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Hollow $CaTiO_3$ cubes modified by La/Cr co-doping for efficient photocatalytic hydrogen production

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ABSTRACT

In this work, we have applied microstructure management and doping techniques to conventional wide band gap semiconductor $CaTiO_3$ with the aim to improve its light absorption and photocatalytic activity. A series of La/Cr co-doping hollow $CaTiO_3$ cubes have been successfully prepared by a template-free hydrothermal method. Their crystal structures, microstructures, optical absorption and photocatalytic hydrogen production have been systematically investigated. Our results suggest that hollow $CaTiO_3$ owns a higher light absorption than solid one and demonstrates a much better photocatalytic activity both under full range ($\lambda \geq 250$ nm) and visible light illumination ($\lambda \geq 400$ nm). These improvements probably originate from the peculiar hollow microstructures that increase photon-matter interactions and shorten the charge migration pathways. The photocatalytic activity for hydrogen production has been further studied by varying the La/Cr content in $CaTiO_3$. An optimal doping point at 5% La/Cr doping level has been reached for full range illumination with apparent quantum efficiency approaching ~2.41%. Nevertheless, the activity under visible light illumination shows a clear dependence on doping level with highest apparent quantum efficiency ~0.40% at 20% La/Cr doping level. DFT calculations reveal the critical role of Cr in forming a new spin-polarized valence band inside the original band gap of $CaTiO_3$ therefore is responsible for band gap reduction and visible light photocatalysis. This work here highlights the importance of microstructure control to the photocatalytic performance and shall shed a light on the design and development of efficient photocatalytic materials/systems.

1. Introduction

How to fulfil the ever-growing energy demand of our modern society is one of the premier targets for this century since current fossil-fuel based economy is not sustainable in essence, let alone various environmental issues associated with fossil fuel usage. There is now a worldwide agreement on searching/developing clean and renewable energy resources that can ultimately relieve us from fossil fuel reliance. In this regard, photocatalytic water splitting into hydrogen and oxygen, with the aid of solar energy, has been considered as a promising means to set up a sustainable energy infrastructure, not only because hydrogen is a clean energy vector but also because solar insolation is inexhaustible and is easily accessible worldwide [1–8]. Ever since the report of photo-electrochemical water splitting on titanium dioxide (TiO_2) in 1972 [9], great efforts have been devoted to the design and the development of new photocatalytic materials or systems yet very few compounds demonstrate photocatalytic activity high enough to warrant commercial interest. In general, the catalytic activity of a semiconductor photocatalyst is a function of various parameters, such as crystallinity, defects, microstructures etc. Control of these parameters has been an effective way to tailor the photocatalytic activity of a particular semiconductor compound. For example, tetrahedral shaped Ag_3PO_4 submicro-crystals exhibit higher photocatalytic activities than normal Ag_3PO_4 particles for the degradation of organic contaminants under visible light irradiation [10]. Several approaches have been developed to fabricate architectures assembled with peculiar nanostructures by the assistance of templates and/or surfactants [11–13]. To avoid the complicated operations using templates, template-free methods with a few steps are highly welcome [14–16]. Along with microstructure management, a number of strategies such as dye sensitizing [17], nitridizing/sulfurizing [18–23], doping with foreign elements [24–26] etc., have been developed to extend the light absorption of wide band gap semiconductors. Among these strategies, doping with foreign atoms has been adopted as the most simple and effective method to enhance the light sensitivity of a semiconductor. This normally involves the formation of additional bands/energy levels within

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the intrinsic band gaps of these compounds, which could significantly reduce the threshold of photon absorption [26]. It is known that metal oxides with perovskite-type structure (ABO_3) often show promising catalytic activity and their structures are extremely flexible and tolerant to cationic and anionic replacements. Applying doping strategies to these perovskites have witnessed a number of successes in improving the photocatalytic activities. For instance, recent reports have showed that Cr seems to be the most simple and cost-effective dopant for $SrTiO_3$ in extending its superior photocatalytic activities into visible light region [27,28].

In this work, we applied both microstructure control and doping strategies to perovskite compound $CaTiO_3$. We successfully synthesized hollow $CaTiO_3$ cubes modified by La/Cr co-doping via a facile template-free hydrothermal method. Their peculiar microstructures are found to be beneficial for light absorption due to enhanced reflection steps, which in turn contributes to a higher photocatalytic performance with respect to normal $CaTiO_3$. The photocatalytic activity of these hollow $CaTiO_3$ cubes was further optimized by adjusting the La/Cr co-doping levels. The microstructure manipulation combined with doping techniques in this study highlights an effective means to boost photocatalytic activity of conventional wide band gap semiconductors.

2. Experimental

2.1. Synthesis

La/Cr co-doped $CaTiO_3$ hollow cubes were synthesized according to previous reports with some modifications [16]. In a typical synthesis of $Ca_{0.80}La_{0.20}Ti_{0.80}Cr_{0.20}O_3$, 0.5725 g $Ca(NO_3)_2{\cdot}4H_2O$ (Aladdin, 99.0%), 0.2624 g $La(NO_3)_3{\cdot}6H_2O$ (Aladdin, 99.0%), 0.2425 g $Cr(NO_3)_3{\cdot}9H_2O$ (Aladdin, 99.0%) were dissolved in 3 ml deionized water according to the stoichiometric ratios. 57 ml polyethylene glycol-200 (PEG-200) was then added to above solution with sonication to promote dissolution. Subsequently, 0.792 ml titanium *n*-butoxide (Aladdin, 99.0%, TNB) were added dropwisely to the solution under magnetic stirring. All cations in the solution were then precipitated by adding 66 mmol sodium hydroxide (Aladdin, 96.0%) under magnetic stirring. The precipitates were transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 15 h. The resulting powders were separated by centrifuging and washed with ethanol (twice), diluted acetic acid (10 vol%, twice), and distilled water until pH reached 7 and dried in an oven at 80 °C for 12 h. The La/Cr co-doping levels were simply controlled by adjusting initial $La(NO_3)_3{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ content. These samples were labeled as Hollow. Normal La/Cr co-doped $CaTiO_3$ was also synthesized for comparison purpose: appropriate amounts of $Ca(NO_3)_2{\cdot}4H_2O$ (Aladdin, 99%), $La(NO_3)_3{\cdot}6H_2O$ (Aladdin, 99.0%), $Cr(NO_3)_3{\cdot}9H_2O$ (Aladdin, 99.0%) were dissolved in 15 ml deionized water to form a transparent solution. Proper amounts of titanium isopropanol (Aladdin, 95%, TIP) ethanol solution were then added slowly to above solution according to stoichiometric ratio. All cations in the solution were precipitated by adding 10 ml 10 M NaOH solution to form slurry. The slurry was transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 15 h. The powders formed were then washed with deionized water until pH reaches 7 and were dried in an oven at 80 °C for 12 h. These samples were labeled as Normal.

2.2. Methods for analysis

Crystal structure and phase composition were examined by using X-ray powder diffraction (XRD) techniques (Bruker D8 Focus diffractometer). The incident radiations were Cu $K_{\alpha 1}$ ($\lambda = 1.5406$ Å) and Cu $K_{\alpha 2}$ ($\lambda = 1.5444$ Å), respectively. The step size for data collection was 0.01° with a collection time of 0.1s at each step. The General Structure Analysis System (GSAS) software package was applied to perform Rietveld refinement on the data collected [29]. Microstructures compositions of all samples were examined using a field emission scanning electron microscope (Hitachi S4800) equipped with a Mica energy dispersive X-ray spectroscopy (EDS) analysis system and a transmission electron microscope (JEOL JEM-2100). Surface conditions and binding energy of constitutional elements were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250 with a monochromatic Al Kα X-ray source). All binding energies were referenced to the adventitious carbon C 1s peak at 284.7 eV [30]. Diffuse reflectance spectra were collected and analyzed on a UV–vis spectrophotometer (JASCO-V750) combined with the JASCO software suite. The reference non-absorbing material is $BaSO_4$ [31]. Specific surface areas were analysed using a Micromeritics instrument TriStar 3000 and were calculated via the Brunauer-Emmett-Teller (BET) model.

2.3. Photocatalytic hydrogen production

Photocatalytic activity of all specimens was performed in a top-irradiation-type reactor connected to a gas-closed circulation and evacuation system (Perfect Light, Labsolar-IIIAG). The typical gas pressure inside the reactor is 100 Pa. In a typical experiment, 100 mg sample powders were distributed in 100 ml aqueous solution, which was then transferred into the reactor and subjected to evacuation to remove air dissolved. Na_2SO_3 (0.05 M) was used as the sacrificial agent while Pt (1 wt%) was loaded as a co-catalyst to enhance the activity of photoreduction [32,33]. Pt was loaded onto the sample powders by a thermal deposition method [34–36]: appropriated amounts of H_2PtCl_6 aqueous solution was impregnated into sample powders which were then heated on a hot plate at 90 °C until dry. Thereafter, the temperature was raised to 180 °C for 2 h to fully convert H_2PtCl_6 into Pt nanoparticles. The solution is irradiated by using a 500 W high-pressure mercury lamp (NBeT, Merc-500) as the light source. The visible light illumination was produced by filtering the output of the lamp with a UV cut-off filter ($\lambda \geq 400$ nm). The photon flux of the lamp is gauged using a quantum meter (Apogee MP-300). A typical emission spectrum of the mercury lamp used in this work is shown in Fig. S1. The recorded photon flux is ~1543.9 $\mu mol\ m^{-2}\ s^{-1}$ for full range irradiation ($\lambda \geq 250$ nm) and ~796.5 $\mu mol\ m^{-2}\ s^{-1}$ for visible light irradiation ($\lambda \geq 400$ nm). Monochromic light irradiation was produced by filtering the output of the lamp with corresponding bandpass filters. The gas component within the reactor was then analyzed using an on-lined gas chromatograph (TECHCOMP, GC7900) with a thermal conductivity detector (5 Å molecular sieve columns and Ar carrier). The apparent quantum efficiency is then calculated using following equation:

Apparent quantum efficiency = 2 × mol of hydrogen production per hour/moles of photon flux per hour × 100%

2.4. Theoretical calculation

Theoretical calculations were performed using the density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) [37]. The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) [38] and the projector augmented-wave pseudopotential were applied [39]. Spin-polarization was also considered during calculation. An orthorhombic unit cell ($a = 5.38$ Å, $b = 5.44$ Å, $c = 7.639$ Å, $\alpha = \beta = \gamma = 90°$) was constructed for simulation. La/Cr co-doping was considered by assuming that 1 Ca atom and 1 Ti atom were replaced by 1 La atom and 1 Cr atom, respectively. There are 20 atoms in the unit cell (1 La, 3Ca, 1 Cr, 3 Ti and 12 O) and the doping level is 25%. All geometry structures were fully relaxed until the forces on each atom are less than 0.01 eV $Å^{-1}$. Static calculations were done with a 9 × 9 × 7 Monkhorst-Pack k-point grid.