Synthesis and characterization of Au-Pd/NaTaO₃ multilayer films for photocatalytic hydrogen production

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ABSTRACT

Sodium tantalate (NaTaO₃) multilayers were prepared on indium–tin oxide (ITO)-coated glass substrates by a facile screen printing method. The surface of multilayer NaTaO₃ 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 photocorrosion test showed a good chemical stability for all NaTaO₃-multilayers prepared. The effect on the hydrogen evolution reaction of the number of NaTaO₃ 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 NaTaO₃ films. The NaTaO₃ bi-layer film with 30 s of Au-Pd coating showed the highest photocatalytic activity producing 3305 μmol H₂/g.

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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 TiO₂ by Fujishima and Honda [3], a wide range of semiconductor materials have been developed as photocatalysts for use under solar irradiation such as TiO₂, SrTiO₃, Nb₂O₅, NaTaO₃, ZrO₂, MnS, CuS, ZnS and so on [4].

Particularly, NaTaO₃ 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 NaTaO₃ 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 NaTaO₃ 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 NaTaO₃ 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 effectiveness of the material [19–21].

Therefore, this work was focused on the development of a multilayer system integrated by NaTaO₃ films and Au-Pd onto ITO-
coated (indium-tin oxide) glass substrate. The prepared multilayer films (ITO/NaTaO₃/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 NaTaO₃ paste

NaTaO₃ 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 NaTaO₃ powder was mixed with acetic acid and then grinded in a mortar, subsequently distilled water and ethanol were incorpo-rated 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 NaTaO₃ paste.

2.1.2. Preparation of NaTaO₃ multilayer films

To prepare the NaTaO₃ 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 NaTaO₃ paste was 0.1 mg to obtain a film of 300 nm thickness and an area of 1.0 cm² (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 NaTaO₃ 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 NaTaO₃ 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 NaTaO₃ and Au-Pd/NaTaO₃ on ITO substrates.

2.2. Structural, morphological, optical and electrical characterization

Crystallinity, morphology and absorbance for all Au-Pd/NaTaO₃ 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 photoelectrochemical 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 NaTaO₃ 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 Na₂SO₄.

2.4. Photocatalytic hydrogen production

The water splitting reaction was carried out in a hermetic glass batch type reactor using a 4400 μW cm⁻² Pen-Ray® lamp of 254 nm. The NaTaO₃ and Au-Pd/NaTaO₃ 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 N₂ 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 NaTaO₃ films obtained by screen-printing method is shown in Fig. 1(a) and it corresponds to a monoclinic structure, according to the JCPDS-01-074-2477 file. The presence of some additional peaks was detected, corresponding to the secondary orthorhombic symmetry phase, Na₂Ta₂O₇ (JCPDS-00-038-0463), [12]. When NaTaO₃ 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 NaTaO₃ 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 NaTaO₃ 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 NaTaO₃ 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>
<thead>
<tr>
<th>Sample</th>
<th>NaTaO₃ (# layers)</th>
<th>Film thickness (nm)</th>
<th>Sheet resistance (Ω/cm²)</th>
<th>Au-Pd alloy Deposition time, (min)</th>
<th>Au-Pd alloy (Weight%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>304</td>
<td>240</td>
<td>–</td>
<td>0.94 ± 0.2</td>
</tr>
<tr>
<td>S2</td>
<td>2</td>
<td>540</td>
<td>225</td>
<td>0.5</td>
<td>6 ± 0.8</td>
</tr>
<tr>
<td>S3</td>
<td>3</td>
<td>770</td>
<td>230</td>
<td>2</td>
<td>9.6 ± 0.51</td>
</tr>
<tr>
<td>S4</td>
<td>4</td>
<td>1113</td>
<td>310</td>
<td>3</td>
<td>16.1 ± 0.32</td>
</tr>
<tr>
<td>S5</td>
<td>2</td>
<td>540</td>
<td>185</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>S6</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>S7</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>S8</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>S9</td>
<td>0</td>
<td>–</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>S10</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>0.5</td>
<td>–</td>
</tr>
</tbody>
</table>
control of thickness and adherence. Furthermore, Table 1 also shows the values of the electrical resistance of NaTaO₃ film with different thickness. The results indicate that the lowest electrical resistance was obtained by the bi-layer film, which indicates that this film has the highest electron mobility. Moreover the addition of Au-Pd bimetallic particles (S5) decreased the value of electrical resistance of bi-layer film.

EDS results revealed that Au-Pd/NaTaO₃ bi-layer films presented an homogeneous atomic distribution of gold and palladium, samples S5–S8. The mass percentage was obtained by the average of the weight measurements in an analytical balance as a function of deposition time and the results are summarized in Table 1.

3.2. Optical properties of samples

From absorbance data and using the Kubelka-Munk function, the band gap ($E_g$) value for NaTaO₃ films was determined. The calculated $E_g$ value for samples S1–S4 were 3.90 ± 0.04 eV. This result indicates that the $E_g$ value does not depend on the thickness of the film.
The addition of Au-Pd bimetallic particles on the NaTaO₃ multilayer films causes a significant increase of the absorbance in the visible region, indicating an enhanced light capture. In this case, as the amount of Au-Pd covering NaTaO₃ film increased, the films were darkened, thus the absorption of irradiation increases and decreases in visible and UV region, respectively. In previous reports [8,9] it has been proven that loading of gold into NaTaO₃ powder causes an absorption band in the visible region. In another work [10] the Pd-doping on NaTaO₃ powder also enhanced absorption in visible region. However, in our work the material is not doped, therefore we could not expect any activity in visible region, just an effect in the absorbance properties of the films, which will provoke that NaTaO₃ allows the improvement of the electron-hole separation in order to show better photocatalytic activity.

3.3. Electrochemical characterization (band structure determination)

The flat-band potential and number of carriers were determined from constructing the Mott-Schottky plots using the next equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_{eo} \varepsilon A N_D} \left( E - E_B - \frac{k_B T}{e} \right)$$

where \(C_{eo}, \varepsilon, \varepsilon_{eo}, N_D, E, E_B, k_B\) and \(T\) are the capacitance of the space charge region, area, dielectric constant of the semiconductor, permittivity of free space \((\varepsilon_{eo} = 8.8542 \times 10^{-12} \text{F/m})\), elementary charge \((e = 1.602 \times 10^{-19} \text{C})\), donor density (electron donor concentration for an n-type semiconductor or hole acceptor concentration for a p-type semiconductor), applied potential, flat band potential, Boltzmann constant and temperature, respectively. Therefore, a plot of \(1/C^2\) vs. \(E\) should yield a straight line from which \(E_B\) can be determined from the intersection on the \(E\) axis. The value of \(N_D\) can also be conveniently obtained from the slope knowing \(\varepsilon\) and \(A\). Fig. 3 shows a comparison of the Mott-Schottky plots for S1 and S4. In this Figure it is clear to observe that in both cases a positive slope is obtained, which is inversely proportional to \(N_D\). From these results it is possible to propose that the NaTaO₃ is a n-type semiconductor, as well as that highest concentration of electron donor is for S1.

The flat-band potential value for NaTaO₃ was \(-1.03 \pm 0.05\) eV vs. NHE and the valence band was calculated from the subtraction of \(E_g\) value of 3.90 eV plus the conduction band value, to obtain 2.87 eV. Kato and Kudo in a previous work [22] calculated a value of \(-1.06\) eV vs. NHE for the conduction band and a value of 2.94 eV value for the valence band, such values are very similar to those obtained here. Moreover, the slope increases with an increment in NaTaO₃ film thickness, suggesting that the four layer film has the lowest donor density according to Eq. (1).

The Schottky barrier height (\(\Phi\)) for an n-type semiconductor is defined as the difference between the work function (\(W\)) of the metal and the electron affinity (\(\chi\)) as is indicated in Eq. (2) [23].

$$\Phi = W - \chi$$

The work function values for Au and Pd are reported in the literature [24], which are 5.1 and 5.2 eV, respectively. From Eq. (2) the calculated \(\Phi\) values were 1.05 and 1.15 eV, which are approximately equal. These results indicate that the Fermi level of Au-Pd bimetallic particles must be located below the conduction band and then act as an electron collector.

Additional analysis (linear sweep voltammetry) was made to find out the Fermi Level of Au-Pd bimetallic particles. Fig. 4 shows the obtained voltammogram on Au-Pd electrode, it is clear to observe that at \(-0.3\) V the current starts to increase; this value can be associated with the Fermi level value for Au-Pd alloy. From these results it is possible to construct the band diagram as shown in Fig. 5.

The energy band diagram illustrated in Fig. 5 indicates that the position of conduction and valence bands are adequate for photocatalytic water splitting and that the incorporation of Au-Pd will enhance the collection of electrons for proton reduction.

3.4. Photocatalytic hydrogen production test

The hydrogen production as a function of number of layers of NaTaO₃ is observed in Fig. 6. It was found that the highest hydrogen production (571.5 μmol/g) was achieved with the bi-layer film (S2) which has a thickness of around 540 nm. These results indicate that when the film thickness is greater than three times the wavelength lamp (254 nm) the electron-hole recombination rate increases and the activity of the material decrease, according to Suib [25].

From the above results, the sample S2 was selected to deposit different amounts of bimetallic particles Au-Pd in order to enhance the hydrogen production. The effect of amount of Au-Pd in NaTaO₃ bi-layer film on the hydrogen production is observed in Fig. 7. According to results, the largest activity was achieved for sample S5, which corresponds to NaTaO₃ film containing 0.94 wt.% of

[Fig. 3. Mott-Schottky plot of NaTaO₃ film indicates that this material is a n-type semiconductor.]

[Fig. 4. Voltamperogram of Au-Pd in NaTaO₃ film allow us to associate it with the Fermi level value of Au-Pd bimetallic particles.]
Fig. 5. Band structure scheme of NaTaO₃ film, which indicates that the position of conduction and valence bands are adequate for photocatalytic water splitting and the incorporation of Au-Pd will enhance the hydrogen production.

![Fig. 5](image)

Fig. 6. Hydrogen production from water splitting using NaTaO₃ films of different thickness. Sample S2 shows higher activity than S1, S3 and S4.

![Fig. 6](image)

Fig. 7. Effect of the amount of Au-Pd in NaTaO₃ films on the hydrogen production, where it is observed that when the amount of Au-Pd increases, the hydrogen production is diminished.

![Fig. 7](image)

bimetallic particles Au-Pd. This film has an increment of 6 times in the activity of the material without the co-catalyst since it promotes charge separation and generation of active sites for hydrogen evolution on NaTaO₃ film. The NaTaO₃ semiconductor film has enough activity compared with other oxides in the form of a film (Table 2), which makes it an excellent material to be used in devices where you need to apply as a semiconductor film.

Fig. 7 also indicates that when the amount of Au-Pd increases, the hydrogen production is diminished. In the literature [23] it is reported that height of the Schottky barrier in the metal-semiconductor junction increases with the amount of metal, which provokes a decrement in the Fermi level value. If the Fermi level is more negative than the conduction band, the electron transference from NaTaO₃ to Au-Pd bimetallic particles is not possible.

On the other hand, hydrogen production efficiency can be also attributed to the better dispersion of bimetallic particles Au-Pd in the surface of NaTaO₃ film. The increment of the percentage in mass of bimetallic particles causes the formation of agglomerates in the surface of the NaTaO₃ film, hindering UV-light absorption (Fig. 6) and reducing the number of excited charges.

In the literature [30] it has been mentioned that the determination of quantum yield is an important parameter to characterize the water splitting process, which is defined as:

\[
AQY(%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100
\]  

(3)

where AQY is an apparent quantum yield because the number of absorbed photons is usually smaller than the incident light. The calculations of AQY are shown in Fig. 8, in which it is possible to observe that the highest values correspond to S2 and S5 for the films without and with Au-Pd film, respectively. These results allow us to propose that high amount of Au-Pd on NaTaO₃ film causes a decrement in the absorption of light. Opposite case is observed at low concentration of Au-Pd, in where this metallic alloy acts as an electron collector.

The quantum yield of the different films was calculated from Eq. (3) and is presented in Fig. 8, it can be observed that the values confirm the previous results. Sample S5 is the one that shows the highest quantum yield because presented a bi-layer film and the minor amount of Au-Pd deposited.

3.5. Photoelectrochemical hydrogen production test

The Nyquist plots (Fig. 9) were obtained for NaTaO₃ films (S1–S5) at a single potential of −0.8 V. It can be seen that bi-layer and three-layer films have a smaller radius of semicircle that the
Comparison of hydrogen production using different oxide materials as films.

<table>
<thead>
<tr>
<th>Material film</th>
<th>Hydrogen production</th>
<th>Experimental conditions</th>
<th>Lamp type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-doped-TiO₂</td>
<td>15.5 μmol/h</td>
<td>Photoelectrochemical process, NaOH 1 M solution at pH 13</td>
<td>250W-Tungsten halogen lamp</td>
<td>[26]</td>
</tr>
<tr>
<td>Cr-doped-TiO₂</td>
<td>5.3 μmol/h</td>
<td>Photoelectrochemical process, NaOH 1 M solution</td>
<td>300W-high pressure mercury lamp</td>
<td>[27]</td>
</tr>
<tr>
<td>Ti[TNT]/N-I-P/NaTaO₃</td>
<td>8.73 μmol/h·cm²</td>
<td>Photocatalytic process Water solution</td>
<td>250W-Tungsten halogen lamp</td>
<td>[28]</td>
</tr>
<tr>
<td>Cr-doped-TiO₂-6 bilayer</td>
<td>24.4 μmol/h</td>
<td>Photoelectrochemical process, NaOH 1 M solution</td>
<td>250W-Tungsten halogen lamp</td>
<td>[29]</td>
</tr>
<tr>
<td>TiO₂ thin film</td>
<td>12.5 μmol/h</td>
<td>Photoelectrochemical process, NaOH 1 M solution</td>
<td>4400 μW cm⁻² Pen-Ray¹ lamp of 254 nm</td>
<td>This work</td>
</tr>
<tr>
<td>NaTaO₃</td>
<td>33 μmol/h</td>
<td>Photocatalytic process Water solution</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. The quantum yield of the different films shows that the highest values correspond to S2 and S5 for the films without and with Au-Pd film, respectively.

Fig. 9. The Nyquist plots for NaTaO₃ films (S1–S5) show that bi-layer and three-layer films have smaller radius of semicircle than single-layer and four-layer films.

Fig. 10. Linear sweep voltammetry for different films (S1–S5), where the bi-layer film exhibits better activity for hydrogen evolution reaction (HER) than S1, S3 and S4 films.

Linear sweep voltammetry was carried out for different films (S1–S5) and it is shown in Fig. 10. As it is observed, bi-layer film exhibits better activity for hydrogen evolution reaction (HER) than the films with another thickness (S1, S3 and S4). By adding Au-Pd the performance of the bi-layer film is enhanced, thus at the same potential the sample S5 showed significantly higher current density. These results can be attributed to the shift in the Fermi level (pseudo-Fermi Level) of the metal-semiconductor system to more negative potentials. The explanation of this phenomena is because when the noble metal-semiconductor system is irradiated with UV light, photoexcited electrons are transferred from the semiconductor to the metal particles until the pseudo-Fermi level equilibrates, getting closer to the conduction band of the semiconductor. This shift in the pseudo-Fermi level improves the charge separation and the reductive potential of the system [25,31].

The generation of photocurrent by varying the NaTaO₃ number of layers was reproducible for several on-off cycles of illumination Fig. 11, as the thickness of the film plays a significant role in charge transport and, hence, in photocurrent output of the system. Sample S5 is also included to observe the effect of Au-Pd addition. On-Off curves indicate that all the current generated by the films is due to the photoresponse of the materials; in darkness there is not current generation. NaTaO₃ bi-layer film (S2) had the highest photoresponse, followed by S3, S1 and S4. This result suggests that there is an optimum thickness that will yield the best results. The transient behavior depends strongly on the density and energy of single-layer and four-layer films, which can be attributed to the lower charge-transfer impedance. Similar behavior was observed on the Au-Pd on NaTaO₃ film, which presented the lowest radius of semicircle in Nyquist plots. These results are in agreement with the electrical resistance values presented in Table 1.
the trapping states, which was previously established in the slope of Mott–Schottky plots. In this case, the photoelectrochemical results are in concordance with the photocatalytic tests, where the NaTaO$_3$ bi-layer film showed the highest activity for the hydrogen evolution.

When Au-Pd are deposited onto the NaTaO$_3$ bi-layer film (S5), the photoresponse decays as the generated electrons are trapped by Au-Pd instead of reaching the ITO back contact and produce current. However, photocurrent generated by S5 shows a more stable behavior than that of S2, suggesting a lower rate of recombination.

4. Conclusions

In conclusion, NaTaO$_3$ films were deposited on ITO-coated glass by a simple, cheap and effective screen-printing method. The films presented good crystallinity, adherence and uniformity. It was found that multilayer configuration of NaTaO$_3$ film favors photocurrent generation and photocatalytic activity since thickness plays an important role in charge transport. The bi-layer film has less electrical resistance value and less charge-transfer impedance than films with other thickness. Moreover, bi-layer film has a greater density of carriers than single-layer film. Au-Pd layer deposition over NaTaO$_3$ film enhances charge separation and creates active sites for hydrogen reduction, improving its photocatalytic performance. The film consisting of two layers of NaTaO$_3$ and 0.5 min of Au-Pd deposition had a hydrogen production of 3305 μmol/g, which was the highest among all samples. These can be attributed to the adequate height of the Schottky barrier in the semiconductor/metal interface and the better dispersion of Au-Pd particles in the surface of NaTaO$_3$.

References