Materials Research Bulletin 84 (2016) 474–479

Contents lists available at ScienceDirect

Materials Research Bulletin

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

A unique approach for high performance photoelectrochemical water splitting: Utilizing coating and doping methods

Aryan Azad, Sun Jae Kim*

Institute/Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, South Korea

ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form 25 July 2016
Accepted 23 August 2016
Available online 24 August 2016

Keywords:
Semiconductors
Thin films
Oxides
Nanostructures
Raman Spectroscopy

ABSTRACT

Hydrogen photocatalytically is generated from water by utilizing solar radiation, and it is identified as one of the renewable energy sources to influence the global warming. We explore a unique approach to compare the effects of Fe-and Ti doped titanium and iron oxide respectively as photoanodes for photocatalytic water splitting. For this reason five different photoanodes prepared by coating and doping methods on Fluorine thin oxide (FTO) glasses and heat-treated at various temperatures. Specifically, Samples were characterized by field emission scanning electronic microscopy (FESEM), photocurrent density (*I–V*), optical band gap energy and Raman spectroscopy. Significant performance can be seen in Ti-doped hematite which was improved the photocurrent density while the band gap energy and electron-hole recombination, were decreased.

1. Introduction

Solar and the wind are the two major sources of renewable energy, and they are also the promising sources for renewable hydrogen production [1]. Semiconductor-based heterogeneous photocatalysis, which allows direct conversion of solar energy into chemical energy via a renewable route, could be the most viable long-term solution with potential to address these environmental and energy issues [2]. Photocatalysis, in which the inexhaustibly abundant and clean solar energy can be harnessed as viable technologies, offers us a promising avenue with the tenet of sustainable chemistry toward solar energy conversion [3]. Early work of TiO_2 photoelectrochemical hydrogen production was reported by Fujishima and Honda [4]. It is often assumed that production of one molecule of oxygen from two water molecules requires four holes and, therefore, four photons. This assumption is based on the four-hole requirement of the water-splitting process in natural photosynthesis [5,6]. Compared with other photocatalysts, TiO_2 is much more promising as it is stable, non-corrosive, environmentally friendly, abundant and affordable. However, the photocatalytic efficiency of TiO_2 for water splitting is limited due to the high recombination rate of photogenerated electron-hole pairs [7]. On the other hand, it has previously shown that electron recombination happens on a microsecond time scale when low intensity excitation is used in degassed acetonitrile [8]. Moreover, Tamaki et al. observed that the geminate recombination of electron and hole did not take place before 1 ns under weak laser intensity in the air [9]. To resolve this problem, many methods have been proposed to enhance the photocatalytic activity of TiO_2, including the doping of transition metal or nonmetal ions, the deposition of noble metals, the surface sensitization of dyes and the preparation of composite semiconductors or coating methods. [10–14] However, problems such as increased carrier recombination centers and decreased incident photon to electron conversion efficiency (IPCE) in the UV light absorption region represent significant limitations for this strategy [15]. Thereby, to further improve the photoelectrochemical (PEC) activity of TiO_2 by a doping strategy, an important issue is to solve the diminution of IPCE in the UV region [16,17]. Since hematite exhibits a much lower dielectric constant when compared to TiO_2 [18], the hematite presence can affect the separation of photogenerated charges and the photocatalytic activity [18,19]. Hematite (α-Fe_2O_3), as the most stable iron oxide with n-type semiconducting properties ($Eg = 2.1$ eV) under ambient conditions, is of great scientific and technological interest. Owing to its low cost and high resistance to corrosion, α-Fe_2O_3 has been investigated as electrode material [20], pigment [21], catalyst [22], gas sensor and anticorrosion protective paints [20–23]. Hydrothermal or solvothermal methods which may use for doping, have some advantages, including mild synthetic conditions, simple manipulation and good crystallization of the products [24]. In this research based on recent research works by hydrothermal and layer by layer methods, the

* Corresponding author.
E-mail address: sjkim1@sejong.ac.kr (S.J. Kim).

http://dx.doi.org/10.1016/j.materresbull.2016.08.033
0025-5408/

enhancement methods for photocatalytic hydrogen production are evaluated by comparing the effect of Fe-doped TiO_2 and Ti-doped Fe_2O_3 on FTO glass.

2. Materials and methods

In this study five different photoanodes were prepared to increase photoelectrochemical water splitting efficiency.

2.1. α-Fe_2O_3/FTO and Ti-doped Fe_2O_3/FTO hydrothermal (HT)

Fluorine tin oxide glasses (FTO) (Asahi Glass Co, Japan, 14 Ωsq^{-1}) were cut (3cm × 3cm × 2 mm) and cleaned by acetone, ethanol, and deionized water. A piece of cleaned FTO glass was placed in the solution containing 0.4 g $FeCl_3 \cdot 6H_2O$ and 0.85 g $NaNO_3$ at pH 1.5 (adjusted by HCl) afterward put in an autoclave and heated at 100 °C for six hours. A uniform layer of yellow film (FeOOH) was formed on the FTO substrate. After cooling down (to room temperature), the FeOOH-coated substrate was washed with deionized water and dried at 80 °C. For phase transition from ß-FeOOH to pure α-Fe_2O_3, samples were annealed at 550 °C for 2 h and additional 10 min at 750 °C [25].

Ti precursor was added to the above solution to prepare Ti-doped hematite nanostructures. Therefore, TiCN (0.5 ml, Sigma-Aldrich Co.) aqueous solution (10 mg/ml) as a precursor was added to the (0.4 g $FeCl_3 \cdot 6H_2O$ and 0.85 g $NaNO_3$ at pH 1.5 (adjusted by HCl) solution). The synthesized samples were washed with deionized water before sintering in air to remove the black powder (TiCN) [26].

2.2. TiO_2/FTO and Fe_2O_3/FTO coating (LBL method)

To clean and ensure a fresh surface, FTO glasses were etched for 20 min in Piranha solution (7:3 = 70% conc. H_2SO_4:30% H_2O_2). By dipping FTO glasses in 0.2 M poly-ethylene imine (PEI, Aldrich Co.) for 20 min at room temperature, the surface of FTO glasses were contained a positive charge. Then negatively charged ions were produced by immersing the FTO glasses for 20 min in an aqueous 10 gL^{-1} H-TiNT particle solution dispersed together with 0.2 M tetra butyl ammonium hydroxide (TBAOH, Aldrich Co.). The same method was used to make positively charged ions by immersing in 0.2 M poly diallyl dimethyl ammonium chloride (PDDA, Aldrich Co.) aqueous solution. The obtained H-TiNT/FTO glasses were dried under UV–vis light irradiation (Hg-Xe 200W lamp, Super-cure,

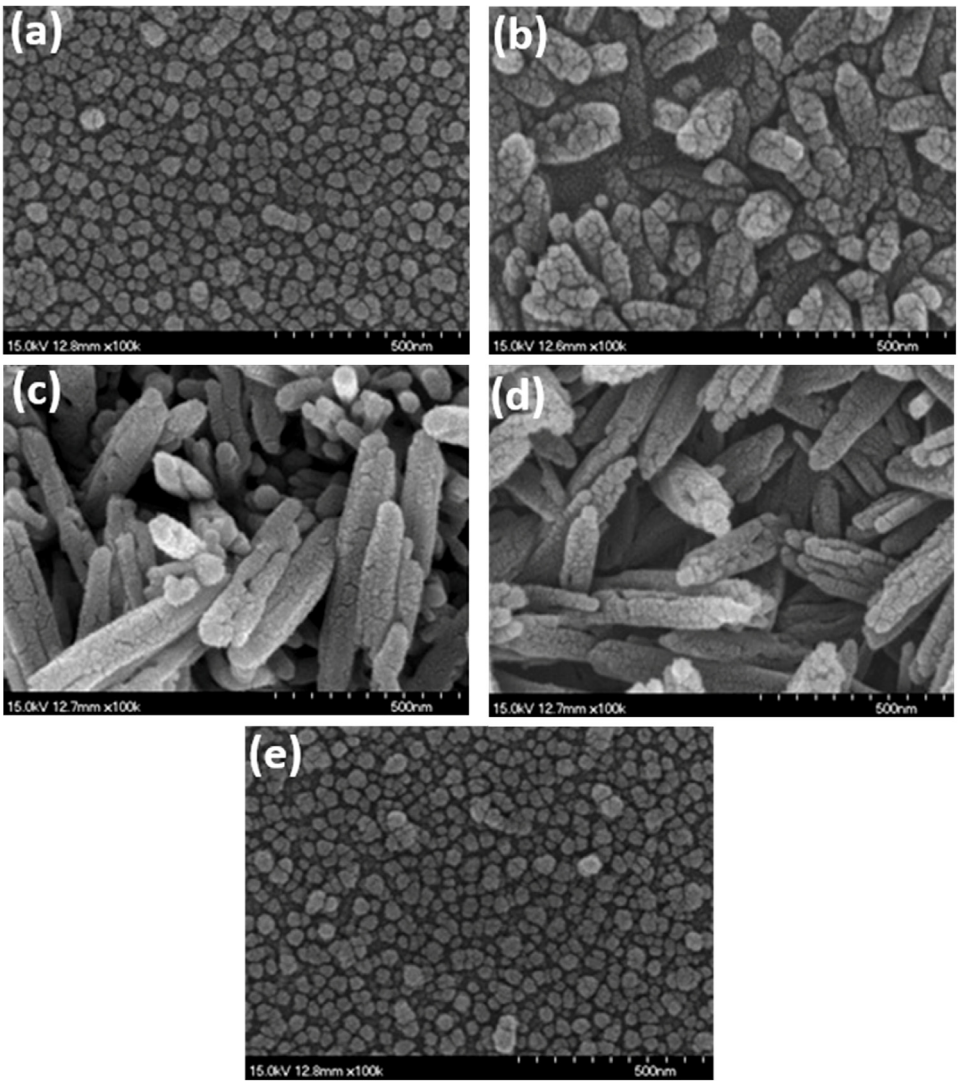

Fig. 1. SEM micrographs at 100 kX magnification of different photoanodes: (a) Fe-doped TiO_2 sintered at 500 °C for 15 min, (b) Ti-doped Fe_2O_3 sintered at 550 °C for 2 h, additional heat-treatment at 750 °C for 10 min, (c) TiO_2/FTO sintered at 500 °C for 10 min, (d) Undoped hematite sintered at 550 °C for 2 h, additional heat-treatment at 750 °C for 10 min and (e) Fe_2O_3/FTO sintered at 500 °C for 10 min.