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Synthesis and characterization of Au-Pd/$NaTaO_3$ multilayer films for photocatalytic hydrogen production

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ABSTRACT

Sodium tantalate ($NaTaO_3$) multilayers were prepared on indium–tin oxide (ITO)-coated glass substrates by a facile screen printing method. The surface of multilayer $NaTaO_3$ films was coated using a gold-palladium (Au-Pd) sputtering target. The films were characterized by UV–vis spectroscopy, X-ray powder diffraction (XRD) scanning electron microscopy (SEM) and electrochemical techniques. The photo-corrosion test showed a good chemical stability for all $NaTaO_3$-multilayers prepared. The effect on the hydrogen evolution reaction of the number of $NaTaO_3$ layers (1–4) and amount of Au-Pd deposited was analyzed through photocatalytic reaction under UV irradiation of 254 nm-wavelength. The presence of Au-Pd alloy enhances the photocatalytic behavior of $NaTaO_3$ films. The $NaTaO_3$ bi-layer film with 30 s of Au-Pd coating showed the highest photocatalytic activity producing 3305 μmol H_2/g.

1. Introduction

In recent years the environmental pollution and depletion of fossil fuels have opened a great area of opportunity for the study of alternative fuels that are nowadays a critical issue for the society. The conversion of solar energy into hydrogen via water-splitting process assisted by a semiconductor catalyst, is one of the most promising technologies among the methods to produce alternative energy for the future [1]. From this manner, large quantities of hydrogen can be potentially generated in a clean and sustainable manner [2]. Since the discovery of hydrogen evolution through photoelectrochemical water splitting on n-type TiO_2 by Fujishima and Honda [3], a wide range of semiconductor materials have been developed as photocatalysts for use under solar irradiation such as TiO_2, $SrTiO_3$, Nb_2O_5, $NaTaO_3$, ZrO_2, MnS, CuS, ZnS and so on [4].

Particularly, $NaTaO_3$ powder has been reported as an efficient catalyst material for water splitting under UV irradiation [5]. Several works have been reported related to the enhancement of the photocatalytic activity of $NaTaO_3$ by the incorporation of metal cations doping and/or loading with metal oxides or pure metals as co-catalysts [5–7]. Moreover, it has been reported that the photocatalytic activity of $NaTaO_3$ is enhanced with the addition of nanoparticles of noble metals like Au and Pd [8–10], where the metal acts as a hydrogen evolution active site. Additionally, the effect of the synthesis methods on the persistent photocatalytic activity of $NaTaO_3$ has been systematically studied by several authors [11,12], since the photocatalytic activity depends on various physical parameters of the photocatalyst, such as the particle size, surface area, morphology, etc.

Since the actual photocatalytic systems requires that the catalyst materials are placed onto a substrate without degradation, several film deposition techniques have been used, like sputtering [13], sol-gel deposition [14], electron beam-induced deposition [15], spin coating [16] and screen printing [17]. Particularly, screen-printing technique is widely applied in the development of solar cells [17] and has also been used in lesser extent for photocatalytic processes [18]. It is cheap, easy to use, has no power consumption and a wide range of materials can be deposited by this method; resulting in films with good adherence and properties. Additionally, the use of a multilayer system of coupled semiconductors and metals with adequate conduction energy levels favors the separation of charge carriers avoiding the recombination of electron-hole pair, which is a phenomenon that reduces the effectivity of the material [19–21].

Therefore, this work was focused on the development of a multilayer system integrated by $NaTaO_3$ films and Au-Pd onto ITO-

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coated (indium-tin oxide) glass substrate. The prepared multilayer films (ITO/$NaTaO_3$/Au-Pd) were used as photocatalyst for hydrogen production from the water splitting reaction.

2. Experimental

2.1. Materials preparation

2.1.1. Preparation of $NaTaO_3$ paste

$NaTaO_3$ used in this work has been synthesized by a solvo-combustion method previously reported by our group elsewhere [12]. In order to form a screen-printable paste, the obtained $NaTaO_3$ powder was mixed with acetic acid and then grinded in a mortar, subsequently distillated water and ethanol were incorporated to the mixture and grinded again for 30 min. The mixture was transferred to a beaker with ethanol, which was sonicated in ultrasonic bath by 30 min. Afterwards, terpineol and ethyl cellulose were added and once again, the mixture was sonicated. Finally, the mixture was placed onto a hot plate to evaporate the solvent excess and thus obtain the $NaTaO_3$ paste.

2.1.2. Preparation of $NaTaO_3$ multilayer films

To prepare the $NaTaO_3$ films, the ITO glass was first cleaned in acetone, isopropyl alcohol and distilled water using an ultrasonic bath for 30 min. One, two, three and four-layer pastes were coated on the ITO glass substrates by screen-printing. The screen is made of polyester, with mesh count 90T mesh/cm and mesh opening 60 μm. For a single-layer film, the employed amount of $NaTaO_3$ paste was 0.1 mg to obtain a film of 300 nm thickness and an area of 1.0 cm^2 (S1). For the double-layer film, the first layer was dried at 120 °C during 10 min under air atmosphere and then a second layer of $NaTaO_3$ was deposited by screen-printing (S2); the same procedure was used to deposit the three and four layers in S3 and S4 samples. Finally, each obtained film was annealed at 400 °C for 2 h to eliminate the organic compounds.

Additionally, a thin film of Au-Pd bimetallic alloy was deposited on $NaTaO_3$ film from an Au-Pd target (60 wt.% Au and 40 wt.% Pd) by means of sputtering technique, using a Denton Vacuum Desk IV coater at different deposition time. Table 1 shows the different configurations of multilayer films of $NaTaO_3$ and Au-Pd/$NaTaO_3$ on ITO substrates.

2.2. Structural, morphological, optical and electrical characterization

Crystallinity, morphology and absorbance for all Au-Pd/$NaTaO_3$ films were determined. The crystalline structure was analyzed with a D-8 Advance X-ray diffractometer (Bruker AXS) with Cu Kα radiation. A scanning electron microscopy (JEOL JSM-6490LV) was used to observe morphology and thickness of the films. The determination of optical properties was carried out using a UV–vis spectrophotometer (Agilent Technologies, Cary 5000). Sample resistance was measured using 4-point probe method for all films.

2.3. Photoelectrochemical characterization

The electrochemical characterization was carried out by means of chronoamperometry, linear voltammetry and electrochemical impedance spectroscopy techniques. The experiments were conducted in a quartz conventional electrochemical cell of three-electrodes under UV light with wavelength of 254 nm and 4400 μW cm^{-2}. To carry out these experiments, the $NaTaO_3$ multilayer films on ITO substrate were used as working electrode; Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The measurements were controlled with a potentiostat-galvanostat equipment (Autolab, PGSTAT302N). The chemical composition of the aqueous electrolytic solution used was 0.5 M Na_2SO_4.

2.4. Photocatalytic hydrogen production

The water splitting reaction was carried out in a hermetic glass bach type reactor using a 4400 μW cm^{-2} Pen-Ray® lamp of 254 nm. The $NaTaO_3$ and Au-Pd/$NaTaO_3$ films were placed into the reactor, and then it was added 200 mL of deionized water; previously, the reaction system was purged during 15 min with N_2 gas. The hydrogen production reaction was conducted without adjusting the pH, at room temperature, and the hydrogen evolution was measured in intervals of 30 min during 3 h with a gas chromatograph equipment (Thermo Scientific, Trace GC Ultra) with a TCD detector using nitrogen gas as carrier.

3. Results and discussion

3.1. Structural and morphological characterization of samples

The XRD pattern of $NaTaO_3$ films obtained by screen-printing method is shown in Fig. 1(a) and it corresponds to a monoclinic structure, accordingly to the JCPDS-01-074-2477 file. The presence of some additional peaks was detected, corresponding to the secondary orthorhombic symmetry phase, $Na_2Ta_4O_{11}$ (JCPDS-00-038-0463), [12]. When $NaTaO_3$ is deposited on the substrate it is possible to observe the peaks corresponding to ITO-coating in glass substrates according to JCPDS 01-089-4598 in all samples.

Fig. 1(b) corresponds to the XRD patterns of $NaTaO_3$ bi-layer films (samples S5–S8), which are coated with Au-Pd bimetallic particles. It can be observed that no changes in the diffraction patterns of $NaTaO_3$ films were detected. Furthermore, no gold or palladium signals were detected in the XRD patterns corresponding to S5 and S6, due to its low-deposited amount.

The cross-sectional SEM image of the four-layer film (S4) presented in Fig. 2 shows that $NaTaO_3$ layer is perfectly stable and adhered to ITO substrate, it is important to indicate that the S1–S3 presented the same behavior, not showed here, but their average measured thickness is shown in Table 1. Accordingly to results, it is possible to observe that screen-printing method allows a good

Table 1
Conditions for the deposition, thickness, sheet resistance and weight% of films.

Sample	$NaTaO_3$ (# layers)	Film thickness (nm)	Sheet resistance (Ω/cm^2)	Au-Pd alloy Deposition time, (min)	Au-Pd alloy (Weight%)
S1	1	304	240	–	
S2	2	540	225	–	
S3	3	770	230	–	
S4	4	1113	310	–	
S5	2	540	185	0.5	0.94 ± 0.2
S6	2	–	–	2	6 ± 0.8
S7	2	–	–	3	9.6 ± 0.51
S8	2	–	–	4	16.1 ± 0.32
S9	0	–	–	0.5	–
S10	2	–	–	0.5	–