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Experimental investigation and analysis of a new photoelectrochemical reactor for hydrogen production

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ARTICLE INFO

Article history:

Received 23 February 2018

Received in revised form

8 April 2018

Accepted 14 April 2018

Available online xxx

Keywords:

Hydrogen production

Electrolysis

Photoelectrochemistry

Titanium dioxide

Exergy

Efficiency

ABSTRACT

In this research paper, an experimental investigation of photoactive material titanium dioxide (TiO₂) coated on 180 cm² 316 stainless steel anode is undertaken to study the photoresponse on photoelectrochemical (PEC) hydrogen production. The TiO₂ nanoparticles are first prepared via sol-gel method. A large surface 316 stainless steel anode is coated with TiO₂ nanoparticles by a dip coating apparatus at a withdraw rate of 2.5 mm/s. The nanoparticles are carried on the stainless steel substrate by two-step annealing procedure. The potentiostatic studies confirm the photoactivity of TiO₂ nanoparticles in a photoelectrochemical reactor when exposed to solar ultraviolet (UV) light. The photon to current efficiency measurements carried out on the PEC reactor with TiO₂ coated large surface stainless steel as photoanode demonstrate a significant increase of photoresponse in UV light compared to the uncoated stainless steel prepared under similar conditions. Upon illumination at a power density of 600 W/m², the hydrogen production is observed in TiO₂ coated stainless steel substrate at a measured rate of 51 ml/h while no illumination conditions show a production rate of 42 ml/h. In comparative assessments, the TiO₂ coated substrate shows an increase in photocurrent of 10 mA with an energy efficiency of 1.32% and exergy efficiency of 3.42% at an applied potential of 1.6 V. The present results show a great potential for titanium nanoparticles semiconductor metal oxide in photoelectrochemical hydrogen production application.

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Introduction

Hydrogen is recognized as the most abundant element in the universe. Nevertheless, it is not inherently present in the environment, but may be produced by means of various processes. One of the most common practices for hydrogen

production is water electrolysis which is decomposition of water into its elements through an electric current being passed through water. In order to achieve more environmentally friendly sources of hydrogen production, solar energy can synergize with the electrolysis process through what is known as photoelectrochemical water splitting (PEC).

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<https://doi.org/10.1016/j.ijhydene.2018.04.110>

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Semiconductor materials in a PEC hydrogen production reactor, convert solar energy to an energy carrier via light stimulated electrochemical processes. The solar illumination is absorbed by one or both of the photosensitive electrodes and it can be converted into either chemical or electrical energy. Photoelectrochemical systems combine both phenomena, electrochemical water splitting and solar energy absorption into a single reactor which brings less external electricity supply requirement and thus gives more compact and environmentally friendly solutions [1]. Theoretically, water splitting requires 1.23 V potential difference in the acidic medium. However, the true cell voltage is higher as 1.8–2.0 V. The part of the required electric potential can be provided by the photoelectrodes in a photoelectrochemical hydrogen production reactor. In this regard, in an electrolyzer cell, electrodes can be either replaced or coated with a semiconductor material to utilize solar energy. This technology is relatively new compared to conventional energy conversion systems and can be considered as a long-term technology pathway, with the potential for low or no greenhouse gas emissions. Despite much research undertaken for the photocatalytic method of hydrogen production, the photocatalytic process is still at the developmental stage for commercialization, and there has been increasing interest in developing more efficient and more cost-effective techniques.

There are numerous types of photoelectrode pairs presented in the open literature. One of these ways is coating a single electrode by a semiconductor base material which is called single photo-electrode PEC system. The electrode can be selected as anode or cathode depending on the semiconductor type (as being p- and n-type). The second way is coating both electrode pairs with dissimilar semiconductor materials which are known as bi-photo-electrode systems. In such systems, p- and n-type materials are utilized as the photocathode and photoanode, respectively and hence the photo-electricity can be induced in both sides [2]. As a third alternative, hybrid photo-electrodes can be formed by combining two different n- or p-type material (depending on the photoanode and photocathode) [3]. However, for the hybrid formations, the external materials exposed to solar illumination have to be transparent to transmit radiation [2].

Several semiconductor-based materials are used in the literature as a catalyst to optimize hydrogen yield such SnO₂, WO₃, ZnO, TiO₂, CdS, MoS₂ [4–9]. Due to the high corrosion resistant nature of TiO₂, it is the most frequently studied material. Even though the high band gap of 3 eV puts some limitation to practical applications, TiO₂ is still showing promising features [2,10,11] and can be utilized under visible spectrum with a combination of other materials for hydrogen production [12]. Anchoring of TiO₂ onto a suitable catalyst support is a promising subject that is studied by applying several techniques [13]. Various methods are reported in the literature for TiO₂ coating [13] such as, chemical vapor deposition [14–17], thermal treatment [18–20], hydrothermal [21], electrodeposition [22,23], sol-spray [24] and sol-gel [25–29]. Among all the aforementioned techniques, the sol-gel method is widely utilized because of the advantages of relatively low cost, as well as, compatibility to small and large-scale applications with various sizes and shapes of the substrates [13,30].

Crisan et al. [31] prepare TiO₂ nanometer films by the alkoxide route of the sol-gel method. The doped materials are obtained by simultaneous gelation of both precursors in the sol-gel technique. Glass is selected as the substrate in the study and effect of dopant, the number of coating layers and thermal treatment on the structure of the film are obtained. The study reports that 2% S-doped TiO₂ samples show the maximum photocatalytic activity due to the smallest crystallite size. Also, the study shows that the distortion of anatase lattice and even the temperature of 500 °C, has a significant effect on the photocatalytic activity positively. Sonawane et al. [32] prepare a sol-gel to deposit the surface of various substrates including glass plates, silica rashing rings and glass helix by iron (Fe) doped TiO₂ (Fe–TiO₂). The study modifies the surface of the coating film surface by adjusting the concentration of the polyethylene glycol (PEG) into the TiO₂ solution. The results show that the addition of Fe into the sol-gel decreases both phase transition temperature and crystallization temperature. The coatings are prepared with 0.6 g of polyethylene glycol containing 2% Fe–TiO₂ and 4% Fe–TiO₂ demonstrates the best photo-catalytic performance after annealing at 450 °C, respectively.

For a dip coating process, the thickness of the film deposited is highly dependent on both the number of dipping and viscosity of the sol-gel. A dip coating with a viscous solution may cause TiO₂ to be peeled off easily from the surface of the electrode. Conversely, having a solution with low viscosity brings the problem of the coating time. More immersion time will be required for such cases to obtain a sustainable substrate. Hence it is critical to keep the balance between them in order to achieve better practices [13]. Shangguan et al. [33] form anatase TiO₂ films on glass samples by utilizing the sol-gel technique. Their titanium isopropoxide is utilized as a precursor of the sol-gel. The thickness of the film is controlled by the number of coating cycles where one coating formed about 140 nm film. The results show that the prepared films are calcinated with temperature range from 500 °C to 600 °C which sustained pure anatase crystallization. It is also determined that 0.3 wt % Pt loading improve the hydrogen yield while no significant effect of dip-coating cycles and calcination temperature on the photoactivity is witnessed. Anitha et al. [34] investigate the influence of the annealing temperature on the structural, optical, electrical and photocatalytic activity of ZrO₂–TiO₂ nanocomposite thin films which are prepared by sol-gel dip coating method. In their study, the annealing temperature varies between 500 °C and 1200 °C. The crystallinity of films increases with higher temperatures. The study shows the direct relationship between the conductivity of the films and annealing temperature. Higher conductivity values are observed at higher annealing temperatures. Moreover, photocatalytic performance of the films is enhanced with the annealing temperature due to a higher amount of crystallization and reduction in bulk defects. The modified sol-gel techniques are also extensively used for improving photo-responses of the substrates. Cheng et al. [35] combine high catalytic activity of titanium dioxide with the superior adsorptive properties of titanates by using the sol-gel method with the solvothermal process. Eventually, they successfully produced dual phase material with a relatively high surface area of 180 m² g⁻¹ which significantly enhances the catalytic

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