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RuO_2–$NaTaO_3$ heterostructure for its application in photoelectrochemical water splitting under simulated sunlight illumination

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ABSTRACT

In this paper, we report the synthesis of RuO_2–$NaTaO_3$ films for their application as photocathodes in photoelectrochemical (PEC) cells for hydrogen generation from water splitting. RuO_2 was electrodeposited on $NaTaO_3$ films at constant current varying the deposition time with the finality to obtain 1–3 wt.% RuO_2–$NaTaO_3$. The characterization of the photoelectrodes RuO_2–$NaTaO_3$ was carried out by linear voltammetry (VL), chronoamperometry (CA), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), X-ray diffraction (XRD), ultraviolet–visible absorption spectroscopy (UV–vis) and X-ray photoelectron spectroscopy (XPS). The hydrogen production was conducted in a photoelectrochemical reactor coupled with a gas chromatograph. One of the main contributions of this work is the incorporation of RuO_2 on $NaTaO_3$ films in order to enhance its activity in the visible region, achieving a maximum photoelectrochemical hydrogen production of 15.7 mmol h^{-1} g^{-1} for the film with 2 wt.% RuO_2 with a solar-to-hydrogen (STH) conversion efficiency of 4.29%.

1. Introduction

The combination of solar energy with water is one of the promising alternatives to solve the energy need that society will demand in future years. This strategy is an option to obtain hydrogen, from water-splitting process, as a clean and sustainable energy source [1,2]. Water splitting can be carried out by heterogeneous photocatalysis (HPC) and photoelectrochemical process (PEC) [3–5]. In the literature [6,7], it is reported that the photoelectrochemical water splitting started in Japan in the late 1960s with the study of Fujishima and Honda, in which TiO_2 was used as semiconductor material. Since then, new materials have been prepared with finality to surmount the high-energy barriers in the water-splitting reaction. Among these materials, $NaTaO_3$ has been widely studied due to its high activity for this reaction under UV-light [8]. Kudo et al., using the HPC system [9–14], have extensively reported the study of tantalates, for its application in the hydrogen production. Recently, our group has reported a photocatalytic hydrogen production of 10 mmol h^{-1} g^{-1} using sodium tantalate [15,16]. Furthermore, other studies about the use of tantalates for hydrogen production can be found in literature [17–27]. Most of those reports are focused on the relation of sodium tantalate performance with hydrogen production rate

Several strategies have been conducted in order to enhance the photocatalytic activity of the tantalates, such as synthesis route, doping of metal cations and incorporation of co-catalysts; also it is reported that different morphologies can increase the amount of hydrogen production. Specifically, the synthesis methods used in these studies are solid state, hydrothermal, sol–gel, molten-salt synthesis, hydrothermal, polymerizable complex, deposition and/or doping of metal cations such as: Zn, La, Sm, Gd, Si, Zr, In, Nb, Ce, and Al [8]. Also the use of co-catalysts like Ni, NiO, Au nanoparticles, RuO_2 and $[Mo_3S_4]^{4+}$ have been applied as a strategy to enhance activity [10,13,15,16].

Despite the fact that there is a huge amount of papers related to hydrogen production using perovskite-type tantalate compounds, only few studies are related to the use of PEC systems [28–31]. These studies have been focused to get information about the electrochemical behavior to understand the mechanism of photocatalysis for water splitting reaction and O_2 photoreverse reaction. Among the metallic materials that can be combined with $NaTaO_3$ to enhance the photocatalytic activity of this semiconductor in visible region, the RuO_2 can be a good candidate due to its high chemical stability, high conductivity and excellent diffusion barrier

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properties. In particular, RuO_2 has been applied as a catalyst in the reaction of water splitting and several organic compounds [32–35] through photoinduced processes. For example, Bloh et al. [33,34] have showed that zinc oxide containing ruthenium oxide is highly active in the visible light spectrum. In our previous studies, the hydrogen production, using HPC system, was enhanced due to the incorporation of RuO_2 as co-catalyst in $NaTaO_3$ [15,16]; however, the heterointerface of RuO_2–$NaTaO_3$ remains uninvestigated. In this work, we focus by first time on the photoelectrochemical hydrogen production using RuO_2 as co-catalyst on $NaTaO_3$; it is used as photocathode under simulated solar irradiation.

2. Experimental

2.1. Synthesis of $NaTaO_3$

$NaTaO_3$ was synthesized by the solvo-combustion method in concordance with the procedure reported by our group [16], where $NaTaO_3$ was formed by a reaction between tantalum (V) ethoxide (99.98% Sigma Aldrich) and sodium acetate (98% DEQ) in stoichiometric amounts. The reaction mixture was kept at 70 °C under stirred and refluxed for a time of 30 min. Then, 1 mL of nitric acid was added and the flask immediately placed onto a hot plate at 180 °C during 5 min. The obtained product was annealed at 600 °C for 2 h. The obtained $NaTaO_3$ powder was applied by screen printing on a copper substrate area ($1 \times 1\ cm^2$) to form the $NaTaO_3$ film. Later, this sample was used as working electrode for electrodeposition of RuO_2 and subsequently, in the experiments of photoelectrochemical hydrogen production. The amount of powder applied on the copper substrate was 1.2 ± 0.1 mg.

2.2. Synthesis of RuO_2 on $NaTaO_3$

RuO_2 was incorporated on each $NaTaO_3$ film by chronopotentiometry technique from an electrolytic solution with a chemical composition of 1.0 M HNO_3 + 0.01 M $RuCl_3$ (both from Sigma Aldrich), which was kept at 40 °C. Before the experiments, the solution was bubbled with O_2 for 1 h. The electrochemical experiments were carried out in a conventional three-electrode cell; platinum wire and saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrochemical tests were conducted using a potentiostat/galvanostat AUTOLAB PGSTAT302N equipment coupled to a computer with the NOVA 1.10 software for control of the experiments and data acquisition. The applied current for electrodeposition of RuO_2 on the $NaTaO_3$ surface was $0.5\ mA\ cm^{-2}$ with different duration time in order to obtain three electrodes containing 1, 2 and 3 wt.%. of RuO_2, respectively.

2.3. Structural, morphological and optical characterization

The crystal structure of the powder was analyzed by X-ray diffraction (XRD) using Cu Kα radiation (1.5406 Å) in a Bruker D8 Advance X-ray diffractometer. The surface morphology and elemental distribution were analyzed using a scanning electron microscope (SEM) in a JEOL 6490 LV equipment coupled with an energy dispersive X-ray spectroscopy detector (EDS). X-ray photoelectron spectra of photocatalysts were recorded using a Perkin-Elmer Phi 560 XPS/Auger system.

In order to determinate the band gap energy (E_g), Tauc's plot was employed from the acquired data of absorbance spectra using the transformed diffuse reflectance technique according to the Kubelka–Munk theory. UV–Vis spectrophotometer (Lambda 35 Perkin Elmer Corporation) equipped with an integrating sphere attachment was used for optical absorption measurements.

2.4. Photoelectrochemical study

The electrochemical experiments were carried out in a conventional three-electrode photoelectrochemical quartz cell in a 0.5 M Na_2SO_4 aqueous solution at room temperature. The photoelectrodes fabricated were used as working electrodes; Platinum wire and saturated Ag/AgCl were used as counter and reference electrodes, respectively. In this work all potentials are reported with respect to Ag/AgCl electrode. The photocurrents were recorded under simulated solar light (AM1.5G, $100\ mW\ cm^{-2}$) with a 450 W Xe-lamp. The experiments were performed under inert atmosphere and at room temperature. The activity of RuO_2–$NaTaO_3$ for the hydrogen evolution reaction (HER) was studied by linear voltammetry and chronoamperometry techniques. The PEC cell was connected to a Shimadzu's versatile GC-2014 (TCD) gas chromatograph equipment for hydrogen quantification. Before measurements, the chromatograph was calibrated for hydrogen and oxygen with the next reference gases containing 99.998% H_2 and 99.999% O_2, respectively.

3. Results and discussion

3.1. Synthesis, preparation and characterization of RuO_2–$NaTaO_3$ electrode

The RuO_2–$NaTaO_3$ photoelectrode was prepared as follow: $NaTaO_3$ nanocubes were firstly synthesized by the solvo-combustion process to obtain a powder, which was coated in the form of a film on ITO substrate by screen printing. The RuO_2 coating on the $NaTaO_3$ films was carried out by electrodeposition technique with a constant applied current from a HNO_3/$RuCl_3$ aqueous solution. Kim et al. [36] have reported the electrodeposition method used in this work to obtain RuO_2.

Fig. 1a shows the XRD patterns registered for the RuO_2–$NaTaO_3$ electrodes. In all cases, the orthorhombic $NaTaO_3$ phase was clearly identifiable in the X-ray diffraction patterns accordingly with the JCPDS 89-8061. Additionally, an enlargement (Fig. 1b) in the 2θ range 27–37° shows the presence of small peaks that have been associated to RuO_2 (JCPDS 70-2662).

Fig. 2 shows: (a) SEM image and its corresponding (b) EDS spectrum of the RuO_2–$NaTaO_3$ film on the copper substrate. Fig. 2a reveals that two different morphologies of RuO_2–$NaTaO_3$ electrode are present. The analysis EDS indicated that cube-like agglomerated structures correspond to $NaTaO_3$, while the small spherical particles are associated to the RuO_2 compound. The chemical analysis by EDS (Fig. 2b) showed that the film contains only Cu, Na, Ta, Ru and O. The measured weight percentage of RuO_2 (2.1 wt.%) agrees with the expected one, i.e., 2.0 wt.%.

In order to determine the optical properties and calculate the energy band gap (E_g) of the RuO_2–$NaTaO_3$ films, additional experiments of UV–vis spectroscopy were conducted. Fig. 3a shows the absorbance spectra of the RuO_2–$NaTaO_3$ films. It is clear to observe that the light absorption in visible region increases with increasing RuO_2 content. This behavior is attributed to the resonant oscillation of conduction electrons at the interface between RuO_2 and $NaTaO_3$ as it has been mentioned in the literature [35]. This phenomenon is stimulated by incident light provoking an enhancement ultraviolet light emission and increase of visible light absorption. Tauc's plot (Fig. 3b) was constructed from the absorbance spectrum. According to the Kubelka–Munk equation [37,38], absorption coefficient (α) can be calculated using reflectance data:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s} \qquad (1)$$