NANOSTRUCTURED TiO$_2$ SENSITIZED WITH PORPHYRINS FOR SOLAR WATER-SPLITTING

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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).

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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 sensitzers 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.

![Fig. 1. Structural formula of: a) acetylacetone, b) polypropylene glycol and c) Triton-X 100 (http://www.sigmaaldrich.com)](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)₃Cl₂ )), see Figure 2. A mixed dichlorethane and chloroform solution was used to prepare the dyes’ solutions. After dye adsorption, the TiO₂-dye layers were rinsed with ethanol.

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)₃Cl₂ (http://www.sigmaaldrich.com)

The optoelectronic properties of TiO₂-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).

![UV-VIS spectrum of TiO$_2$ sample without sensitizer](image1)

**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)$_3$Cl$_2$) are shown in Figure 4.

![UV-VIS absorption spectra of TiO$_2$-sensitized samples](image2)

**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)$_3$Cl$_2$ compounds do not produce a significant absorption and they cannot be considered 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.

![Fluorescence spectra of TiO$_2$ samples](image)

**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 that 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.
REFERENCES