as the shuttle redox mediator. In comparison, under the same experimental conditions, the Pt-loaded $SrTiO_3$(La,Cr)-PCM sample [Pt/$SrTiO_3$(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 $Cr(NO_3)_3{\cdot}9H_2O$ (99%) were purchased from Beijing J&K Scientific Ltd., China; $Sr(NO_3)_2$ (99.5%) was purchased from Tianjin Guangfu Chemical Co., China; $La(NO_3)_3{\cdot}6H_2O$ (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 WO_3 were purchased from SinoPharm Chemical Reagent Co., Ltd., China. All chemicals were used as received without further purification.

Two types of $SrTiO_3$(La,Cr) samples; namely, $SrTiO_3$(La,Cr)-PCM and $SrTiO_3$(La,Cr)-SHM, were prepared by the PCM [18] and SHM methods as depicted in Fig. S1. Typically, for the synthesis of the $SrTiO_3$(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 $Sr(NO_3)_2$ (3.02 g), $La(NO_3)_3{\cdot}6H_2O$ (0.33 g), and $Cr(NO_3)_3{\cdot}9H_2O$ (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 $SrTiO_3$(La,Cr)-SHM sample was synthesized by following the procedure reported in the literature, except that $Sr(NO_3)_2$ was used as the Sr precursor instead of $Sr(Ac)_2{\cdot}0.5H_2O$ [33]. Typically, titanium tetra-isopropoxide (5.40 g) was dissolved in an ethylene glycol (55 mL) solution, and the metal precursors $Sr(NO_3)_2$ (4.02 g), $La(NO_3)_3{\cdot}6H_2O$ (0.43 g), and $Cr(NO_3)_3{\cdot}9H_2O$ (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 $SrTiO_3$(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 H_2PtCl_6. 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