

# Preparation and Characterization of Titanium Dioxide Photoelectrodes for Generation of Hydrogen by Photoelectrochemical Water Splitting

Alvaro Realpe<sup>#1</sup>, Diana Núñez<sup>#2</sup>, Isabel Carbal<sup>#3</sup>, María T. Acevedo<sup>#4</sup>, Gezira De Avila<sup>#5</sup>

<sup>#</sup>Department of Chemical Engineering,  
Research Group of Particles and Processes Modeling, Engineering Faculty,  
University of Cartagena, Cartagena, Colombia

<sup>1</sup>arealpe@unicartagena.edu.co

<sup>2</sup>diana.p30@hotmail.com

<sup>3</sup>cristy\_8538@hotmail.com

**Abstract**—The photoelectrochemical water splitting for the production of hydrogen was evaluated through the preparation of photoelectrodes of different substrates (glass, aluminium, graphite) with TiO<sub>2</sub> film. The film on each substrate was characterized by scanning electron microscope (SEM) and x-ray diffraction (XRD). The results show that the TiO<sub>2</sub> was deposited in dispersed form and in small clusters on the surface of the substrate and it had no effect on the crystal structure of the semiconductor; furthermore, good adhesion of the films on substrates was obtained except with graphite substrate. The hydrogen production process was carried out using UV light, halogen light and sunlight as photon sources, and it was evaluated by the current flow through the external circuit of the cell. The highest photocurrent values were obtained with the aluminium photoelectrode, averaging 1092.03  $\mu$ A.

**Keyword**- Titanium dioxide, photoelectrochemical cells, photoelectrodes.

## I. INTRODUCTION

In today's world, energy and its processing play an essential role in life and have a direct impact on all sectors of the economy, areas where it is used include transportation, domestic work and industry, with the ever growing of global population there is a continuous increase in this energy demand [1], [2]. Fossil fuels such as coal, oil and natural gas satisfy more than 85% of these energy needs, which associated leads a combustion process to transform the chemical energy of these fuels in other forms of useful energy, this situation has unleashed a global problems associated with pollution, generated gases and the non-renewable nature of these fuels [1]. This has stimulated exploration of new systems that guarantee energy sustainability and at the same time limiting greenhouse gas emissions, and thus to mitigate high levels and adverse effects of the current contamination [3].

As alternative energy source, hydrogen is considered an ideal fuel which can be obtained from various sources of energy, the success of the use of hydrogen energy lies in the development of efficient and cost-effective technologies for their production as when it is made from water and sunlight through of a dissociation photo-electrochemical process [4],[5],[6]. Recognized as one of the most promising ways for the development of hydrogen as an energy carrier, considering the resources, environment and costs [7]. In turn, the implementation of the photoelectrochemical process for obtaining hydrogen, offers in according with [8] the potential to produce hydrogen using sunlight without an external cost for insertion of a photovoltaic system and the losses associated with this external source, in addition, an effective conversion of photons to hydrogen of 43.4% has been obtained using TiO<sub>2</sub> nanotubes [9]. Furthermore, the selection of an appropriate substrate is an important preliminary step in accurately evaluating electrochemically active materials including photoelectrodes, the substrate is typically defined as an inert, electrically conductive support onto which a material of interest can be deposited, but the substrate also needs to fulfill a variety of additional requirements for specialized studies. Key properties of the substrate may include thermal stability, mechanical strength, and chemical stability, among others. Thus, the selection of an appropriate substrate can be very important [10]. This research is based on the preparation and evaluation of glass, aluminium and graphite to be used as support for the preparation of TiO<sub>2</sub> photoelectrodes to obtain hydrogen through a photoelectrochemical water splitting process.

## 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) as solvent for preparation of suspension. Distilled water and sulfuric acid 98% (manufactured by MERK) were used for the preparation of the electrolyte solution. As substrate for TiO<sub>2</sub> films were used glass, graphite and aluminium sheets (6 cm<sup>2</sup>). Two lamps of 4W power and wavelength of 365 nm were used as a UV light source, a lamp of 500W with wavelength of 600 nm as visible light source.

### B. Preparation of photoelectrodes

The technique of spray painting was used for the preparation of photo- electrodes. The dispersion was carried out using P25 TiO<sub>2</sub> (0.5 g) in a solution of water and Acronal (ratio 30% v/v) to ensure proper adhesion of the films on the substrates. Solution dispersion was subjected to a process of agitation of 850 rpm on a plate with magnetic stirring for 20 minutes. To coat the substrates was used a spray gun, in this process the application distance was kept constant; film adhesion to substrates was enhanced by heat treatment (250 °C for 3 hours - the temperature used for this treatment was determined by the thermal resistance of the glass). This procedure resulted in the formation of the TiO<sub>2</sub> film on the substrates, constituting the photoelectrodes.

### C. Photoelectrode Characterization

1) *X – Ray diffraction (XRD)*: XRD analysis was used in this research in the supported films in order to check the composition and structure of the crystalline phases of Degussa P25 TiO<sub>2</sub> altered after being deposited on different substrates and the respective heat treatment. The crystal size was determined by the following equation [11]:

$$D_c = \frac{\kappa\lambda}{B \cos\theta} \quad (1)$$

where  $D_c$  is size of crystal in nm,  $\kappa$  is a dimensionless constant which varies according to the geometry of the particles,  $\lambda$  wavelength of the incident radiation (0.15406 nm),  $B$  is the width of the height half of each peak of diffraction (measurement in radians) and  $\theta$  is the Bragg angle of each diffraction peak.

The content of the anatase phase was determined by the following equation [12]:

$$\% \text{ anatase phase} = \frac{100}{1 + 1.26 \left(\frac{I_R}{I_A}\right)} \quad (2)$$

where  $I_R$  and  $I_A$  represent the greatest Intensity of rutile and anatase crystalline phases respectively.

1) *Scanning electron microscope (SEM)*: The films morphology deposited on different substrates was observed using a scanning electron microscope, to an acceleration of voltage of 10 kV, 10 μm resolution and magnifications of X2000. An elemental chemical analysis was performed to identify the elemental composition of the films by means energy dispersive x-ray spectroscopy (EDS).

### D. Cell assembly

The photoelectrochemical solar cell consists of a glass box with a useful volume of 255 cm<sup>3</sup>, and an external cooling system, which controls the temperature of the electrolyte solution inside the cell, through the input and output of water flow. Figure 1 shows a schematic representation of the PEC used in this research. In this design a photoelectrode and a counter-electrode are immersed in aqueous electrolyte (H<sub>2</sub>SO<sub>4</sub> solution), which were connected through an external circuit integrated with a system current meter. Photonic source is localized in front of the cell to illuminate the TiO<sub>2</sub> photoelectrode and the light passes through the cell and the electrolyte.

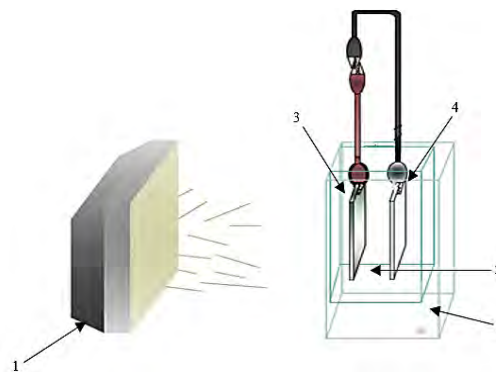


Fig 1. Schematic representation of the PEC used in this research, 1: photon source, 2: cooling system, 3: TiO<sub>2</sub> photoelectrode, 4: cathode of stainless steel of 2cm × 3cm, 5: H<sub>2</sub>SO<sub>4</sub> electrolyte.

### E. Electrolyte

Pure water has a limited capacity of ionization, so it doesn't have enough free ions to the electricity circulation (electrolysis), in this way the addition of sulfuric acid will act as a catalyst to promote the  $H^+$  circulation and also to promote the hydrogen production. 2 ml sulfuric acid were added to 255 ml of distilled water to obtain an electrolytic solution with a pH of 1.

### E. Quantification of the produced hydrogen

The system was exposed to two different wavelengths, UV light, visible light and a third exhibition was performed with sunlight, to determine the performance of the photoelectrodes at each of these variations. The exposure was held during a period of 2 hours. Quantification was effected by quantitative assessment of the pure hydrogen detachment in Steel electrode (counter-electrode), this was carried out by calculation the mass through Faraday law [13], expressed in the following equation:

$$m = \frac{It}{F} * \frac{M}{n} \quad (3)$$

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

## III. RESULTS AND DISCUSSION

### F. X-Ray diffraction (XRD)

The X-ray diffraction patterns of the  $TiO_2$  films supported on different substrates are shown in Figure 2. Film deposited on glass and aluminium present mainly anatase phase where observed the characteristic peaks of this structure at  $2\theta$  of 25.30°, 37.76°, 48.04°, 55.06°, and 62.76°. There are also characteristic peaks of the crystalline rutile phase at  $2\theta$  of 27.36°, 36.06° and 41.22° [12].

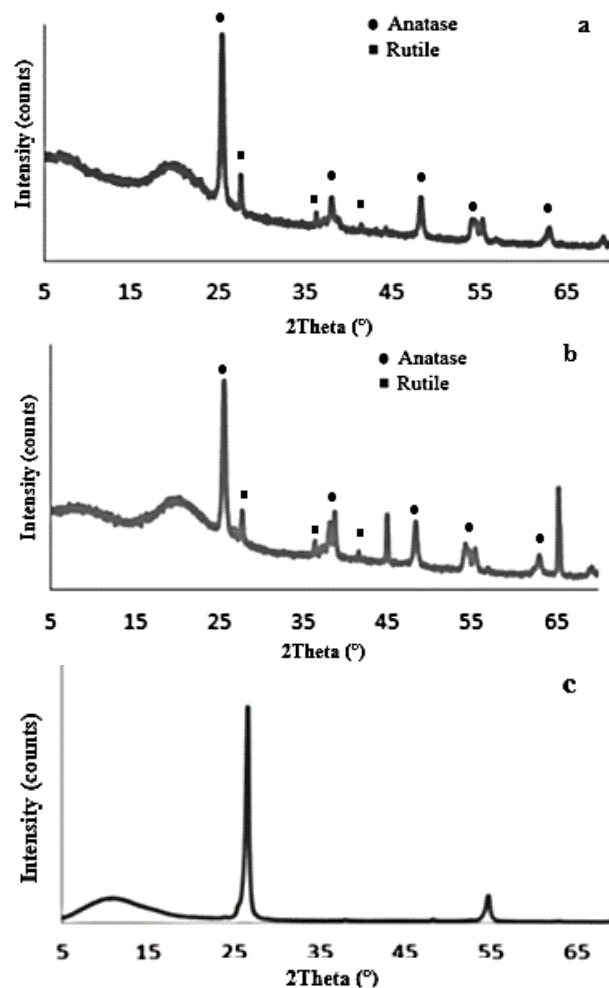


Fig 2. XRD patterns of  $TiO_2$  films supported on: a. Glass, b. Aluminium, c. Graphite.

In the case of the film deposited on graphite, the diffractogram does not show the characteristic peaks of  $\text{TiO}_2$ , this is attributable to the gradual loosening of the film, which did not allow the realization of the corresponding analysis.

Also, it is observed that the intensity of the peak for both patterns (film supported in aluminium and glass) are not different, which ensures that there is no difference in grain size, applying a form factor of 0.9 and employing the angle  $2\theta$  of 25.4. The crystal size is 19.8 nm, which is a resemblance value to the reported [15] for the  $\text{TiO}_2$  that is 21 nm. This crystal size is an important parameter in photoinduced processes since the reactions take place at semiconductor-electrolyte interface, the decrease in the crystal size generates a greater number of active sites in the surface, which improves the photon absorption process and results in a high speed of photo-electrochemical reaction in the photo-electrode [15]. Percentages of 80.6% and 19.4% of the anatase and rutile crystalline phases, respectively, values similar to those reported in the literature, 80% anatase phase and 20% rutile phase form precursor [12]. From these results it was determined that the structure of substrate does not exerts any direct effect on the  $\text{TiO}_2$  crystalline structure, as well as the solvent for the suspension and the heat treatment applied; similar results have been reported on the effect of the glass, aluminium and other substrates [16], which states that any change in the crystalline phase would be associated with the nature of the  $\text{TiO}_2$  slurry and the heat treatment conditions, instead of effect of the substrate structure.

#### G. Scanning electron microscope (SEM)

Fig. 3 shows the surface of the different photoelectrodes, it was observed the  $\text{TiO}_2$  distributed over the whole surface; however, this distribution is not uniform throughout the area of the material, in some regions presented agglomerates, these images showed that the  $\text{TiO}_2$  has a more compact and homogeneous morphology in aluminium substrate, and followed by glass and graphite

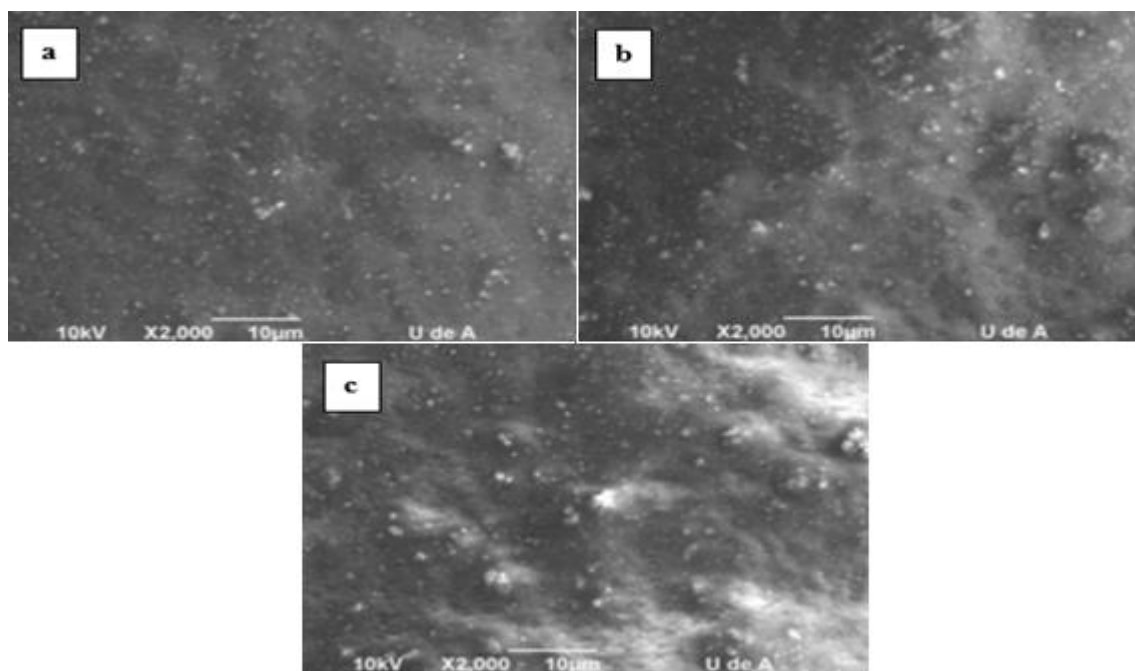


Fig. 3. SEM images for  $\text{TiO}_2$  films supported on: a. Glass, b. Aluminium. C. Graphite

The surface roughness of the substrate, the adhesion strength of the film with the support, preparation protocol and the calcination treatments are determinant factors in the adherence and distribution of  $\text{TiO}_2$  [16],[17]. In this instance, the clusters presented in the film were originated by preparation and impregnation protocol, since the solvent used in its elaboration did not allow proper dispersion of the semiconductor particles. These clusters reduce the surface area available to photonics absorption, which is the main feature that should have a photoelectrode to ensure its efficiency [18]; these imperfections also affect the contact of the charge carriers with the conductive substrate to the external circuit.

Table I shows elemental chemical analysis (EDS) and was found C, O and Ti, which indicates that  $\text{TiO}_2$  is in the support surface. The weight percentage and atomic percentage of each element is shown, where C has highest proportion, due to solvent used, consisting of copolymer based on acrylate n-butyl and styrene, which is constituted by carbonated chains in its molecular structure.

TABLE I  
Elemental analysis, by weight percent and atomic percent

Element	TiO <sub>2</sub> in Aluminium		TiO <sub>2</sub> in Graphite		TiO <sub>2</sub> in Glass	
	% weight	% Atomic	% weight	% Atomic	% weight	% Atomic
C	68.65	76.31	68.32	76.52	68.79	75.67
O	26.90	22.45	26.04	21.90	28.59	23.61
Ti	4.46	1.24	5.64	1.59	2.62	0.72

H. Quantification of the produced hydrogen

- Photoelectrolysis under the Irradiation of UV light

Figure 4 shows the dynamic behavior of the current flowing in the cell, where the current is greater in photoelectrode with TiO<sub>2</sub> film supported in aluminium, followed by photoelectrode with glass and graphite substrate.

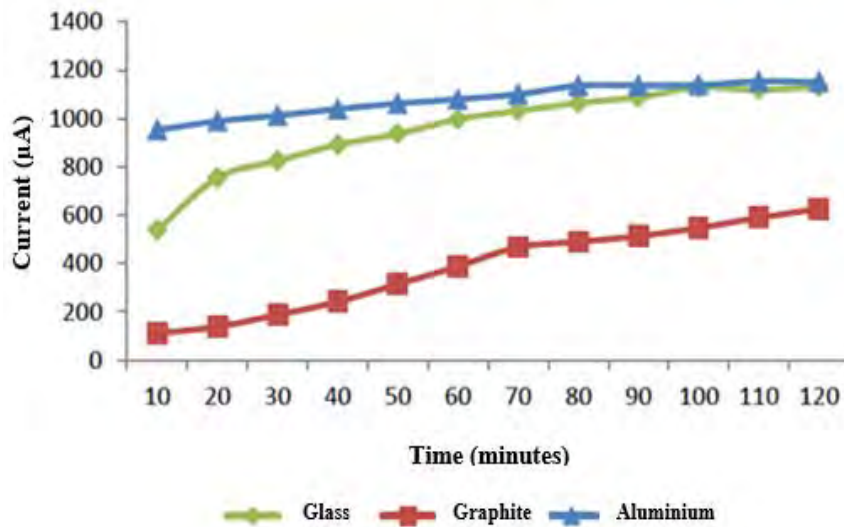


Fig. 4. Current generated by photoelectrochemical cell

The quantity of current generated by cell is associated with imperfections in crystalline structure, surface properties of the film (clusters, detachment), photo-electrodes and, cell capacity to conduct the dissociation reaction, which determined the transfer of hollows across the interface, the transport of electrons from semiconductor and the barriers existence in the interface semiconductor-substrate and semiconductor-electrolyte [16]. The aluminum photoelectrode behavior is due to its conductive character, ensuring a higher speed in the electrons transport. It was expected higher current flow in graphite photoelectrode than glass photo-electrode due to the high resistance of glass to current flow. Previous investigations relating to the use of graphite as substrate for the photoelectrodes manufacture have demonstrated that the roughness graphite surface exerts a favorable effect, ensuring a greater area of contact of the TiO<sub>2</sub> film with substrate [19]. Results obtained with graphite are attributed to low adhesion of the film and its detachment and the low roughness of graphite employed.

TABLE II  
Current and mass values obtained with the different photo-electrodes with UV light

Substrate	Film	I <sub>Avg</sub> (µA)	Mass of H <sub>2</sub> (µg)
Aluminium	TiO <sub>2</sub>	1079.85	80.58
Graphite	TiO <sub>2</sub>	726.13	54.19
Glass	TiO <sub>2</sub>	974.95	72.14

The hydrogen mass produced by each photoelectrode is shown in Table II and these were calculated using the current circulating across the external circuit of the cell (during 120 minutes of irradiation). Quantitative evaluation of pure hydrogen detachment in steel electrode, was carried by calculate the mass using the Faraday's laws equation (3). The amount of hydrogen produced is proportional to the current in the external circuit.

- *Photoelectrolysis under the Irradiation of visible light*

Oxygen and hydrogen gases were not generated by exposing photoelectrode to the visible light source, because the photoexcitation of semiconductor occurs under the incidence of photons with higher energy ( $\lambda \leq 380$  nm) and this light is emitting photons of lower energy (600-700 nm) [20] which is outside the absorption range of TiO<sub>2</sub>.

- *Photoelectrolysis under the Irradiation of sunlight*

With an accumulated radiation of 1310880 J/m<sup>2</sup> (this accumulated radiation is total, the whole electromagnetic spectrum).

TABLE III  
Current and mass values obtained with the different photoelectrodes with sunlight

Substrate	Film	I <sub>Avg</sub> ( $\mu$ A)	Mass of H <sub>2</sub> ( $\mu$ g)
Aluminium	TiO <sub>2</sub>	1092.03	81.49
Graphite	TiO <sub>2</sub>	461.63	34.45
Glass	TiO <sub>2</sub>	830.92	61.94

The table III shows the current and H<sub>2</sub> mass obtained with TiO<sub>2</sub> photo-electrodes exposed to solar radiation. The low performance of these photo-electrodes in the hydrogen production is due to low UV radiation of sunlight (5%) that reaches the earth [21].

#### IV. CONCLUSION

In the present investigation, photo-electrodes of titanium dioxide supported on aluminum, glass and graphite were prepared. It was established that any of these materials has an effect that would alter the crystal structure of titanium dioxide, and consequently the photonics exhibition; however, the surface characteristics of graphite do not allow adequate adhesion of the TiO<sub>2</sub> film, which is a limiting factor for the occurrence of the photo-electrochemical process. Aluminum substrate has the best performance in the process of photo-electrochemical water splitting by its capacity of electrical conduction, which favored the movement of photocurrent. Therefore, the aluminum provides stability during thermal treatments in the preparation of the photoelectrode. The solvent employed favored the adhesion of the films, however too much can promote agglomeration of the particles.

#### ACKNOWLEDGMENT

The authors wish to thank professors who collaborated on this research, and the University of Cartagena for providing the means for the realization of this work.

#### REFERENCES

- [1] M. Orhan, I. Dincer, M. Rosen, M. Kanoglu, Integrated hydrogen production options based on renewable and nuclear energy sources, *Renewable and Sustainable Energy Reviews* 16 (2012) 6059-6082.
- [2] G. Wang, Y. Ling, H. Wang, X. Lu, Y. Li, Chemically modified nanostructures for photoelectrochemical water splitting, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 19 (2014) 35 – 51.
- [3] A. Realpe, J. Diazgranados, M. Acevedo, Electricity generation and wind potential assessment in regions of Colombia, *DYNA*, Vol. 79, núm. 171 (2012).
- [4] L. Jeffery Minggu, W. Ramli Wan Daud, M. B. Kassim, An overview of photocells and photoreactors for photoelectrochemical water splitting, *International Journal of Hydrogen Energy* 35 (2010) 5233 - 5244.
- [5] A. Realpe, L.G. Ricardo, Y. Venecia, M. Cabarca, M. Acevedo, Evaluación Económica de La Energía Solar en Colombia, *Revista Ciencias e Ingeniería al Día*, 5(2010), 21-33
- [6] G. Cipriani, V. Di Dio, F. Genduso, D. La Cascia, R. Liga, R. Miceli, G. Ricco Galluzzo, Perspective on hydrogen energy carrier and its automotive applications, *International Journal of Hydrogen Energy* 39(2014), 8482-8494
- [7] M. Tian, H. Wang, D. Sun, W. Peng, W. Tao, Visible light driven nanocrystal anatase TiO<sub>2</sub> doed by Ce from sol – gel method and its photoelectrochemical water splitting properties, *International Journal of Hydrogen Energy* 39 (2014) 13448 – 13453.
- [8] S. Lindquist, Fuels – Hydrogen production/ Photoelectrolysis, *Encyclopedia of Electrochemical Power Sources* (2009) 369 – 383.
- [9] Z. Zhang, Md. F. Hossain, T. Takahashi, Photoelectrochemical water splitting on highly smooth and ordered TiO<sub>2</sub> nanotube arrays for hydrogen generation, *International Journal of Hydrogen Energy* 35 (2010) 8528 – 8535.
- [10] J. Benck, B. Pinaud, Y. Gorlin, T. Jaramillo, Substrate selection for fundamental studies of electrocatalysts and photoelectrodes: Inert potential Windows in acidic, neutral, and basic electrolyte, *PLoS ONE* 9(10): e107942. doi:10.1371/journal.pone.0107942.
- [11] A. Monshi, M. Reza Foroughi, M. Reza Monshi, Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD, *World Journal of Nano Science and Engineering* (2012) 2, 154-160.
- [12] H. He, A. Chen, M. Chang, L. Ma, C. Li, A feasible hydrogen process of water electrolysis assisted by TiO<sub>2</sub> nanotube photocatalysis, *Journal of Industrial and Engineering Chemistry* 19 (2013) 1112 – 1116.

- [13] G. Zini, P. Tartarini, *Solar Energy Systems: Science and Technology for the Hydrogen Economy*, Springer Science & Business Media, 2012.
- [14] K. Raj, B. Viswanathan, Effect of Surface area, pore volume and particle size of P25 titania on the phase transformation of anatase to rutile, *Indian Journal of chemistry* 48 (2009) 1378 – 1382.
- [15] J. Nowotny, T. Bak, M. Nowotny, L. Sheppard, Titanium dioxide for solar-hydrogen I. Functional properties, *International Journal of Hydrogen Energy*, 32, 2609-2629.
- [16] L. Lopez, W. Daoud, D. Dutta, B. Panther, T. Turney, Effect of substrate on Surface morphology and photocatalysis of large – scale TiO<sub>2</sub> films, *Applied Surface Science* 265 (2013) 162 – 168.
- [17] F. Gracia, Películas delgadas basadas en TiO<sub>2</sub> y MOX /TiO<sub>2</sub> con aplicaciones fotoelectroquímicas y ópticas, Tesis doctoral, Instituto de ciencia de materiales de Sevilla, Sevilla (2005).
- [18] R. Pessoa, M. Fraga, L. Santos, M. Massi, H. Maciel, Nanostructured thin films based on TiO<sub>2</sub> and/or SiC for use in photoelectrochemical cells: A review of the material characteristics, synthesis and recent applications, *Materials Science Semiconductor Processing* 29 (2015) 56-68.
- [19] X. Yua, X. Hana, Z. Zhaob, J. Zhanga, W. Guoa, C. Pan, A. Li, H. Liu, Z. Lin Wang, Hierarchical TiO<sub>2</sub> nanowire/graphite fiber photoelectrocatalysis setup powered by a wind-driven nanogenerator: A highly efficient photoelectrocatalytic device entirely based on renewable energy, *Nano Energy* (2015) 11, 19–27.
- [20] J. Xi, Q. Zhanga, K. Parka, Y. Sunb, G. Caoa, Enhanced power conversion efficiency in dye-sensitized solar cells with TiO<sub>2</sub> aggregates/nanocrystallites mixed photoelectrodes, *Electrochimica Acta* 56 (2011) 1960–1966.
- [21] E. Vargas, R. Vargas, O. Núñez, A TiO<sub>2</sub> surface modified with copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt as a catalyst during photoinduced dichlorvos mineralization by visible solar light. *Applied Catalysis B: Environmental*, 156–157(2014), 8-14.

#### AUTHOR PROFILE

Alvaro Realpe Jiménez is an Assistant Professor of Chemical Engineering Department of University of Cartagena. He received his B.S. in chemical engineering from University of Atlantico, Barranquilla, Colombia, 1998. He received his M.Sc. in chemical engineering from University of Puerto Rico, Puerto Rico, USA, 2002. He received his Ph.D. in chemical engineering from University of Puerto Rico, Puerto Rico, USA, 2007. His research areas include polymeric membrane for fuel cell, renewable energy, photoelectrochemical process and powder mixing.

Diana Nuñez is a chemical engineer of University of Cartagena, Colombia, 2014. She is a research scholar in the Chemical Engineering Program, University of Cartagena. Her area of research interest is hydrogen generation by photoelectrochemical water splitting process.

Isabel Carbal is a chemical engineer of University of Cartagena, Colombia 2014. Her area of research interest is hydrogen generation by photoelectrochemical water splitting process.

Maria Teresa Acevedo is an Assistant Professor of Chemical Engineering Department of University of Cartagena. She received his B.S. in chemical engineering from Universidad Industrial de Santander, Bucaramanga, Colombia, 1999. She received her M.Sc. in chemical engineering from University of Puerto Rico, Puerto Rico, USA, 2005. Her research focuses on polymeric membrane for electrolytic process, carbon dioxide separation and fuel cell. Moreover, she has developed other researches in medical applications as encapsulating of medical drugs and synthesis of polyanhydrides for cancer treatment. Her publications have been reported in the *Desalination Journal* and *Drug Delivery*.

Gezira De Avila is an Assistant Professor of Chemical Engineering Department of University of Cartagena. She received his B.S. in chemical engineering from Universidad de Antioquia, Medellin, Colombia, 1993. She received her M.Sc. in chemical engineering from University Nacional of Colombia, 2007. Her research focuses on biotechnology and biopolymer.