



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Photocatalytic hydrogen production by water splitting over Au/Al-SrTiO₃

Dilara Saadetnejad, Ramazan Yıldırım*

Boğaziçi University, İstanbul, Turkey

ARTICLE INFO

Article history:

Received 18 April 2017

Received in revised form

10 October 2017

Accepted 26 October 2017

Available online xxx

Keywords:

Water splitting

Photocatalysis

Gold

Perovskites

Au-Al/SrTiO₃

ABSTRACT

Visible light water splitting activity of Au-Al/SrTiO₃ was tested in this work. Al/SrTiO₃ was synthesized via solid state reaction while Au loading was done with homogenous deposition precipitation method. The effects of Au loading and Al doping were investigated in 10, 20 and 30% aqueous solutions of methanol, ethanol, and isopropyl alcohol. The methanol was performed better over 0.25%Au-1.0%Al/SrTiO₃ at 20% alcohol concentration while the isopropyl alcohol resulted in better performance over the same catalyst at 30% concentration; the latter was also the best result obtained in this work with the hydrogen evolution rate of 347 $\mu\text{mol/h.gcat}$. Ethanol showed lower performance than other two alcohols. It was found from UV–vis analysis that Al doping increased the band energy of SrTiO₃. XRD and XPS analyses clearly showed that the dominant structure was SrTiO₃ in all samples. Au was found to be generally loaded as 30–40 nm particles by SEM.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Developing new renewable energy technologies has become an important task in recent years due to increase in population of the world, excessive utilization and rapid depletion of fossil fuels and increasing environmental problems (like air pollution and global warming) created by conventional energy technologies [1]. Conversion of solar energy into the chemical energy in an effective manner can contribute the solution of the energy problem significantly considering its abundance; the solar radiation on earth for about 30 min can supply a one-year energy demand of the world [2]. Hydrogen, which is an excellent and clean energy carrier, can be used to utilize solar energy through technologies like photocatalytic water splitting.

The hydrogen production using photo-electrochemical cell by Fujishima and Honda in 1972 [3] was the milestone for solar driven water splitting reaction this work initiated various

research projects in this fields. The photocatalytic water splitting research over particulate photocatalyst was started in early 80's [4] and developed gradually; today it is one of the most extensively studied field for clean hydrogen production as the numerous reviews in the field also indicated [5–7].

Semiconductor combined with a cocatalyst is the heart of overall water splitting reactions; the bandgap of the semiconductor should be suitable for the visible light or it should be tuned by some modifications. TiO₂ has been one of the earliest and the most commonly used semiconductors for water splitting as well as the other photocatalytic applications thanks to its stability, low cost, nontoxicity, and environmental-friendliness [8,9]. Unfortunately, however, its band gap is suitable for UV light harvesting; hence it was doped by various metals to shift the bandgap for visible light [10–12]. For example, in 1982, Borgarello et al. [13] studied photocatalytic water splitting over Cr³⁺doped TiO₂ nanoparticles. The observation of visible light activity of Cr³⁺ doped TiO₂ nanoparticles is attributed to contribution of Cr³⁺ 3d

* Corresponding author.

E-mail address: yildirra@boun.edu.tr (R. Yıldırım).<https://doi.org/10.1016/j.ijhydene.2017.10.154>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

electrons to the conduction band of TiO_2 . Similarly Anpo and co-workers [14] prepared diverse cation (V, Cr, Mn, Fe, and Ni) doped TiO_2 materials by ion implantation method, and they found that the absorption band of doped TiO_2 shifted toward the visible-light region. Asahi et al. [15] also reported a similar work involving C, N, F, P and S doping of TiO_2 for photocatalytic water splitting.

Although researches using TiO_2 is still continuing, other semiconductors were also tested [5,6,16–18]. Among them, perovskites are the most commonly studied material in the recent years since they are visible-light active or can be easily modified to be so by ion doping or ion replacement, and as multi-component solid solutions or multi-component composites [19–21].

SrTiO_3 is one of the most commonly studied perovskite structure for photocatalytic water splitting although it has large band gap, which make it UV-light responsive [22]. Its band gap is usually modified to make it active under visible light by doping with cations or anions since perovskite structures have a great capacity to accommodate impurities [23–26]. These impurities may also result in formation of defects, which might lead to better interactions with adsorbed molecules [27]; there are many studies showing that doped SrTiO_3 gives good response to visible light. For example SrTiO_3 doped with Rh, Ru, and Ir demonstrated higher efficiencies for hydrogen evolution [28]. Koto et al. [29] studied a series of co-doped SrTiO_3 photocatalysts with the pairs of Cr-Sb, Cr-Ta and Ni-Ta, and used them under visible-light for H_2 production in methanol solution. They found that Cr-Sb doping showed high photocatalytic activity in the visible light region; the results obtained over Cr-Ta co-doped catalyst also exhibited higher photocatalytic activity as compared to Ta doping alone. Cr/N doping to SrTiO_3 was also investigated and proven to be beneficial [30].

Co-catalysts chosen for water splitting should enhance either H_2 evolution. Through history of this field, low-cost and abundant elements such as Ni, Co and Cu have been used. For example Korzhak et al. [31] compared Cu and Ni co-catalyst over TiO_2 , and they found that Cu leads higher photocatalytic H_2 evolution rate than Ni; they attributed this to the stronger electronic interactions between Cu and TiO_2 . In 1980, Domen et al. [4]. Studied water splitting over SrTiO_3 in the absence and presence of co-catalyst of NiO and Ni; they showed that H_2 evolution rate was higher with NiO, which might have impeded back reaction. Rh or Pt has also proven to be active under visible light as co-catalyst over SrTiO_3 [32].

Gold was considered as inactive for catalysis until Haruta et al. [33] showed that it can have significant activity in CO oxidation at low temperatures if it is used as nanoparticles. Later on, this metal was also used as co-catalysts (as hydrogen evolution site) for water splitting as well as other photocatalytic applications. In addition to the role of gold as hydrogen evolution site, some studies show that its interband transition and surface plasmon resonance effect also play a significant role for visible light activation in photocatalytic applications, although the nature of this role is not clear yet [34–36].

In this work, the water splitting activity of Au/SrTiO_3 was investigated. We also tested the effect of Al doping to SrTiO_3 considering that it enhanced the water splitting activity of

SrTiO_3 in the presence of Rh and Cr co-catalyst [37]. Our preliminary works indicated that it may also enhance the performance of Au/SrTiO_3 system; as far as we know, this has not been tested before in the literature. The effects of Au loading (0.1–0.5%), Al (0.5–1.5%) doping, type and concentration of sacrificial agent (10%, 20% and 30% methanol, ethanol and isopropyl alcohol) were investigated. The reaction tests were performed in a semi batch reactor equipped with a 150 W xenon arc lamp, and hydrogen produced was measured using an on-line mass spectrometer. The catalysts were also characterized using UV–visible spectroscopy, scanning electron microscope (SEM), X-ray diffraction technique (XRD) and X-ray photoelectron spectroscopy (XPS). Indeed, it turned out that Au/SrTiO_3 constituted an effective catalyst system for water splitting probably due to the interaction between Au-Al pair and possible formation of Au-Al alloys as discussed in characterization part.

Experimental

Strontium carbonate (SrCO_3), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), and tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were purchased from Sigma-Aldrich company and used in the preparation of strontium titanate (SrTiO_3); all materials were used as received. Aluminum doped SrTiO_3 was prepared via solid state reaction, the procedure was carried out as explained elsewhere [28]. SrCO_3 , TiO_2 and Al_2O_3 were mixed with the molar ratio of Sr:Ti:Al:1:1:0.005–0.01–0.015 in a porcelain dish and heated to 1273 K with 30 K/min and kept at this temperature for 10 h in air. Then Al/SrTiO_3 was loaded with Au via homogenous deposition-precipitation method (using urea) as described by Leba et al. [38], followed by drying at 373 K overnight and calcination at 673 K for 4 h. The use of urea may prevent sudden peaks in pH of the solution, which may decrease Au loading, as it happens when NaOH is used as the base [39]. The particle size of Au may be also smaller when the urea is used [40].

Photocatalytic reactions for H_2 evolution were carried out in a semi batch reaction system in which He is used as inert gas with the flow rate of 20 ml/min. The powder form of photocatalyst as 2.5 gcat/L was suspended in the 1000 ml reaction solution; one third of the reactor volume was kept empty for the gas phase products. The reactor was irradiated from top through Quartz cover by ABET 10500 Solar Simulator equipped with 150 W xenon lamp and continuously stirred with a magnetic stirrer. Helium was bubbled through the water solution together with the hydrogen and oxygen generated, accumulated in the empty space over the liquid phase and left the reactor for analysis. A HIDEN HPR 20 QIC Mass Spectrometry was integrated to the system to determine H_2 production rate.

The reflectance spectra of photocatalysts were determined by diffuse reflectance UV–visible spectroscopy (Shimadzu 2600) and were converted from reflection to absorbance by the Kubelka-Munk method, which enabled to determine band gap energy of photocatalysts [28,29,41].

SEM analysis for surface morphology and Au dispersion was conducted using Philips XL30 ESEM-FEG system at Bogazici University Advanced Technologies R&D Laboratory. The

Download English Version:

<https://daneshyari.com/en/article/7708871>

Download Persian Version:

<https://daneshyari.com/article/7708871>

[Daneshyari.com](https://daneshyari.com)