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Polymerizable complex synthesis of $SrTiO_3$:(Cr/Ta) photocatalysts to improve photocatalytic water splitting activity under visible light

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ABSTRACT

Cr/Ta co-doped $SrTiO_3$ (STO:Cr/Ta) photocatalysts with high photocatalytic activity for water splitting under visible light have been synthesized by a polymerizable complex (PC) method. UV–vis diffuse reflectance spectra (DRS) showed that the Cr/Ta co-doping extended the absorption edge of STO to visible light region at the wavelength of 540 nm. Calculations based on density functional theory (DFT) indicated that, after doping, Cr 3d and O 2p orbits formed new impurity states within the forbidden gap of STO and facilitated the excitation of photons with low energy, as the Ta was mainly used to restrain the appearance of undesired Cr^{6+}. The photoelectrochemical measurements and XRD, SEM, BET analysis revealed that the excellent photocatalytic performance of photocatalyst prepared by a PC method was attributed to the high crystalline quality as well as relative large specific surface area. The photocatalytic activity of STO: (1% Cr/Ta) for H_2 evolution prepared by a PC method is 10 times higher than that of the sample prepared by a solid state reaction (SSR) method. The Pt/STO: (2% Cr/Ta) calcined at 1100 °C possessed the highest photocatalyitc activity for water splitting under visible light, thereby producing the average rate of H_2 evolution of 122.6 μmol h^{-1} (ca. 2.6% AYQ) measured at $\lambda = 420$ nm. Also, under a Z-scheme system, the Pt/STO: (2% Cr/Ta) exhibited AQY as high as 1.52% at $\lambda = 420$ nm for overall water splitting while Pt/WO_3 acting as an O_2 evolution photocatalyst.

1. Introduction

Photocatalytic water splitting has been considered as a promising method to generate clean energy H_2 directly from solar energy since the discovery of the Honda-Fujishima effect [1–3]. So far, although a large number of photocatalysts such as TiO_2 [4–6], $NaTaO_3$ [7–9], Ge_3N_4 [10], $K_2La_2Ti_3O_{10}$ [11], CdS [12–14], C_3N_4 [15–18] etc. have been explored for water splitting, most of them only response UV light ($\lambda < 420$ nm, 4% in the full solar energy) due to too wide energy gaps of semicondutors ($E_g > 3.0$ eV), which seriously restricts the efficiency of hydrogen production [19]. Therefore, the development of visible-light-driven photocatalysts is also a key task in this research field.

Generally speaking, metal oxide photocatalysts with large bandgap fail to absorb visible light due to deep energy level of O 2p orbits which mainly constitute valence band (VB) of photocatalysts. To obtain visible-light-driven photocatalysts, two strategies are used in the preparation of photocatalyic materials. First, S, N elements with stronger electron negativity than O are introduced into the formation of VB thus allowing narrower band gaps (e.g. TaON [20,21], Ta_3N_5 [22], GaN:ZnO [23]). Besides, metal ions doping also are used to extend the absorption spectra into the visible region, because the dopants assume mediators to decrease the band gaps of photocatalysts [24–26]. Nevertheless, considering the shortcoming of stability of (oxy)nitrides and (oxy)sulfides in photocatalytic reactions, metal ion doping is a very important method to develop the visible-light-driven photocatalysts.

$SrTiO_3$(STO) have been verified as one of the few promising materials that can split pure water into H_2 and O_2 [27]. However, STO can only respond to UV light due to its too large band gap (ca. 3.1 eV) [28,29]. It was reported doping Mn, Cr, Rh, Ir in STO extended the absorption spectra to 500–600 nm by forming impurity energy level near VB of STO [30,31]. Sayama et al. [32] first reported that Cr, Ta co-doping in STO could split water to either H_2 in the presence of methanol as a sacrificial reagent or stoichiometric H_2 and O_2 under a Z-scheme system under visible light, indicating

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STO: (Cr/Ta) as a good candidate for photocatalytic water splitting under visible light. The STO: (Cr/Ta) exhibits robust stability, its photocatalytic activity is nonetheless relative low. Presumably, the low activity is ascribed to the lack of enough active sites related to the low specific surface area of photocatalysts after treatment under high temperature. It is well known that, both the specific surface area (corresponding to active sites) and crystalline quality (corresponding to the density of surface defect) of photocatalytic materials are two important factors to influence the photocatalytic activity [33]. The cooperation of large specific surface area and high crystalline quality facilitates the occurrence of photocatalytic reaction. Unfortunately, as the general method for the preparation of photocatalysts, conventional solid sate reaction (SSR) usually need high reaction temperature with long duration thus causing low surface area and the low photocatalytic activity. Recently, sol-gel hydrothermal [34–36], spray pyrolysis [37] and hydrothermal methods [38] have applied to respectively synthesize STO: Cr, STO: (Cr/Ta) and STO: (Sb/Rh) to enhance the photocatalytic activity by increasing the specific surface area of photocatalysts or inhibiting the formation of recombination centre of photogenerated electrons and holes, indicating the enhance of photocatalytic activity of STO: (Cr/Ta) by controlling its particle morphology and crystalline intensity.

Herein, we prepared co-doping visible-light-driven photocatalysts STO: (Cr/Ta) with relative large specific surface area and high crystalline quality by a PC method. The optimum reaction temperature and doping amounts were studied. The roles of doping ions in increasing the absorption of light and enhancing the photocatalytic activity were also investigated in light of density functional theory (DFT). Moreover, the photocatalytic performance of photocatalysts for overall water splitting was examined under a Z scheme system exposed to visible light.

2. Experimental

2.1. Material synthesis

The Cr/Ta co-doping STO was prepared by a PC method [39]. All materials were obtained from commercial sources and used without further purification. $TaCl_5$ was obtained from J&K Co. Ltd. and others from Sinopharm Chemical Reagent Co. Ltd. Typically, 80 mL methanol was used as a solvent to dissolve 5.11 g $TiC_{16}H_{36}O_4$. A large excess of citric acid CA, 19.9 g was added into the methanol solution with continuous stirring. After complete dissolution of the CA, 2.21 g $SrCO_3$, 0.062 g $Cr(NO_3)_3{\cdot}9H_2O$ and 0.053 g $TaCl_5$ were added to the solution. The mixture was then magnetically stirred for 1 h to afford a transparent solution and 30 mL ethylene glycol (EG) was added to this solution. Then, the solution was heated at 130 °C to promote esterification between EG and CA, yielding green-yellow resin. The resin was then calcined at 350 °C for 1 h to form black solid monolith. The resulting black powder was calcined on an Al_2O_3 plate at 650 °C for 2 h in air, then calcined at 900–1200 °C for 8 h to obtain 1% Cr and 1% Ta co-doping $SrTiO_3$, $SrTi_{0.98}Cr_{0.01}Ta_{0.01}O_3$ (denoted as STO: (1% Cr/Ta)). Additionally, to obtain 2–6% Cr/Ta co-doping STO samples, only appropriate amounts of $Cr(NO_3)_3{\cdot}9H_2O$ and $TaCl_5$ were added into the solution *via* the same synthesis route described above.

For a direct comparison, STO: (Cr/Ta) sample was synthesized *via* a SSR method reported by Kudo et al. [40]. stoichiometric amounts of $SrCO_3$, TiO_2, Cr_2O_3 and Ta_2O_5 were weighed and mixed with full grinding in a mortar. Then, the mixture was calcined in air at 1150 °C for 20 h.

2.2. Characterization

The crystal structure of the photocatalytic materials was confirmed by X-ray diffraction (Rigaku D/max-2200/PC Japan). The UV–vis diffuse reflection spectra (DRS) was determined by a UV–vis spectrophotometer UV-2450 (Shimadzu, Japan) and was converted to absorbance by the Kubelka–Munk method. The morphology of the samples was studied by scanning electron microscopy (FEI SIRION 200, USA). The specific areas of photocatalytic materials were determined by a BET method from N_2 absorption isotherms at 77 K (Micromeritics TriStarII3020 USA). The surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu-Kratos, Axis UltraDLD, Japan). All the binding energy (BE) values were calibrated by using the standard BE value of contaminant carbon (C1s = 284.8 eV) as a reference.

2.3. Photoelectrochemical measurements

The photoelectrochemical measurements for photocurrent response were performed using a CHI660D electrochemical workstation with three-electrode system according to our previous report [41]. In this study, all potentials were converted into the potentials of reversible hydrogen electrode (RHE). The photocatalysts electrodes as the working electrodes were prepared by coating paste onto FTO glasses (15 $\Omega\,sq^{-1}$, transparency 84%, thickness 1.1 mm) with an area of 1 cm × 2 cm. The working electrodes were prepared as follow: 6 mg ground powder was immersed into mixed solution containing 10 μL acetylacetone, 10 μL Triton 100 and 300 μL distilled water to obtain viscous slurry. The slurry was then injected onto FTO glass and was calcined in air at 350 °C for 1 h. Measurements were performed using a quartz electrochemical cell with a Pt wire as a counter electrode and an Ag/AgCl as a reference electrode. Current–time curves were measured in a 0.1 M KOH aqueous solution as a supporting electrolyte. A 300 W Xenon lamp with a 420 nm cutoff was used as a light source. The effective surface area of the electrodes was 1 cm × 1.5 cm.

2.4. Calculation

The energy bands and density of states (DOS) were calculated by using the standard CASTEP package based on the density functional theory (DFT). Perdew–Burke–Ernzerh (PBE) was used the correlation. The cutoff energy was selected at 500 eV and 4 × 4 × 4 *k*-points for samples were chosen in the calculation. During the geometry optimization, the parameters of convergence criteria were set as: energy tolerance 5×10^{-6} eV per atom, max. force 0.01 eV per Å, max. stress 0.02 GPa, max. displacement 5×10^{-4} eV Å.

2.5. Photocatalytic reactions

Photocatalytic reactions for water splitting were carried out in a 350 mL top irradiation reaction quartz cell at room temperature. The catalyst powder (0.1 g) was suspended in 65 mL methanol solution(10 vol%) containing a certain amount of H_2PtCl_6 under magnetic stirring. The reaction cell was connected to a vacuum system, and a 300 W Xe lamp with a cut-off filter to remove UV light ($\lambda < 420$ nm) was used as a light source. At initial stage, Pt species were gradually deposited and loaded on the surface of photocatalysts. After reaction, 0.3 wt% Pt/STO: (Cr/Ta) was filtered and dried at 60 °C for 2 h as a H_2 evolution photocatalyst for Z-Scheme water splitting reaction. The Z-Scheme water splitting reaction was performed in the same system. 0.05 g 0.3% wt Pt/STO: (Cr/Ta) as a H_2 evolution photocatalyst and 0.05 g 0.5% wt Pt/WO_3 as an O_2 evolution photocatalyst were suspended in 65 mL NaI aqueous solution (5 mmol/L). The gases evolved were analyzed by GC with a TCD detector (Huaai, GC9560, China, MS-5A, argon as carrier gas).