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Ruddlesden-Popper compound Sr_2TiO_4 co-doped with La and Fe for efficient photocatalytic hydrogen production

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ABSTRACT

Doping techniques generally serve as effective means for tailoring the physicochemical properties of a target compound. In this work, we successfully co-doped La/Fe into Ruddlesden-Popper (RP) compound Sr_2TiO_4 and performed a detailed investigation on the crystal structure, morphology, optical absorption and photocatalytic hydrogen production reactions after doping. Our findings suggest that La/Fe co-doping slightly expand the unit cell of Sr_2TiO_4 while maintains the structure lamination. Incorporating La/Fe into Sr_2TiO_4 efficiently reduces the band gap and the level of band gap reduction can be controlled by varying the amounts of dopants. La/Fe co-doping significantly improves the photocatalytic properties of Sr_2TiO_4 under both full range ($\lambda \geq 250$ nm) and visible light illumination ($\lambda \geq 420$ nm). A fivefold enhancement in hydrogen production rate (~106.2 μmol/h) is seen in sample $Sr_{1.9}La_{0.1}Ti_{0.9}Fe_{0.1}O_4$ (x = 0.1). Efficient photocatalytic hydrogen production under visible light illumination ($\lambda \geq 420$ nm) is also achieved in sample $Sr_{1.7}La_{0.3}Ti_{0.7}Fe_{0.3}O_4$ (x = 0.3) with AQE as high as ~1.18% at 420 nm. DFT calculations confirm the critical role of Fe in reducing the band gap of Sr_2TiO_4 by forming additional spin-polarized bands (SPB). The anisotropic charge transportation in Sr_2TiO_4 is also verified by our calculations as both conduction band minimum (CBM) and valence band maximum (VBM) are buried in TiO_6 octahedron layers. The 2D charge transportation properties are particularly useful for photocatalytic reactions since interlayer charge recombination is essentially prevented.

1. Introduction

Storing solar energy into chemical fuels such as hydrogen through photocatalytic water splitting reactions has been recognized as a promising prospect to construct a clean and sustainable energy infrastructure [1–12], particularly under the contexts that we are jeopardized by severe fossil fuel shortage and formidable environmental degradations [13–15]. However, most semiconductor photocatalysts demonstrate a solar to hydrogen (STH) efficiency too low to warrant commercial utilizations, being the major obstacle for practical deployment of this intriguing technique [16,17]. This is either because of their low light absorption capability (e.g. wide band gap semiconductors) or due to their poor utilization of photo-generated charges (e.g. rapid charge recombination) [18–20]. In light of these shortcomings, great efforts have been devoted to modifying or improving conventional semiconductor in terms of light absorption and charge utilizations. Among various strategies adopted for this purpose, doping generally serves as one of the most facile and efficient means to tailor the optical properties of a semiconductor [5,21]. For instance, by introducing Cr [22–25], Ni [26], Fe [27], Mn [28,29], Rh [30] etc. into the crystal structure of $SrTiO_3$, substantial visible light absorption and photocatalytic activity can be achieved. For different types of dopants, Cr and Rh often stand out as the most effective ones for improving the photocatalytic performance [31,32]. Nevertheless, the toxicity of Cr to the environment and the scarcity of Rh on earth essentially hamper their wide application. Thereby, developing alternative dopants that are environmental benign and earth-abundant is one of the premier targets for doping strategy. However, previous studies have witnessed some negative effects on doping where degraded photocatalytic activity is often seen [33,34]. This is reasonable as dopants *per se* are defects which may trap photo-generated charges and serve as charge recombination centers. In this regard, how to balance the side effects of dopants so as to optimize the outcomes of doping is still worth investigation. It has been realized that semiconductors with layered crystal structures often exhibit superior performance for

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photocatalytic water splitting, probably correlated with their peculiar layered crystal structures that facilitate charge separations [35–38]. It would be quite interesting to investigate how doping strategy is applied to layered semiconductors. In this work, we perform an investigation on layered Ruddlesden-Popper (RP) compound Sr_2TiO_4 co-doped with La and Fe for photocatalytic hydrogen production. Sr_2TiO_4 has the highest level of structure lamination among all RP series $Sr_{n+1}Ti_nO_{3n+1}$ ($1 \leq n \leq \infty$) and has typical 2D charge transportation properties [39,40]. It would be of great interest to incorporate dopants into its layered framework, particularly earth-abundant and environmental friendly Fe species.

2. Experimental

2.1. Materials preparation

All samples with nominal chemical formula $Sr_{2-x}La_xTi_{1-x}Fe_xO_4$ ($0 \leq x \leq 1$) were prepared by a standard polymerized complex method. Specifically, proper amounts of tetrabutyl titanate (Aladdin, 99%), anhydrous citric acid (Aladdin, 99.5%), strontium nitrate (SCR, 99.5%), lanthanum nitrate (Aladdin, 99%), iron (III) nitrate nonahydrate (SCR, 98.5%) were dissolved into ethylene glycol (Aladdin, GC grade) with the aid of small amounts of deionized water to reach a transparent solution. The solution was then heated at 423 K under magnetic stirring to promote polymerization reactions between citric acid and ethylene glycol. As the reactions proceeded, the solution became more and more viscous and a brown resin-like gel was formed. The gel was then transferred into alumina crucibles and calcined at 823 K for 15 h to remove residual solvents and burn out organic species. The resultant powders was ground, pelletized and calcined at 1373 K for 10 h to promote phase formation. The calcined pellets were ground into powders and collected for further analysis.

2.2. Materials characterization

We examined phase purity and crystal structure by using X-ray powder diffraction (XRD) techniques (Bruker D8 Focus diffractometer). Incident radiation used were Cu $K_{\alpha1}$ ($\lambda = 1.5406$ Å) and Cu $K_{\alpha2}$ ($\lambda = 1.5444$ Å). The step size for data collection was 0.01° with a collection time of 10 s for each step. The General Structure Analysis System (GSAS) software package was applied to perform Rietveld refinement on the data collected [41]. Microstructures of prepared samples were analyzed by a field emission scanning electron microscope (HitachiS4800) and transmission electron microscope (JEOL JEM-2100). Chemical compositions and binding energy of individual elements were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250 with a monochromatic Al K_α X-ray source). All binding energies were referenced to the C 1s peak at 284.7 eV from adventitious carbon [42]. Optical absorption spectra were collected and analyzed using a UV – vis spectrophotometer (JASCO-V750) and the JASCO software suite, and the reference non-absorbing material is $BaSO_4$ [43]. Surface areas of freshly prepared samples were evaluated by using a Micromeritics instrument Tristar 3000 and were calculated based on the Brunauer-Emmett-Teller (BET) model.

2.3. Photocatalytic hydrogen production

Photocatalytic activity of freshly samples was evaluated in a top-irradiation-type reactor connected to a gas-closed circulation and evacuation system (Perfect Light, Labsolar-IIIAG). In a typical experiment, 100 mg sample powders was ultrasonically dispersed into 100 mL Na_2SO_3 aqueous solution (0.05 M). The reactor was then evacuated to remove air dissolved in the solution. Appropriate amounts of Pt were loaded onto sample powders as a co-catalyst to promote photocatalytic reactions: proper amounts of H_2PtCl_6 aqueous solution were impregnated into sample powders to form slurry. The slurry was heated on a hot plate at 90 °C until dry and then calcined at 250 °C for 2 h to fully decompose H_2PtCl_6 into Pt nanoparticles. A 500 W high-pressure mercury lamp (NBeT, Merc-500) was used as a light source. Visible light was generated by filtering the output of the lamp using a UV cutoff filter ($\lambda \geq$ 420 nm). Monochromic light irradiation was produced by filtering the output of the lamp with corresponding bandpass filters. The photon flux of the lamp is calibrated using a quantum meter (Apogee MP-300). A water jacket was used to stabilize the reactor temperature around 20 °C. An on-line gas chromatograph (TECHCOMP, GC7900) with a TCD detector (5 Å molecular sieve columns and Ar carrier) was used to analyze the gas component within the reactor. The apparent quantum efficiency is then calculated using the following equation:

$$\begin{aligned}\text{Apparent quantum efficiency} &= 2 \\ &\times \text{moles of hydrogen production per hour} \\ &/\text{moles of photon flux per hour} \times 100\%\end{aligned}$$

2.4. Theoretical calculations

Electronic structures of La/Fe co-doped Sr_2TiO_4 were probed by theoretical calculations using the density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) [44]. We applied the Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) [45] and the projector augmented-wave pseudopotential for the calculations [46]. A $2 \times 2 \times 1$ super cell ($a = b = 7.8$ Å, $c = 12.6$ Å, $\alpha = \beta = \gamma = 90°$) was built for simulations of La/Fe co-doped Sr_2TiO_4. La/Fe co-doping was considered by substituting 1 Sr and 1 Ti with 1 La and 1 Fe randomly. Pristine Sr_2TiO_4 was also calculated by constructing a tetragonal unit cell ($a = b =$ 3.9 Å, $c = 12.6$ Å, $\alpha = \beta = \gamma = 90°$). All geometry structures were fully relaxed until the forces on each atom are less than 0.01 eV·Å^{-1}. Static calculations were carried out using $7 \times 7 \times 5$ and $12 \times 12 \times 5$ Monkhorst-Pack k-point grid for La/Fe co-doped Sr_2TiO_4 and pristine Sr_2TiO_4, respectively [47].

3. Results and discussions

3.1. Phase analysis and crystal structure

X-ray powder diffraction (XRD) patterns of samples $Sr_{2-x}La_xTi_{1-x}Fe_xO_4$ ($0 \leq x \leq 1$) are displayed in Fig. 1. All samples demonstrate similar diffraction patterns that can be indexed by a tetragonal symmetry, indicative of single phase formation. However, for individual sample, there is a clear trend for the main peak to shift towards low angles along with La/Fe incorporation, implying that unit cell of Sr_2TiO_4 is gradually expanded upon doping. This is consistent with Vegard's law as Fe^{3+} cation is slightly larger than Ti^{4+} cation in octahedral coordination ($r_{Fe3+} = 0.645$ Å, $r_{Ti4+} = 0.605$ Å) [48,49]. Super-lattice peaks due to cation ordering is not detected, indicating that substitution of Sr/Ti with La/Fe is probably random. We then performed Rietveld refinement on all XRD data using a tetragonal lattice (space group *I 4/mmm*) and placed constraints that Sr/La and Ti/Fe cations were accommodated in the same crystallographic position with equal isotropic temperature factor, respectively. Reasonable goodness-of-fit parameters were all achieved, confirming the accuracy of the structure model. The refined structural information is listed in Table 1. A typical refined XRD patterns of sample $Sr_{1.9}La_{0.1}Ti_{0.9}Fe_{0.1}O_4$ ($x = 0.1$) is illustrated in Fig. 2 with good *R* and χ^2 factor