

Sensitization of TiO₂ Photoelectrodes Using Copper Phthalocyanine for Hydrogen Production

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Abstract—The effect of the photoelectrode sensitization with copper phthalocyanine (CuPc) was studied by means of the absorption of this organometallic compound on the surface of TiO₂ film. Infrared absorption spectra (FTIR analysis) was used for characterization of CuPc thin film deposited, then, the hydrogen production was evaluated by exposure to a source of visible light and sunlight. The results showed activation of the photoelectrode in the visible region, and under sunlight the current flow in sensitized photoelectrode is higher than to non-sensitized photoelectrode.

Keywords: Titanium dioxide, sensitization, phthalocyanine, photoelectrochemical cells.

I. INTRODUCTION

The increase in energy demand, the almost exclusive dependence on fossil fuels and the intensification of the environmental pollution problems are sufficient reasons to implement alternatives that guarantee energetic sustainability, the preservation of the environment and the sustainable development [1] [2]. In this sense, one of the biggest challenges in today is to reduce the dependence of these fuels through abundant and clean alternatives, in such a way that are viable compared to existing, as it is the case of the sunlight. It is estimated that the energy radiated from the sun that reaches the earth's surface is 10.000 times more than what is used today, whereby, is one of the most important sources of green energy, however and in spite of this has contributed little to the total energy production [3]. The conversion of solar energy into other useful energy source involves different types of process, among which is the photonic process, in which solar photons are absorbed to convert its energy into electricity (photovoltaic cell), or stored as chemical energy through a chemical reaction (water photoelectrolysis) [4].

The photoelectrochemical water splitting process is a low-cost method for the generating of hydrogen fuel, which is based on semiconductor materials to be used as photoelectrodes, which absorb solar photons with energy equal or higher than its band gap to generate the electron-hole pair, that constitutes the starting point of the process, here the efficiency conversion of energy is mainly determined by the properties of the materials to be employed as photoelectrodes [5], [6]. TiO₂ has been one of the most widely used materials in these type process due to their stability in aqueous electrolytes, however, the absorption threshold of this semiconductor does not allow the use of visible light, its band gap energy (3.2eV) allows it to absorb electromagnetic radiation in the ultraviolet range, that constitutes about 4% of the incident solar energy on earth [7], [8]. To overcome the problems of high energy required due to the separation of the bands in the TiO₂ which leads to inefficient utilization of the solar spectrum. Sensitization with organometallic pigments as phthalocyanine has been an alternative, where the sensitizing compound absorbs incident light, to continue the injection of electrons from its excited state to the conduction band of the TiO₂ and the photogenerated hole was scavenged by a redox couple in solution [9]. The objective of this research is to observe the sensitization effect with copper phthalocyanine in TiO₂ photoelectrodes for the hydrogen production in a photoelectrochemical cell.

II. MATERIALS AND METHODS

A. Materials and instruments

Titanium dioxide (Degussa P25) was used as semiconductor, and a copolymer based on acrylate-n-butyl and styrene (ACRONAL 295D) for the elaboration of films, foils aluminium, graphite and glass (6 cm² area, 1 mm thick) were used as substrate. Copper phthalocyanine was used for sensitization of photoelectrodes. As visible light source was used a lamp of 500 W and wavelength of 600 nm. The cell assembly and quantification of hydrogen produced in the process were performed using procedures and conditions described in [10].

B. Preparation of photoelectrodes

The procedure described in [10] was used for the preparation of photoelectrodes. For the sensitization process, the photoelectrodes were introduced into a solution containing 0.0115 g of Copper phthalocyanine for 50 ml of ethyl alcohol during 12 hours at room temperature in a free-contaminants environment [11]; then, they were washed with distilled water to remove the excess of sensitizing particles.

C. Photoelectrode Characterization

1) *Fourier Transform Infrared Spectroscopy (FTIR)*: FTIR spectroscopy analysis of the sensitized film was carried out to identify the interaction of the sensitizer agent with semiconductor films. The analysis was performed in a transformed of Fourier Spectrometer (Nicolet 6700) in a range measurement of wavelength from 600 to 4000 cm^{-1} .

D. Quantification of the hydrogen production

The system was exposed to visible light and sunlight to determine the performance of the sensitized photoelectrodes. Exposure was held during a period of 2 hours. Quantification of hydrogen production was performed as described in [10]. The mass was calculated using Faraday law [12], which is expressed in the following equation:

$$m = \frac{It}{F} * \frac{M}{n} \quad (1)$$

where m is hydrogen mass (g), I electric current (A), t is the time (s), F is the Faraday constant (96485 C/mol), M is the molar mass of the substance (g/mol), n is the number of electrons exchanged in electrochemical reaction.

III. RESULTS AND DISCUSSION

E. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 shows the spectrum of the thin film of CuPc consisting in a macrocyclic compounds containing four pyrrole units, each of the pyrrole nuclei is fused to an aromatic nucleus (phthalocyanine compounds), the copper atom is located in the center of the molecule and coordinated to the nitrogen atoms of pyrrole units.

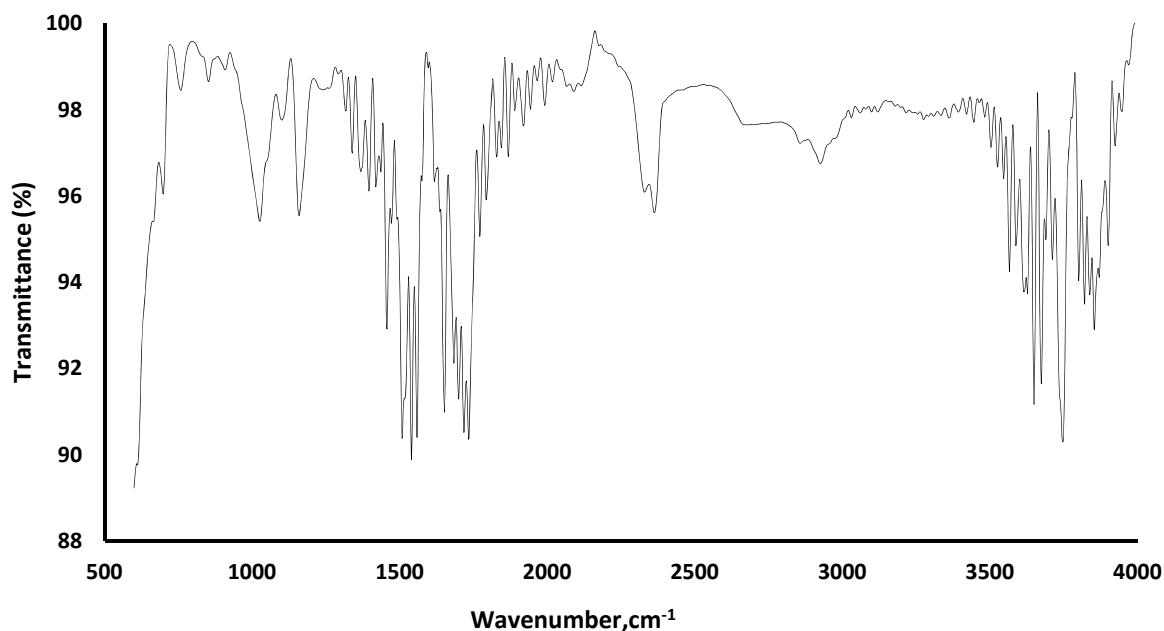


Fig. 1. FTIR spectrum of film supported

The weak vibrations between 1600 – 2000 cm^{-1} containing overtones corresponding to the C – C bond present in the aromatic ring [13]. In the area between 1605 and 1450 cm^{-1} there are four bands corresponding to bending vibration of the C=C bond, the band located at 1508 cm^{-1} are assigned to the vibration caused by C = N bond of the pyrrole ring [14]. The characteristic absorption band corresponding to the N-Cu bond, which is outside the range of wavenumber worked (lower wave number) for that reason is not identified in this IR spectrum [15].

In this spectrum the presence of the C – Cl bond is observed at 700 cm^{-1} [16], because it is a halogenated phthalocyanine with chlorine, where the hydrogen atoms of the aromatic rings have been substituted by chlorine, gaining the compound greater resistance to light, thermal stability and resistance to acidic medium [17].

F. Quantification of the hydrogen production with sensitized photoelectrodes

- *Photoelectrolysis under the irradiation of visible light*

Figure 2 represents the behavior of the photocurrent generated in the cell during the exposure of photoelectrodes to visible light source. The current has a non-linear behavior. The maximum photocurrent registered was $1845\text{ }\mu\text{A}$, corresponding to the film deposited on aluminium, followed by $1421\text{ }\mu\text{A}$ with film on glass and $1202\text{ }\mu\text{A}$ with film on graphite. The hydrogen flow is shown in Table 1.

Hydrogen production at the cathode and oxygen at the anode under exposure to visible light source is attributed to the phthalocyanine absorbed over the TiO_2 film as sensitizing, for being this a photoactive compound in the visible region [18], where the sensitizer molecules on the TiO_2 surface absorb visible light to excitation loads, which generates an electronic vacancy in the HOMO level, to generate a photoexcited electron on LUMO level, then the electron transfer occurs to the conduction band of TiO_2 . According to [10], the exposure to visible light of the photoelectrodes without sensitizing had no effect of charge separation on the semiconductor, so this complex sensitizing extend the absorption range of the photoelectrode to this spectrum. In addition, there are recent reports of this process, where hydrogen production is more efficient under visible light illumination with photoelectrodes coated with sensitizing substances [19].

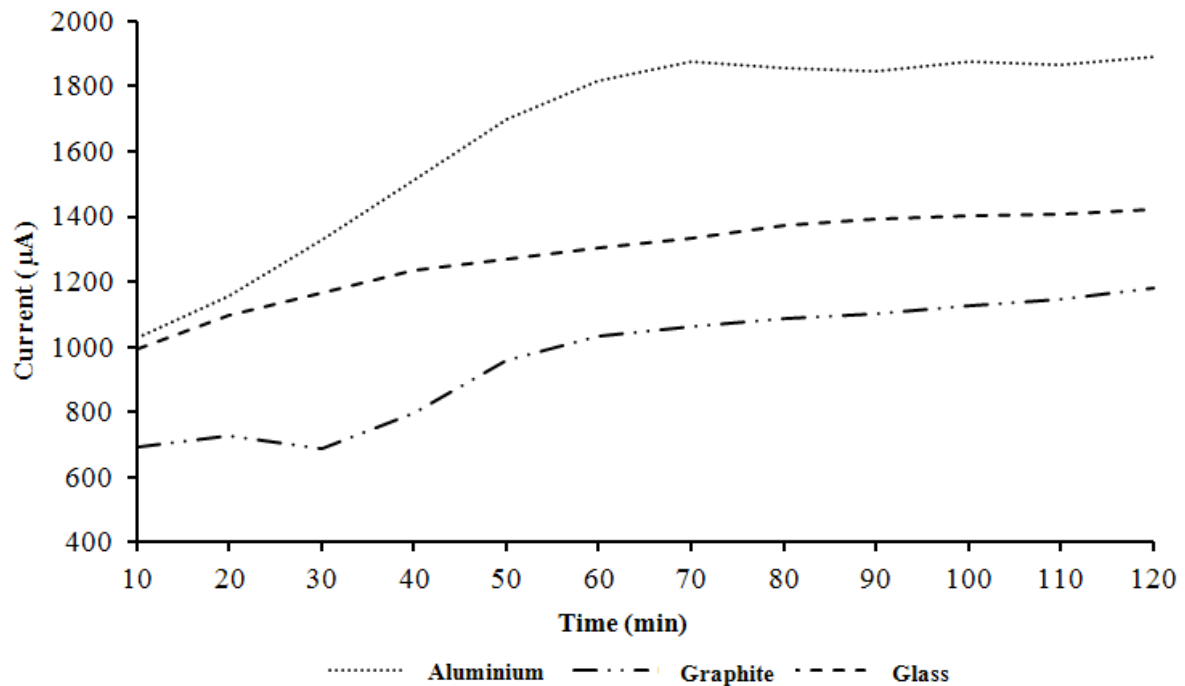


Fig. 2. Current generated with cell irradiated using visible light

TABLE I. Current and mass values obtained with the different photo-electrodes sensitized irradiated with visible light

Substrate	Film	I_{Avg} (µA)	Mass flow of H_2 (µg/s)
Aluminium	TiO_2	1624.67	0.0168
Graphite	TiO_2	939.65	0.0097
Glass	TiO_2	1268.52	0.0131

- *Photoelectrolysis under the irradiation of sunlight*

Table 2 shows the results of the hydrogen flow obtained with each photoelectrode exposed to sunlight, resulting highest production on aluminium photoelectrode, followed by glass and finally the graphite in the same way as in the previous tests.

TABLE II. Current and mass values obtained with the different photoelectrodes sensitized irradiated with sunlight

Substrate	Film	I _{Avg} (μ A)	Mass flow of H ₂ (μ g/s)
Aluminium	TiO ₂	1301.41	0.0135
Graphite	TiO ₂	517.39	0.0053
Glass	TiO ₂	884.28	0.0092

IV. CONCLUSIONS

The photocurrent generation and consequent hydrogen generation in a PEC was achieved through sensitized TiO₂ photoelectrodes. The sensitization with halogenated copper phthalocyanine allowed to extend the range of light absorption of photoelectrodes into visible region of the electromagnetic spectrum, generating better use of sunlight, manifested in a small increase in the flow of hydrogen generated with each of the photoelectrodes. The photoelectrode of aluminium showed a higher performance than the other photoelectrodes during exposure to light.

ACKNOWLEDGMENT

The authors of this paper are grateful to the University of Cartagena by providing the means employed to carry this research.

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