NANOSTRUCTURED TiO_2 SENSITIZED WITH PORPHYRINS FOR SOLAR WATER-SPLITTING

MARCELA-CORINA ROŞU[1], RAMONA-CRINA SUCIU, SIMINA DREVE, T.D. SILIPAŞ, I. BRATU AND E. INDREA

ABSTRACT. – Nanostructured TiO_2 sensitized with porphyrins for Solar water-splitting. The production of hydrogen from water using solar light is very promising for generations of an ecologically pure carrier contributing to a clean, sustainable and renewable energy system. The selection of specific photocatalyst material for hydrogen production in photoelectrochemical cells (PECs) is based on some important characteristics of semiconductor, such as photo-corrosion and chemical corrosion stability, photocatalytic potential, high sensitivity for UV-visible light. In the present paper, different nanocrystalline TiO_2 photoanodes have been prepared via wet-chemical techniques followed by annealing treatment and sensitized with porphyrins and supramolecular complexes of porphyrins. The so obtained photocatalysts were characterized with UV-VIS absorption spectroscopy and spectrofluorimetry. The purpose of these experiments is to show if the prepared materials possess the necessary photocatalytic characteristics and if they can be used with success in H_2 production from water decomposition in PECs.

Keywords: TiO_2, Porphyrins, Ruthenium complex compounds, Sensitizers.

1. INTRODUCTION

The production of hydrogen from water using solar light is a very promising, as a sustainable and renewable energy system. The selection of specific photocatalyst material for hydrogen production in photoelectrochemical cells (PECs) is based on some important characteristics of semiconductor, such as photo-corrosion and chemical corrosion stability, photocatalytic potential, high sensitivity for UV-visible light (Peharz et al., 2007; Zhu and Zäch, 2009).

Photosensitization of wide-band gap semiconductors, such as TiO_2 by visible light absorbing dyes, has become more practical for solar cell applications in the conversion of light into electricity. The sensitization of TiO_2 has been studied extensively in the past (Amao et al., 2004; Campbell et al., 2004; Peng et al., 2008; Rochford and Galoppini, 2008; Kathiravan and Renganathan, 2009a; Zhou et al., 2009).

Porphyrin and porphyrin derivatives are very effective dyes, suitable photosensitizers for photovoltaic conversion of solar to electrical energy due to their strong absorption in the region of 400–450 nm (B or Soret band) as well as in the 500–700 nm (Q bands) (Wang et al., 2007; Kathiravan and Renganathan, 2009b).

[1] National Institute for Research and Development of Isotopic and Molecular Technologies 400293 Cluj-Napoca, Romania, e-mail: marcela.rosu@itim-cj.ro

The presence of different functional anchoring groups (*i.e.* hydroxyl, carboxylate and sulfonate groups) broadens the absorption of photons in the visible region, improves the electron injection efficiency of porphyrins into the conduction band of TiO_2 and it has a good influence to the efficiency of TiO_2–porphyrin systems (Kathiravan and Renganathan, 2009b; Wang et al., 2009).

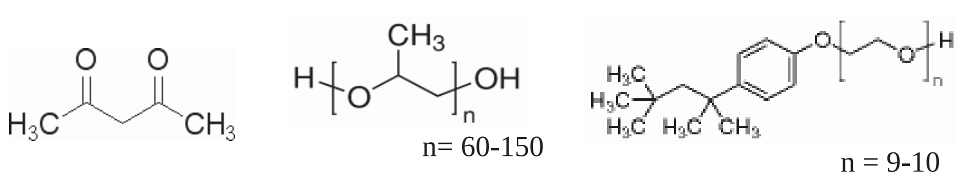
In the present paper, different photoanodes types of nanocrystalline TiO_2 have been prepared via wet-chemical techniques followed by annealing treatment and sensitized with porphyrins and supramolecular complexes of porphyrins. The obtained photocatalysts were characterized using UV-VIS absorption spectroscopy and spectrofluorimetry. The purpose of these experiments is to show if the prepared materials possess the necessary photocatalytic characteristics and if they can be used with success in H_2 production from water decomposition in PECs.

2. EXPERIMENTAL

TiO_2 P25 powder (ca. 80% anatase and 20% rutile; ~ 30 nm in diameter particles) was obtained from Degussa AG, Germany. Besides TiO_2, as starting materials, acetylacetone (Merck, Germany), poly-propylene-glycol (Machery-Nagel, Germany) and Triton X-100 (Fluka, Switzerland) were used without further purification. The solvents, dichlorethane and chloroform were purchased from Merck, Germany and ethanol was obtained from SC PAM Corporation SRL, Romania. The sensitizers used in this work were: protoporphyrin IX (Fluka, USA), *meso*-tetraphenylporphyrin (Alfa Aesar, Germany), tetra-(4-pyridyl)porphyrin (Fluka, USA), tetra-sulfonato-phenyl porphyrin (Fluka, USA) and tris(2,2'-bipyridyl) ruthenium (II) chloride (Fluka, Switzerland). The conductive indium tin oxide glass (ITO, ≤ 20 ohms/sq.) was obtained by Praezision Glas & Optik, Germany. Bi-distilled water was used throughout all the experiments.

In an agate mortar with pestle, 0.6 g TiO_2 was mixed with bi-distilled water, acetylacetone, Triton X-100 and polypropylene glycol in 200:10:5:1 volumetric ratio, until completely homogeneous dispersion.

The structural formulas for the used organic additives are presented in the Figure 1.

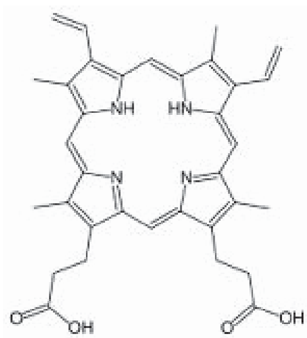


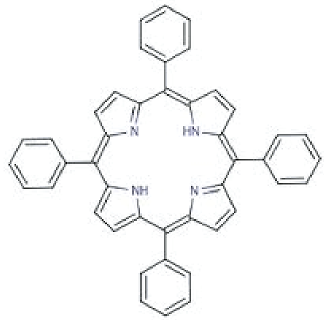
a) *b)* *c)*

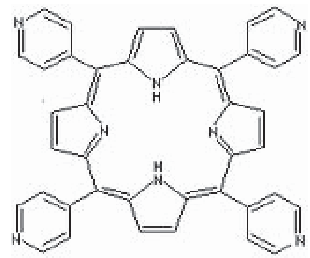
Fig. 1. ***Structural formula of: a) acetylacetone, b) polypropylene glycol and c) Triton-X 100 (http://www.sigmaaldrich.com)***

The prepared paste was deposited onto a ITO glass by doctor blade method in order to obtain five samples. These samples were dried in normal conditions for

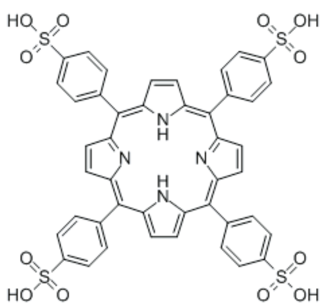
24 hours, and then were heat-treated at 600°C for 90 min., with an increase rate of temperature of 10°C/min. While still warm, the samples were immersed in 10^{-3} M solutions of protoporphyrin IX (PPF-IX), *meso*-tetraphenylporphyrin (TPP), tetra(4-pyridyl)porphyrin (TPyP), tetra-sulfonato-phenyl porphyrin (TSPP) and tris(2,2'-bipyridyl)ruthenium (II) chloride ($(Ru(bpy)_3Cl_2)$), see Figure 2. A mixed dichlorethane and chloroform solution was used to prepare the dyes' solutions. After dye adsorption, the TiO_2-dye layers were rinsed with ethanol.

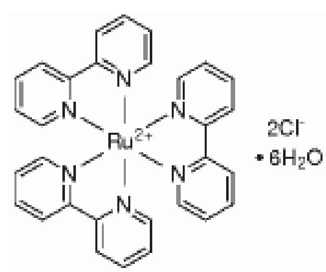






a) ***b)*** ***c)***





d) ***e)***

Fig. 2. ***Structural formula of the used sensitizers:***
a) PPF IX (http://en.wikipedia.org),
b)TPP (http://www.scbt.kr),
c) TPyP (http://www.chemicalland21.com),
d) TSPP (http://www.chemicalbook.com)
e) $Ru(bpy)_3Cl_2$. (http://www.sigmaaldrich.com)

The optoelectronic properties of TiO_2-sensitizer samples have been investigated by using UV-VIS absorption spectroscopy (JASCO V-550 spectrometer) and spectrofluorimetry (ABL&E JASCO V 6500 spectrofluorimeter with xenon lamp).

3. RESULTS AND DISCUSSION

The UV–VIS spectrum of TiO_2 layer without dyes presents an absorption peak maximum at about 320 nm corresponding to the photoactivation of titania by light with energy higher than 3.0-3.2 eV or wavelength less than 400 nm (Fig. 3).

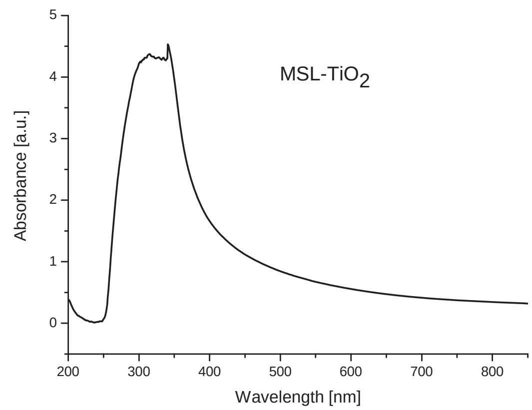


Fig. 3. ***UV-VIS spectrum of TiO_2 sample without sensitizer***

The UV-VIS absorption spectra for nanostructured TiO_2 layers sensitized with porphyrin-type compounds (noted: MSL-PPF IX, MSL-TPP, MSL-TPyP, MSL-TSPP and MSL-$Ru(bpy)_3Cl_2$) are shown in Figure 4.

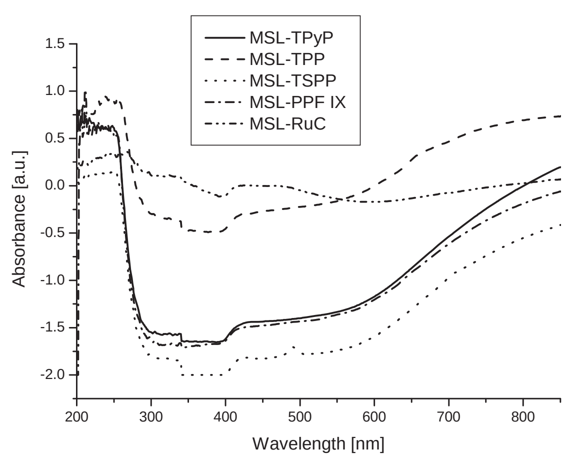


Fig. 4. ***UV-VIS absorption spectra of TiO_2-sensitized samples***

The TiO_2-sensitized layers absorption spectra show the maximum absorption between 230 nm and 260 nm, *i.e.* the sensitized TiO_2 layers absorb light radiation in the UV region. It can be noted that the same types of layers, TPP sensitizer presents a maximum absorption, while TSPP and $Ru(bpy)_3Cl_2$ compounds do not produce a significant absorption and they can not consider the most efficient sensitizers for UV.

The TiO_2 layers sensitized with porphyrins or porphyrin-type compounds are part of photoelectrocatalytic materials class and their efficiency can be determined by measuring the fluorescence spectra of these materials.

Figure 5 illustrates the fluorescence spectra of TiO_2 samples excited at wavelength of 250 nm, whose energy was used to excite the valence electrons and to promote them to the conduction band.

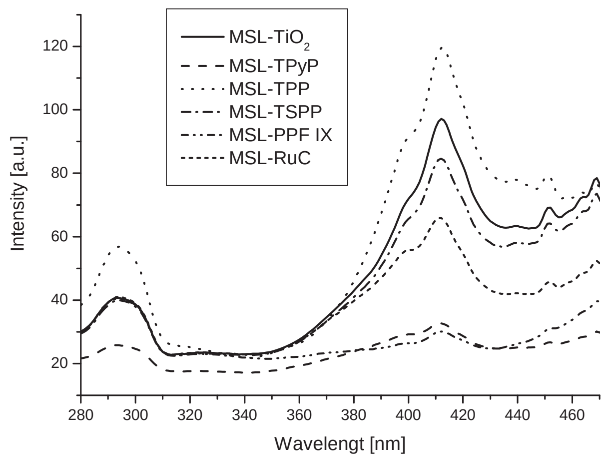


Fig. 5. ***Fluorescence spectra of TiO_2 and TiO_2-sensitized samples***

Two intense emission peaks for all samples can be seen, one in the UV region (~ 295 nm) and another in the visible region (~ 420 nm). The electronic phenomena who give fluorescence are more intense for TiO_2 layer sensitized with TPP in both UV and visible region. The TSPP, PPF IX and ruthenium complex show fluorescence emission of the same intensity as that of titanium dioxide in UV domain but less intense than TiO_2 in the visible region.

3. CONCLUSIONS

Different TiO_2-based layers with various porphyrins-type compounds were prepared and their photoelectrochemical properties were comparatively investigated by UV-VIS absorption and fluorescence.

A correlation between TiO_2 and the five mentioned compounds used in the TiO_2-sensitizer layers was observed. The results are promising regarding the preparation of layers of titanium dioxide sensitized with porphyrin-type compounds in order to obtain photoanodes with applications in PECs for H_2 production from water decomposition.

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