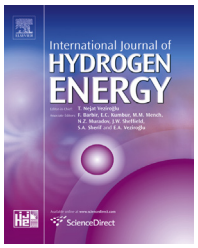
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Improved performance of tri-doped photocatalyst $SrTiO_3$:Rh/Ta/F for H_2 evolution under visible light irradiation

Hyun Woo Kang [a,*], *Seung Bin Park* [b]

[a] *Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Yuseong-gu, Daejeon 305-353, Republic of Korea*
[b] *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daehak-ro 291, Yuseong-gu, Daejeon 305-701, Republic of Korea*

ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form
10 June 2016
Accepted 24 June 2016
Available online 9 July 2016

Keywords:
Photocatalyst
Hydrogen production
Visible light
Spray pyrolysis
Tri-doping

ABSTRACT

A photocatalyst for visible light irradiation was prepared by simultaneously doping $SrTiO_3$ with F^- anion and Rh^{3+} and Ta^{5+} cations for the first time through a spray pyrolysis process. The ternary doping of F^- contributed to the reduction of Ti^{4+} and Rh^{4+} to Ti^{3+} and Rh^{3+}, respectively, by generating extra electron in the lattice. The partially substituted structure of the photocatalyst could be expressed as $Sr(Ti^{4+}_{1-2x-z}Ti^{3+}_{z}Rh^{3+}_{x-y}Rh^{4+}_{y}Ta^{5+}_{x})(O^{2-}_{3-w}F^{-}_{w})$. The doping of F^- into $SrTiO_3$:Rh/Ta increased the photocatalytic hydrogen evolution rate to 4123.7 μmol g^{-1} h^{-1} (quantum efficiency: 6.60%) under visible light irradiation, which was 1.93 times higher than that of $SrTiO_3$:Rh/Ta. The optimum composition of dopants for maximum hydrogen evolution rate was Rh (0.15 mol%), Ta (0.15 mol%), and F (6.0 mol%).

Introduction

To utilize solar energy, various kinds of photocatalysts have been investigated. One of the most efficient methods to store solar energy is hydrogen production by the photocatalyst. To produce hydrogen by water splitting, the photocatalyst should possess both holes in the valence band and electrons in the conduction band with sufficient potential [1–8].

Among the photocatalysts, $SrTiO_3$ is well known for hydrogen production. However, due to its large band gap energy (3.2 eV), $SrTiO_3$ does not absorb and utilize visible light. This large band gap energy could be reduced for visible light absorption by doping with foreign elements. Many investigators have focused on the selection of dopants and the doping method for $SrTiO_3$ host material. The modification of the $SrTiO_3$ band gap structure by doping has been carried out successfully due to the accommodating space in its ABO_3-type perovskite structure. The doping of transition metals (Mn, Fe, Mo, Co, Ru, Ir, Pt, Pd, Rh, Cr, or Ni) into the B site of $SrTiO_3$ creates a new acceptor or donor level in the forbidden band, which decreases the band gap and activates $SrTiO_3$ under visible light [1,9–20].

In previous studies, co-doping of transition metals such as La or Ta enhances the activity of the $SrTiO_3$. It was revealed that the second dopant does not create a new energy level in

* *Corresponding author*. Tel.: +82 42 868 2625; Fax: +82 42 868 8317.
E-mail address: hyunwookang@kaeri.re.kr (H.W. Kang).
http://dx.doi.org/10.1016/j.ijhydene.2016.06.213

the forbidden band; instead, it suppresses further oxidation of the first dopant such as Rh, Cr, or Ni. Such intrinsic reduction of the dopant by the addition of a second dopant leads to improved photocatalytic activity of doped $SrTiO_3$ [21–29].

Doping of anions, on the other hand, is believed to modify the lattice structure and electron configuration of the host material. Anions of N, S, P, and F have been employed as dopants, and they have been shown to improve the visible light absorption and activity of the photocatalyst [30–48]. Fluorine in particular can improve the activity of photocatalyst for pollutant decomposition. Fluorine-doped $SrTiO_3$ and TiO_2 showed enhanced activity under visible light irradiation. The doping of fluorine leads to a narrower band gap by reducing Ti^{4+} to Ti^{3+} and/or forming cation vacancies, so that the photocatalyst is active under visible light [37–48].

In addition to the dopants, the surface morphology of a photocatalyst is also a key factor in determining its potential activity, since the surface is the heterogeneous interface between the photocatalyst and water molecules in the liquid medium. Effective surface morphology with large Brunauer–Emmett–Teller (BET) surface area has been realized in photocatalyst powder by employing the spray pyrolysis process, which can prepare porous and spherical photocatalyst particles with uniform size and consistent composition [49,50].

In this work, the tri-doped photocatalyst $SrTiO_3$:Rh/Ta/F was prepared by a spray pyrolysis process, which produced a more homogeneous product than that produced by the solid state reaction. This process also simultaneously introduced F^- anion and Rh^{3+} and Ta^{5+} cations into $SrTiO_3$. Effects of the ternary dopant fluorine on the electron configuration in the lattice of the host material and on the hydrogen evolution rate under visible light were discussed. The factors affecting the photocatalytic activity were also examined.

Experimental

Preparation of photocatalyst

Tri-doped photocatalyst, $SrTiO_3$:Rh/Ta/F, was prepared by a spray pyrolysis process. The detail of the process is described elsewhere [49,50]. The main pyrolysis reactor was made of a quartz tube, the diameter and height of which were 30 mm and 1.2 m, respectively. An ultrasonic atomizer (Dong-Lim Eng.) operating at a frequency of 1.7 MHz was used to produce liquid droplets from an aqueous precursor solution (described below). The liquid droplets were continuously transported to the pyrolysis reactor using air as the carrier gas, with a flow rate of 5 L min^{-1}. The mean residence time of the droplets in the vertical pyrolysis reactor was 1.80 s. The reactor temperature was kept at 1173 K. The photocatalyst powder was collected by means of a thimble filter (28 mm × 100 mm; Toyo Roshi Kaisha Ltd.) connected to the end of the pyrolysis reactor.

The aqueous precursor solution was prepared with $Sr(NO_3)_2$ (Aldrich, 99.0%) and $Ti[OCH(CH_3)_2]_4$ (Aldrich, 97%). $RhCl_3$ (Aldrich, 99.98%), $Ta(OC_2H_5)_5$ (Aldrich, 99.98%), and NH_4F (Aldrich, 98.0%) were added to the precursor solution as sources of Rh, Ta, and F dopants. The molar ratio of Rh/Ta was kept at 1 in the precursor solution to adjust the charge balance of the host material. The concentrations of both Rh and Ta ions were fixed to 0.15 mol%, which showed the maximum H_2 evolution rate for $SrTiO_3$ under visible light irradiation [29]. All the starting materials were dissolved in 40 mL of distilled water with 10 mL of nitric acid to form a 0.5 mol L^{-1} colloidal solution. After the spray pyrolysis process, a platinum cocatalyst was loaded onto the surface of each photocatalyst sample by photo-deposition method using H_2PtCl_6 (Aldrich, 99.9%) aqueous solution [26–29].

Characterization

The successful preparation of tri-doped $SrTiO_3$ was confirmed by X-ray diffraction (XRD, Rigaku, D/MAX-2500) analysis. The crystal size was determined by the Scherrer equation, $D = 0.9\lambda/(\beta\cos\theta)$, where λ is the wavelength of incident X-ray radiation, β is the full width at half of maximum intensity (FWHM), and θ is the Bragg's diffraction angle. The visible light absorption of each sample was characterized by diffuse reflectance spectra (DRS) obtained by using an ultraviolet–visible–near infrared (UV–Vis–NIR) spectrophotometer (Shimadzu, UV-3101PC) with the Kubelka–Munk equation. The surface morphologies of the as-prepared powders were analyzed using a field-emission scanning electron microscope (FE-SEM, FEI Company, Magellan 400). The BET surface area, pore size, and pore volume were assessed from the nitrogen adsorption–desorption isotherms (Micromeritics, ASAP 2010). The chemical states of doped Rh and F were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, Sigma Probe).

Photocatalytic reaction for H_2 evolution

The photocatalytic reaction for hydrogen evolution was conducted in a closed gas circulation reactor with a Pyrex top window at room temperature and atmospheric pressure. The experimental system consisted of a reactor and a gas chromatographic detector, as previously described [46]. The reactor was designed to allow the direct installation of Xe lamp window at the center of the reactor top window, so that light from the lamp can effectively interact with the reactant mixture. Each sample of the as-prepared photocatalyst powder (0.1 g) was dispersed in 20 vol.% aqueous methanol solution to adjust the powder concentration to 5 g L^{-1} in the reactor. A 300 W Xe lamp (Newport, 6258) was used as the visible light source, with a cut-off filter (Newport, 59472) to produce the desired wavelength $\lambda > 415$ nm. The amount of hydrogen evolution was measured by a gas chromatograph (HP 5890) equipped with an on-line thermal conductivity detector (TCD).

To measure the incident photon flux, a quantum radiometer (Delta ohm, HD2302.0) was used. The quantum efficiency was obtained by the equation: Quantum efficiency = (moles of product formed)/(moles of photons absorbed) = (2 × moles of H_2)/(moles of photons absorbed by photocatalyst).

A blank test was conducted with nondoped $SrTiO_3$ prepared under the same experimental conditions. No gas evolution was detected with pure $SrTiO_3$, indicating that it is not active under this experimental condition.