Renewable and Sustainable Energy Reviews 41 (2015) 1205–1216

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Novel nano-structured for the improvement of photo-catalyzed hydrogen production via water splitting with in-situ nano-carbon formation

Ahmed M.A. El Naggar, Heba M. Gobara, Ibrahim M. Nassar *

Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor Street, Nasr City, 11727 Cairo, Egypt

ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form
5 August 2014
Accepted 1 September 2014
Available online 3 October 2014

Keywords:
II–VI semiconductors nanomaterials
Perovskite
Mixed metal oxides
H_2 production
Electron–hole bear effect
Nano-carbon

ABSTRACT

Photocatalytic water splitting is a promising process for producing H_2 from two abundant renewable sources, namely, water and solar light, with the aid of suitable photocatalysts. In a previous research study, the team of this work succeeded in enhancing the production of H_2 during the water splitting using synthesized Chalcogenide photocatalytic nanoparticles of d-group elements based semiconductors (ZnO and CdS) via a photochemical reaction under UV-light in the presence of methanol as a hole-scavenger. In the current work, a new nano-structured mixed oxide based material in a Perovskite structure is introduced as a novel semiconductor for the water splitting application. The combination of the aforementioned semiconductors and Perovskite in order to improve the photocatalytic activity for an enhanced hydrogen production through water splitting process under visible light irradiation (sunlight) is also discussed through this study. Unpredictable results based on the utilization of Perovskite individually or combined with the other semiconductors were obtained. Hydrogen was aggrandized (since a pioneering and unexpected hydrogen yield was obtained) accompanied with the formation of carbon-species which disclose an innovative reaction mechanism through this research. These results were emphasized by different tools analysis, namely Raman microscopy, SEM, TEM, and surface area. The results obtained in this work reveal that the nano-structured semiconductor/Perovskite system introduced through this work is a promising candidate in the field of hydrogen production with a simultaneous carbon based materials formation.

Contents

* Corresponding author. Tel.: +20 2 227 45902; fax: +20 2 227 727433.
E-mail address: inassar_76@yahoo.com (I.M. Nassar).

http://dx.doi.org/10.1016/j.rser.2014.09.001
1364-0321/

1. Introduction

An important process for future energy supplies is 'photo-hydrogen' production from water splitting; the photocatalytic processes are clean and employ a renewable source as reported for various systems [1–3]. The band gap of a semiconductor should be larger than 1.23 eV, corresponding to the water splitting potential, where the conduction and valence band levels should satisfy the energy requirements to match the reduction and oxidation potentials of H_2O, respectively [4]. Several semiconductor oxides such as TiO_2, ZrO_2, $NbTaO_3$, and $NaTaO_3$, including transition metal oxides, have been studied [5–7]; also the design of nanocomposite nanomaterials has attracted attention due to their high response in UV–visible region for photocatalytic reactions [8,9].

Titanium dioxide (TiO_2) is considered as the best photocatalyst. However, the use of TiO_2 as photocatalysts for water splitting is limited by its redox potential with reference to the normal hydrogen electrode (NHE) [10]. Important studies have been made to improve the photocatalytic activity of titanium dioxide for the water splitting reaction. Modified titanium dioxide was prepared by doping with Fe, Zn, Cu, V, Mg, Be and Ni [11], or by impregnating TiO_2 with noble metals such as Pt, Pd, Ir, Rh and Ru [12]. In particular, the preparation of mixed oxides like CuO, ZnO, NiO and CeO [13–17] has attracted attention for researchers because of the low-cost materials and as they show important photocatalytic properties. The incorporated oxide effect has been related to oxygen vacancies in its crystal structure [18,19].

In a previous work by the authors of this study [20], the photo-electrochemical water splitting for hydrogen production from water–methanol mixture decomposition using either ZnO with energy band gap of 3.37 eV or CdS with energy band gap of 2.42 eV separately or combined together was demonstrated. It is clearly reported that CdS and ZnO have reasonable photocatalytic activity for hydrogen production from water, in the presence of methanol as the hole scavenger, under UV and visible light. A colloidal CdS/ZnO composite system with small particles size (less than 10 nm for each component) was introduced. The CdS electrons homo-generated during its band gap excitation can then be transferred to the conduction band (CB) of ZnO while the holes remain in the CdS particle. This charge separation in a colloidal composite system might help in increasing H_2 production rate especially for those which have particle sizes less than 10 nm. The overall activity of hydrogen production was nearly 6 mmol/h when both semiconductors were physically combined together [20].

The development of new semiconductor based photocatalytic materials is a very challenging task; it involves different deciding factors such as the band gap, carrier transport, catalytic activity, surface related absorption properties and chemical stability [21]. Searches for alternateing photocatalysts are carried out to develop materials that are capable of absorbing visible light, which constitutes a larger portion of the solar light.

One approach that has been studied is to modify the band gap as well as to discover new photocatalysts for identification of new materials with appropriate band gaps. Many mixed metal oxides with early transition metal ions having d^0 configuration (Ti^{4+}, Nb^{5+}, Ta^{5+}) have been explored, specifically several layered Perovskitess, such as $K_2La_2Ti_3O_{10}$, $RbPb_2Nb_3O_{10}$, and $KLaNb_2O_7$, identified as photocatalysts in the presence of co-catalysts (Pt, NiO, etc.) for the evolution of H_2 from water under UV light radiation [22].

These oxides are attractive photocatalytic materials for the following reasons. (1) Their structures consist of two-dimensional Perovskite slabs interleaved with cations, which is expected to increase the lifetime of the photo-generated electrons and holes, and thereby increase the efficiency of the materials [23]. (2) The Perovskite slabs normally made up of metals such as Ti, Nb, or Ta have been preferred as photocatalysts under UV irradiation. (3) Numerous low-temperature synthetic possibilities exist [24] to study the influence of cationic and/or anionic substitutions by the appropriate tuning of the band gaps. For the aforementioned reasons the authors of this study were interested to investigate the Perovskite oxide $K_2La_2Ti_3O_{10}$, as part of their ongoing efforts to identify visible light active photocatalysts for water decomposition.

Various kinds of new mixed oxide semiconductor materials which could absorb visible light were synthesized by Arakawa et al. [25]. The first group is Bi_2MNbO_7 ($M=Al^{3+}$, Ga^{3+}, In^{3+}, Y^{3+}, Rare $Earth^{3+}$) [26] of $A_2B_2O_7$ pyrochlore structure. The second group is $BiMO_4$ ($M=Nb^{5+}$, Ta^{5+}) [27] of stibotantalite structure and the third group is $InMO_4$ ($M=Nb^{5+}$, Ta^{5+}) of wolframite structure. These materials crystallize in different structures; however, they contain the same octahedral TaO_6 and/or NbO_6 in the structures. The band structure of these materials shows that the conduction band is mainly composed of Ta/Nb d-level and the valence band is mainly composed of O 2p level. The band gaps of these materials determined by UV–visible reflectance spectra were between 2.7 and 2.4 eV. Among these materials NiO_x (surface oxidized Ni) or RuO_2 that promoted $InTaO_4$ and $InNbO_4$ photocatalysts, such as $NiO_x/InTaO_4$, $RuO_2/InTaO_4$ and $NiO_x/InNbO_4$, showed photocatalytic activities for pure water splitting under visible light irradiation ($\lambda=420$ nm, 300 W Xe lamp). However, the activities were very low.

Solar energy is one of the most promising renewable energy sources. Therefore, several solar energy conversion technologies were studied for several decades [28]. The thermochemical cycles for hydrogen production with solar energy were proposed since the 1960s [29]. The thermochemical cycles of halogen and sulfur compounds as intermediates are efficient for hydrogen production by water splitting, but a slight release of those compounds can impose serious environmental problems. The thermochemical cycle with the redox pairs of metal oxides is regarded as the simplest, as well as the most environmentally benign. In the redox cycle of metal oxides, solar energy can convert metal oxides into their reduced form, which can be oxidized by water to produce hydrogen [30,31]. The effects of various synthetic conditions of the semiconductor/Perovskite photocatalysts on their physicochemical properties and photocatalytic H_2 production activity were investigated.

The coupling of two or more semiconductors with different energy gaps is useful to achieve effective charge separation. Accordingly, the present research review focuses on the combination of various semiconductors using either LSCF [Perovskite] individually or combined with ZnO or CdS as well as a ternary mixture of LSCF–CdS–ZnO having different band energies in order to enhance the photocatalytic activity toward water splitting.