

A Novel $\text{Sr}_2\text{CuInO}_3\text{S}$ p-type semiconductor photocatalyst for hydrogen production under visible light irradiation

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Abstract

A novel $\text{Sr}_2\text{CuInO}_3\text{S}$ oxysulfide p-type semiconductor photocatalyst has been prepared by solid state reaction method and it exhibits intriguing visible light absorption properties with a bandgap of 2.3 eV. The p-type semiconductor character of the synthesized $\text{Sr}_2\text{CuInO}_3\text{S}$ was confirmed by Hall efficient measurement and Mott-Schottky plot analysis. First-principles density functional theory calculations (DFT) and electrochemical measurements were performed to elucidate the electronic structure and the energy band locations. It was found that the as-synthesized $\text{Sr}_2\text{CuInO}_3\text{S}$ photocatalyst has appreciate conduction and valence band positions for hydrogen and oxygen evolution, respectively. Photocatalytic hydrogen production experiments under a visible light irradiation ($\lambda > 420$ nm) were carried out by loading different metal and metal-like cocatalysts on $\text{Sr}_2\text{CuInO}_3\text{S}$ and Rh was found to be the best one among the tested ones.

Key words

hydrogen production; photocatalyst; p-type semiconductor; $\text{Sr}_2\text{CuInO}_3\text{S}$ oxysulfide; visible light; cocatalyst

1. Introduction

Photocatalytic water splitting has been extensively explored in recent years because it is considered as a viable and sustainable means to produce hydrogen, a clean energy carrier [1,2]. Energetically uphill and four electron transfer processes of water splitting make it to be an extremely difficult reaction to achieve [3–5]. However, the development of semiconductor-based photocatalysts has been proved that it is the most promising approach for water splitting. Up to date, the majority of the photocatalysts explored for water splitting, including water oxidation and reduction photocatalysts in the presence of sacrificial reagents, are n-type semiconductors [1]. It is not only that the n-type semiconductors are more readily available while p-types are much relatively rare in nature, but also that most of the known p-type semiconductors have some fatal problems, such as none-active for water splitting (e.g., Co_2O_3 and Co_3O_4 , NiO and Ni_2O_3), insufficient bandgaps or band levels to split water [6–8], or too large overpotential for water oxidation (Cu_2O and CaFe_2O_4)

[9,10].

One of the key issues related to the photocatalysis is efficient charge separation. Junction approach for build-up of internal field or potential difference at the interfaces of different semiconductor is a useful strategy to achieve efficient charge separation [11–14]. We have reported that the formation of surface phase junction [15,16] and/or heterojunction [17] can lead to efficient charge separation and hence, promote the photocatalytic activities. But the driving forces built up by these junctions are usually relatively small. For example, the potential difference of n-n surface phase junction of anatase/rutile is only ca. 0.2 eV [18]. In order to further improve charge separation for promoting photocatalytic activity, more efficient junctions with much stronger driving forces are certainly needed. To this end, p-n junction may provide much large drive force and may be an attractive approach for the development of water splitting photocatalysts [19–21]. Obviously, exploration of novel p-type semiconductors with enough bandgaps and proper band-levels for water splitting is in highly demand. Recently, sulfides [22,23] and oxysulfides [24] have been reported to be promising candidates for visible

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light driven photocatalysts. Especially, the p-type semiconductors of $\text{La}_5\text{Ti}_2\text{MS}_5\text{O}_7$ ($M = \text{Ag}, \text{Cu}$) have been reported to be efficient photocatalysts for water oxidation and proton reduction half reactions [25,26].

Herein, we have synthesized a layered $\text{Sr}_2\text{CuInO}_3\text{S}$ oxy-sulfide semiconductor by solid-state reaction method. Band structure analyses show that it is a visible light responsive p-type semiconductor with an intrinsic bandgap of 2.3 eV. Importantly, this p-type semiconductor also has suitable conduction band and reduction band levels for water splitting. Our photocatalytic study demonstrates that $\text{Sr}_2\text{CuInO}_3\text{S}$, once in combination with nanoparticles of noble metal or metal sulfide as cocatalyst, is an effective hydrogen evolution catalyst. Moreover, it might be available for the assembly of p-n junction photocatalysts by combining with other n-type semiconductors.

2. Experimental

2.1. Synthesis of materials

$\text{Sr}_2\text{CuInO}_3\text{S}$ was prepared by solid-state reaction method [27]. The starting materials, SrS, SrO, Cu_2O and In_2O_3 were stoichiometrically (the corresponding molar ratio of SrS : SrO : Cu_2O : In_2O_3 was 2 : 2 : 1 : 1) mixed in a mortar and placed on a quartz basket. The mixture was sintered at 1073–1223 K for 10 h under Ar atmosphere. After cooling down to room temperature, the samples were kept in vials and stored in a desiccator. Modification of $\text{Sr}_2\text{CuInO}_3\text{S}$ with nanoparticulate metal cocatalysts (Pt, NiS, Pd, Rh, RuS_2) was accomplished by in-situ photodeposition method in the presence of the sacrificial electron donors (0.01 mol/L Na_2S and 0.01 mol/L Na_2SO_3). The precursors for Pt, NiS, PdS, Rh and RuS_2 are $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{PdCl}_4$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, respectively.

2.2. Characterizations of materials

The crystallinity of the synthesized samples was studied by X-ray diffraction (XRD) technique on a Rigaku D/Max-2500/PC powder diffractometer. The measurements were performed using $\text{Cu } K_\alpha$ as the radiation source with operating voltage of 40 kV and current of 200 mA. The scanning rate was kept at 5 °/min with a step size of 0.02° in the 2θ range of 10°–80°. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a UV-Vis spectrophotometer (JASCO V-550) equipped with an integrating BaSO_4 sphere. The morphologies of the samples were examined by scanning electron microscopy (SEM) images taken with a Quanta 200FEG scanning electron microscope. The Brunauer-Emmett-Teller (BET) surface areas of the samples were calculated based on the nitrogen adsorption isotherms at 77 K performed on a Micromeritics ASAP 2000 adsorption analyzer. X-ray photoelectron spectroscopy (XPS) were recorded on a Thermo Escalab 250 equipped with a monochromatic Al K_α X-ray source. Hall coefficient was measured using a 4-point probe on a Hall effect measurement system (HL5550 LN2) under a

magnetic field of 0.51 T at room temperature.

2.3. Photocatalytic reactions

The photocatalytic H_2 production reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Photocatalyst (0.2 g) was suspended in 200 mL of aqueous solution containing 0.01 mol/L Na_2S and 0.01 M Na_2SO_3 as the sacrificial reagents and thoroughly degassed by evacuation. The photocatalytic reaction was performed by photoirradiation of the reaction mixture using a 300 W Xe lamp (Ushio-CERMAX LX300) equipped with an optical cutoff filter (Kenko, L-42; $\lambda > 420$ nm) and a water filter to prevent passing of the ultraviolet and infrared light, respectively. The temperature of the reaction mixture was maintained at 288 ± 1 K by a continuous flow of cooling water. The amounts of the evolved H_2 were determined by an on line gas chromatography (Shimadzu; GC-8A, MS-5A column, TCD, Ar Carrier).

2.4. Electrochemical measurements

The flat-band potential of $\text{Sr}_2\text{CuInO}_3\text{S}$ was determined by extrapolation of the Mott-Schottky plots measured on a standard three-electrode cell electrochemical workstation (CHI660A, Shanghai Chenhua Instruments, China). In this system, a Pt plate was used as counter electrode, a saturated calomel electrode (SCE) were employed as reference electrode, and the thin films of the photocatalyst samples fabricated by electrophoretic deposition method were used as the working electrode. The electrolyte was 0.5 mol/L Na_2SO_4 solution.

2.5. Band structure calculations

All the DFT calculations have been performed by the CASTEP codes. The Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) was adopted for the exchange correlation. The norm-converging pseudopotentials were adopted with the energy cutoff of 800 eV for basis function. We used $6 \times 6 \times 2$ k-points sampling for $\text{Sr}_2\text{CuInO}_3\text{S}$ bulk. The iterative process was considered to be convergence, as soon as the energy change, the maximum force and the atomic displacement were less than 1×10^{-6} eV, 0.03 eV/Å, and 0.001 Å, respectively. The calculated lattice parameters for a conventional cell are $a = b = 3.9122$ Å, $c = 15.8476$ Å, $\alpha = \beta = \gamma = 90^\circ$, which are in good agreement with the experiment data.

3. Results and discussion

The as-synthesized $\text{Sr}_2\text{CuInO}_3\text{S}$ is isostructural to a series of oxysulfides $\text{Sr}_2\text{CuMO}_3\text{S}$ ($M = \text{Cr}, \text{Fe}$ and Ga) with the tetragonal space group P4/nmm [28,29]. As illustrated in Figure 1, it features a layer structure constructed by Cu-S layers, In-O layers and Sr^{2+} cation along the c -axis. The Cu^+ cation

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