



## THE INFLUENCE OF PEG/PPG AND OF THE ANNEALING TEMPERATURE ON TiO<sub>2</sub>-BASED LAYERS PROPERTIES

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The TiO<sub>2</sub>-based layers were prepared by deposition of the colloidal suspensions on conductive ITO glass and treated one hour at two different temperatures (500°C and 600°C). The TiO<sub>2</sub> colloidal suspensions were prepared in the presence of PEG (polyethylene glycol) and PPG (polypropylene glycol). The effect of the PEG or PPG and the heating temperature on the structural and morphological properties of the TiO<sub>2</sub> photocatalytic layers has been studied by FT/IR spectroscopy, FT/IR microscopy and X-ray diffraction. The optoelectronic properties of the above mentioned photocatalytic layers have been investigated using UV-VIS absorption spectroscopy and spectrofluorimetry. The results of these experiments allowed the selection of PEG as a reasonable additive that determines a better dispersion and adhesion of TiO<sub>2</sub> particles on ITO substrates. Also, the heating temperature of TiO<sub>2</sub> layers at 500°C enhanced their photocatalytic activity due to optimum anatase/rutile ratio in TiO<sub>2</sub> powders.

### INTRODUCTION

Nanocrystalline TiO<sub>2</sub> has gained a great popularity in the semiconductor photoelectrochemical field, the reason being its special chemical (photo corrosion and chemical corrosion stability, photocatalytic potential), electrical (higher electrical conductivity) and optical (optical stability, high sensitivity for UV-visible light) properties.

In recent years, a significant attention has been attributed to nanocrystalline TiO<sub>2</sub> because of its potential applications in a variety of fields such as photoelectrocatalysis,<sup>1-2</sup> solar cells,<sup>3-4</sup> as gas sensor,<sup>5-6</sup> electrochromic devices,<sup>7-8</sup> or in air and water purification systems.<sup>9-10</sup>

Special attention is focused on the preparation and characterization of nano-sized TiO<sub>2</sub>, which is one of the most promising photocatalysts due to its chemical/photochemical stability, high resistance to corrosion and photocorrosion, non-toxicity, economical and available in large amounts.<sup>11-12</sup>

Unfortunately, TiO<sub>2</sub> has a large band gap ~ 3.0–3.2 eV (for the rutile and anatase phases, respectively) which is too large for an efficient photocatalytic activity.<sup>13</sup> Thus, titania (TiO<sub>2</sub>) absorbs only ultraviolet (UV) irradiations of solar light. This part represents about 4% of the incoming solar energy on the earth's surface and therefore it is important to extend the optical absorption of TiO<sub>2</sub> and its photocatalytic activity to the visible-light region that is the main field of solar spectrum.<sup>14-15</sup>

The majority of the layers properties are susceptible to the preparation method, technological parameters of the deposition process and thermal treatment.

The TiO<sub>2</sub> powder (Degussa, P-25) is considered one of the most interesting semiconductors used in photocatalytic processes. It contains anatase and rutile crystalline phases in a percentage proportion of ca. 80% anatase and 20% rutile, which has the optimum ratio between anatase and rutile to show a higher photocatalytic activity.<sup>16</sup> Many previous<sup>17-20</sup>

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studies have characterized the anatase, with a band gap of 3.2 eV corresponding to ultraviolet light region to excite electrons, more photoactive than rutile, which has a band gap of 3.0 eV. However, in thermodynamic terms, rutile is more stable than anatase. So, a combination of the two TiO<sub>2</sub> phases demonstrates a better performance in photocatalytic processes.<sup>21</sup> In agreement with literature, the interaction between these phases at interfaces is a source to the enhancement of the photocatalytic activity and the synergetic effects were described.<sup>18</sup> The lower photoactivity of rutile phase is due in part to rapid rates of recombination between electrons and holes. The coupling of anatase and rutile phases TiO<sub>2</sub> allows the transfer of electrons from anatase to rutile TiO<sub>2</sub> excited by ultraviolet light as a result of the slightly lower conduction band energy of the rutile phase. Consequently, the charges recombination can be suppressed. The charges produced by visible light on rutile are stabilized through electron transfer to lower energy anatase lattice trapping sites.<sup>19</sup> These findings indicate that in mixed-phase TiO<sub>2</sub>, such as Degussa P25, the photogenerated holes are trapped exclusively on the particle surface, while photogenerated electrons are trapped within the nanoparticles lattice. The recombination reactions are dominated by surface reactions that follow charge migration. These facts indicate that, in mixed-phase TiO<sub>2</sub> a random flight mechanism of recombination predominates.<sup>20</sup> The coupled rutile and anatase phase TiO<sub>2</sub> is favorable to enhance the effects of using visible light. Contrarily, excessive adsorption usually prohibits nanometer TiO<sub>2</sub> particles from absorbing both ultraviolet and visible light. It makes the partial surface of the nanometer TiO<sub>2</sub> photocatalyst probably become unavailable for photon absorption, thus bringing little stimulation to the catalytic reaction. Anyhow, the existence of coupled rutile–anatase phase on the surface of heat-treated TiO<sub>2</sub> particles cannot only extend the range of absorption wavelengths. Also, it properly reduces the recombination of photogenerated electron–hole pairs and the adsorption capacity of nanometer anatase TiO<sub>2</sub> particles.<sup>21</sup>

The effects of different additives (*i.e.* polymers) used in the preparation of materials based on titania were also the subject of many studies due to their influence on the surface area and the porosity of the so obtained layers, in general with increasing the surface area and porosity of the prepared materials.<sup>22</sup> PEG is a flexible, water-

soluble polymer that can be used as surfactant, dispersing or solvent in foods, pharmaceuticals or cosmetics industry. It has the chain units of ethylene oxide as the hydrophilic groups and it contains hydroxyl group at each end of the ethylene oxide chain, advantage for wetting performance of TiO<sub>2</sub> nanoparticles (benefit to the wetting performance of TiO<sub>2</sub> nanoparticles). PPG has many properties in common with polyethylene glycol, consequently PPG is used as a surfactant, dispersant or wetting agent and it is less toxic than PEG, reason so the area of biotechnology is more often used than PEG. However, secondary hydroxyl groups in PPG are less reactive than primary hydroxyl groups in polyethylene glycol.

Also, the annealing temperature of TiO<sub>2</sub> layers in obtaining photoelectrodes/photocatalysis is a significant factor affecting the macro/microstructures and their physical-chemical properties (crystal structure, surface area, crystallite size, surface hydroxyl groups) that are correlated with photocatalytic activity.<sup>23</sup>

The aim of this paper was to evaluate the effect of two polymers: PEG and PPG used as additives for colloidal suspensions of TiO<sub>2</sub> particles and the influence of the treatment temperature for TiO<sub>2</sub> prepared layers. The TiO<sub>2</sub> colloidal suspensions were prepared in the presence/absence of PEG or PPG that were chosen because they have terminal hydroxyl groups that may produce hydrogen bond with the surface OH groups in order to form C - O - Ti covalent bonds with the oxide network.

The samples were heat-treated at two different temperatures: 500°C and 600°C. It is known that the process of anatase phase transformation in rutile takes place slowly between 500-600°C. Consequently, the influence of the annealing temperature of the TiO<sub>2</sub> layers on light absorbance in the UV-VIS field and the photocatalytic activity was investigated.

## EXPERIMENTAL

### Coating layers preparation

Titania P-25 (cca. 80% anatase and 20% rutile) was kindly supplied by Degussa AG, Germany. The TiO<sub>2</sub> colloidal suspensions were prepared via wet-chemical techniques, using bi-distilled water, acetylacetone (Merck, Germany), Triton X-100 (Fluka, Switzerland) and PPG (Macherey-Nagel, Germany) or PEG 600 (Macherey-Nagel, Germany) as additives.<sup>24</sup> The 0.3 g TiO<sub>2</sub> was mixed with acetylacetone, Triton X-100 and bi-distilled in the same volumetric ratio, namely 2:3:20. The volume of the two polymers, PEG and PPG, was the same in all experiments - 0.06 mL. The

preparations obtained were processed in an ultrasonic bath for 45 min. Then, the colloidal suspensions were deposited on a conductive indium tin oxide glass (ITO, 20 Ω/square) by spin-coating, 60", 1000 rpm and then were dried in air for 48 hours.

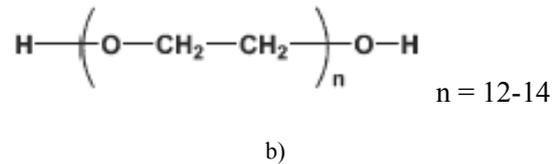
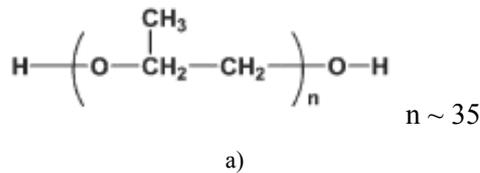


Fig. 1 – The structural formula of polymers: a) PPG si respectively, b) PEG.<sup>25</sup>

The samples were heat-treated one hour at two different temperatures: 500°C and 600°C for 1 hour, with an increase rate of temperature of 10°C/min. The investigated samples were: TP1-500 and TP1-600 (samples with PPG), respectively TP2-500 and TP2-600 (samples with PEG), annealing at mentioned above temperatures. All additives were used without any further purification.

### Coating layers characterization

The thicknesses of the TiO<sub>2</sub> layers were evaluated by weighing method by using Analytical Balance Radwag, Poland, with an accuracy of 0.00001g.

The optoelectronic properties of TiO<sub>2</sub> samples have been investigated using UV-VIS absorption spectroscopy and spectrofluorimetry. The UV-VIS absorption spectra of the prepared layers were registered on a JASCO V-550 spectrometer. The fluorescence spectra were obtained using an ABL&E JASCO V 6500 spectrofluorimeter with xenon lamp.

The effect of the PPG or PEG and of the heating temperature on the structural and morphological properties of the TiO<sub>2</sub> layers has been studied by FT/IR spectroscopy, FT/IR microscopy and X-ray diffraction.

FT/IR spectra of the materials were recorded using JASCO FT/IR - 6100 Fourier Transform Infrared Spectrometer using KBr pellet technique and the FT/IR microscopy images were obtained using by JASCO IRT - 3000 Irtron Infrared Microscope in transmission mode. X-ray diffraction (XRD) measurements were performed using a BRUKER D8 Advance X-ray diffractometer, working at 40 kV and 40mA. The CuK<sub>α</sub> radiation was collimated with Soller slits and a germanium monochromator was used.

## RESULTS AND DISCUSSION

The diffraction patterns of the investigated samples (Fig. 2) illustrate the fact that all titania layers obtained in our synthesis conditions are multiple phase materials containing mainly the tetragonal TiO<sub>2</sub> anatase crystalline phase (PDF card n. 21-1272) and tetragonal TiO<sub>2</sub> rutile crystalline phase (PDF card n. 21-1276).

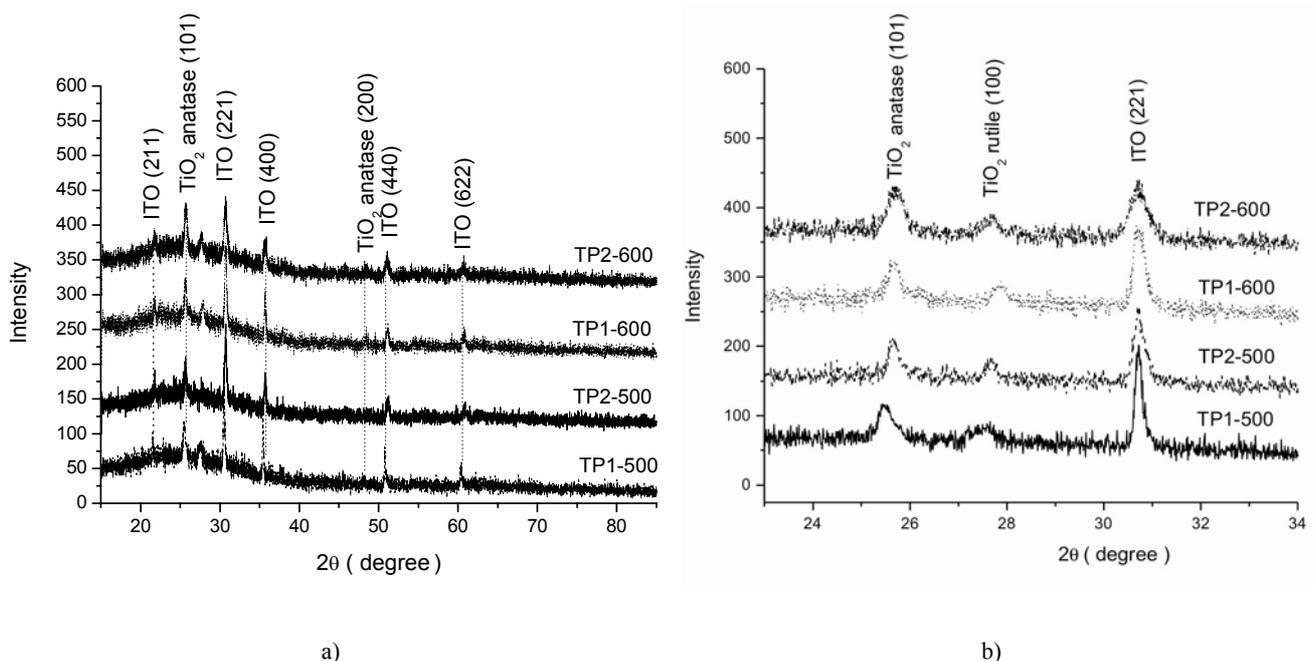


Fig. 2 – X-ray diffraction pattern for TiO<sub>2</sub> samples : a) full 2θ domain and b) 24-34 2θ domain.

The microstructural data obtained by single X-ray profile Fourier analysis of the TiO<sub>2</sub> anatase nanoparticles were the effective crystallite mean size ( $D_{eff}$ ) and the root mean square (rms) of the microstrains, averaged along the  $[hkl]$  direction,  $\langle \epsilon^2 \rangle^{1/2}_{hkl}$ .<sup>26</sup> The Warren-Averbach X-ray profile Fourier analysis of the (101) and of (200) anatase peak profiles were processed by the XRLINE computer program.<sup>27</sup> The unit cell parameters were calculated by Rietveld refinement using the PowderCell software.<sup>28</sup> PowderCell program enables a quantitative phase (volume fractions) analysis method by comparison of the different scattering powers of the component materials. Table 1 presents the change of the relative proportions of rutile phase at different temperatures treatments and different polymer additives. The microstructural properties of TiO<sub>2</sub> layers are also presented in the Table 1.

The  $\langle \epsilon^2 \rangle^{1/2}_{hkl}$  lattice microstrain for TiO<sub>2</sub>/PEG layer shows an increasing value in the intercrystallite zones that suggests an anatase nanocrystallite-PEG additive increasing interaction for photocatalysts annealed above 600°C.

The microstructural parameters of the investigated titania layers show an increase in the average size of the anatase particles from 40 nm to 60 nm for TiO<sub>2</sub>/PPG nanocrystals calcinated at 500°C and 600°C, respectively. For the layers composed by more interactive anatase nanocrystallites-PEG additive the average size of the anatase particles showed an increase from 20

nm to 40 nm when the layers have been thermally treated at 500°C and 600°C, respectively.

In the Table 2 are presented the prepared samples, the thickness of the TiO<sub>2</sub> layers and the values of band gap energy ( $E_g$ ) of TiO<sub>2</sub>.

It was observed that the samples prepared with PEG are thinner than those prepared with PPG, probably due to different kinematic viscosity (~ 50 cSt for PEG and 75 cSt for PPG). Also, the layer thickness is higher for samples treated at 600°C than for the samples heat treated at 500°C. This behavior is based on the crystallite size increase due a temperature rise from 500°C to 600°C (see Table 1).

The band gap energy for the prepared layers was obtained from the UV-VIS spectra. From the solid-state band theory, the absorption coefficient for the direct allowed transition can be described as a function of incident photon energy:<sup>29</sup>  $(\alpha h\nu)^2 = A (h\nu - E_g)$ , where,  $\alpha$  is the absorption coefficient (cm<sup>-1</sup>),  $A$  is a constant,  $h\nu$  (eV) the energy of excitation and  $E_g$  the band gap energy. A quantitative evaluation of the band gap energy can be performed by plotting  $(\alpha h\nu)^2$  vs.  $h\nu$ . The linear extrapolation in the transition region using Tauc's plot<sup>29</sup> on the photon energy-axis gives the value of the direct band gap semiconductors.

It was found that the values of band gap energies of the TiO<sub>2</sub> layers prepared with PPG are lower than the samples prepared with PEG.

Table 1

Anatase/rutile volume fractions and anatase unit cell volume  $V_c$ , effective crystallite mean size,  $D_{eff}$ , mean root mean square (rms) of the microstrains,  $\langle \epsilon^2 \rangle^{1/2}_{hkl}$ , of TiO<sub>2</sub> based samples

Samples	TiO <sub>2</sub> anatase vol. fraction [%]	TiO <sub>2</sub> rutile vol. fraction [%]	Parameter		Anatase unit cell volume [ $\text{\AA}^3$ ]	$D_{eff}$ [nm]	$\langle \epsilon^2 \rangle^{1/2}_{hkl} \times 10^3$
			a [ $\text{\AA}$ ]	c [ $\text{\AA}$ ]			
TP1-500	82	18	3.7425	9.5093	133.190	42.68	2.127
TP2-500	81	19	3.7675	9.4875	134.666	19.33	4.439
TP1-600	78	22	3.7235	9.4324	130.775	60.64	1.246
TP2-600	76	24	3.7291	9.4516	131.434	38.54	2.768

Table 2

TiO<sub>2</sub> samples properties

Samples code	Polymer additive	Temperature treatment (°C)	Layer thickness ( $\mu\text{m}$ )	$E_g$ (eV)
TP1-500	PPG	500	0.258± 6.31%	2.87
TP2-500	PEG	500	0.047±40.42%	2.98
TP1-600	PPG	600	0.326± 5.39%	2.78
TP2-600	PEG	600	0.192±14.16%	3.01

Fig. 3 shows the UV–VIS absorption spectra of the TiO<sub>2</sub>-based layers prepared with PPG or PEG at different annealing temperatures and Fig. 4 presents the fluorescence emission spectra for the same samples at the exciting wavelength of 320 nm.

UV–VIS spectra were recorded in the range of 200–850 nm and it can be seen that absorption edge shifts to shorter wavelengths (about 320 nm) for all TiO<sub>2</sub> samples corresponding to the photoactivation of titania by light with energy higher than 3.0–3.2 eV or wavelength less than 400 nm. However, the absorption of TiO<sub>2</sub> samples prepared with PEG is more intense than those prepared with PPG at the same annealing temperature. Also, the absorption increases for sample of TiO<sub>2</sub> prepared with PPG and heat-treated at 500°C compared with the sample annealing at 600°C. For samples prepared with PEG the absorption intensity is reversed: the sample treated at 600°C shows a peak higher than the one treated at 500°C.

In Fig. 4 are illustrated the fluorescence spectra of TiO<sub>2</sub> samples excited at wavelength of 320 nm, corresponding to photon energy of 3.87 eV (larger

than the band gap of TiO<sub>2</sub>). This energy was used to excite the valence electrons and to promote them to the conduction band.<sup>18</sup> The fluorescence spectra show a broadband emission formed between 350 and 550 nm for all samples and there are several emission peaks superimposed on broadband emission. However, the fluorescence spectra for all four samples are adequate, indicating that the electronic state distributions of TiO<sub>2</sub> samples are similar within the band gap.

The FT/IR microscopy images of the TiO<sub>2</sub> samples upon annealing at high temperatures, are shown in Fig. 5.

The micrograph shows (square dimensions of 100x100 μm<sup>2</sup>) agglomerates with irregular morphology and sizes ranging from few micrometers down to hundreds of nanometer. These images show different distributions of the TiO<sub>2</sub> particles (in dark) but without particle clusters. There are no significant modifications in the morphology of TiO<sub>2</sub> layer surfaces, which suggest that the used polymers have a small effect of surfaces modification.

FT/IR spectra of the TiO<sub>2</sub> samples are shown in Fig. 6.

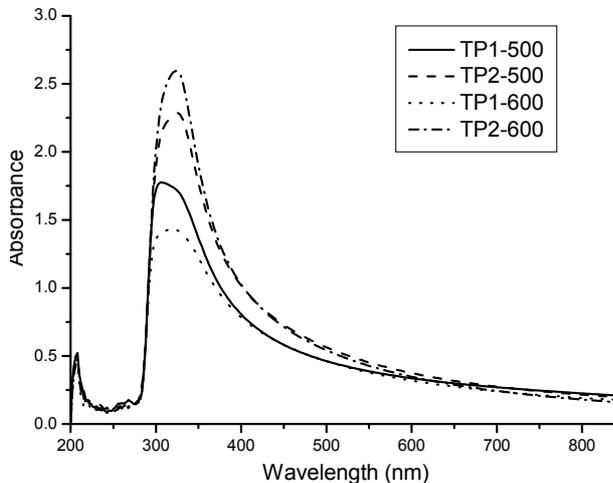


Fig. 3 – UV-VIS spectra of TiO<sub>2</sub> samples.

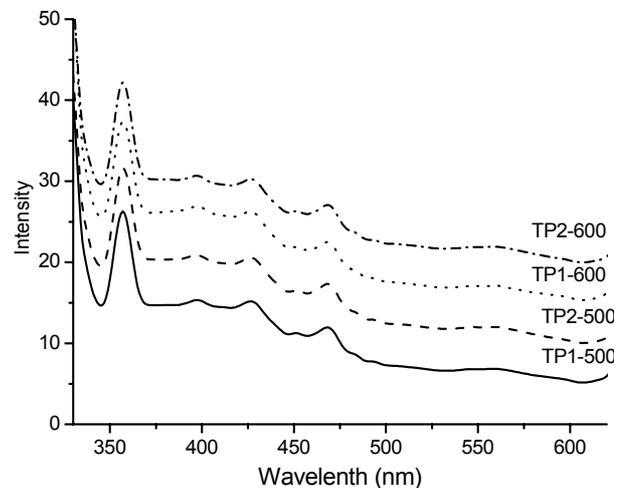
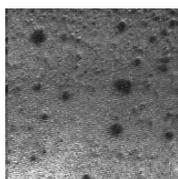
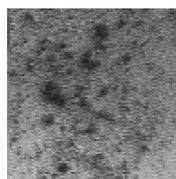


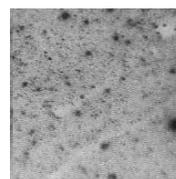
Fig. 4 – Fluorescence spectra of TiO<sub>2</sub> samples.



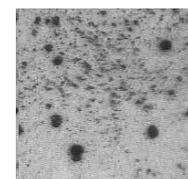
TP 1-500



TP 2-500



TP 1-600



TP 2-600

Fig. 5 – The FT/IR microscopy images of the TiO<sub>2</sub> samples.

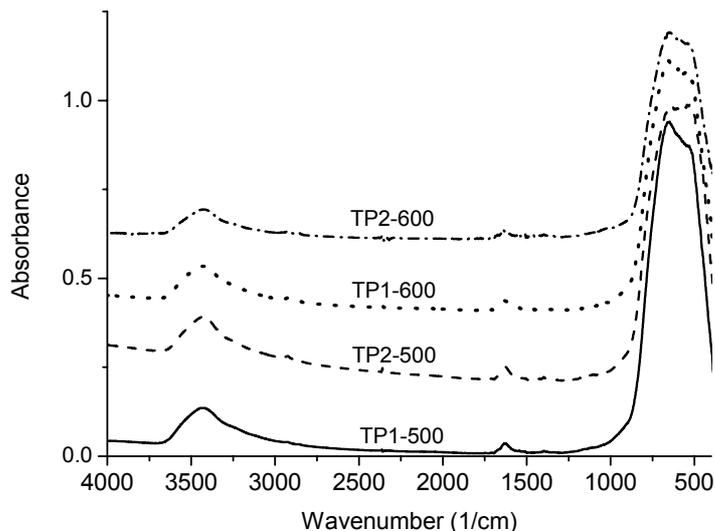


Fig. 6 – FT/IR spectra of TiO<sub>2</sub> samples.

As it is seen from Fig. 6, the broad intense band at  $\sim 650 \text{ cm}^{-1}$  is due to Ti-O-Ti vibrations.<sup>30</sup> There is a broad intense band with maxima at  $3450 \text{ cm}^{-1}$  and a band of lower intensity with maxima at  $1630 \text{ cm}^{-1}$ , both due to (O-H) vibrations of the hydroxyl groups of the adsorbed water molecules and of polymers end hydroxyls. The first band corresponds to the O-H stretching vibration and the other one to the H-O-H bending vibration.<sup>30-31</sup> Also, it can be seen that the intensity of peaks decreases with increasing temperature due to removal of greater amounts of the hydroxyls from TiO<sub>2</sub>. These results show the structural network still retain some hydroxyls.<sup>31</sup> However, the spectrum does not show absorption peaks due to additives used to prepare the TiO<sub>2</sub> samples, which indicates that the organic compounds decompose until the temperature of 500°C.

An adherence test for the titania based layers has been proposed by evaluating the weight loss

after the immersion the TiO<sub>2</sub> layers into a solution of Triton X 1% as surfactant and ultrasonicated for 60 min at 30°C. The samples were dried at 220°C for one hour in order to remove the Triton-X molecules adsorbed on TiO<sub>2</sub> particles. The quantities of titanium dioxide remained on ITO glasses was approximated by weighing method.

The efficiency adherence defined by the percentage-quantitative representation of titanium dioxide remained adherent on ITO glass substrate after the adherence test is shown in Fig. 7.

It was found that the TiO<sub>2</sub> adhesion layer at a temperature of 500°C, in mass percentage, is similar. Instead, at temperature of 600°C, the layers prepared with PPG lose significant initial amount deposited on the substrate.

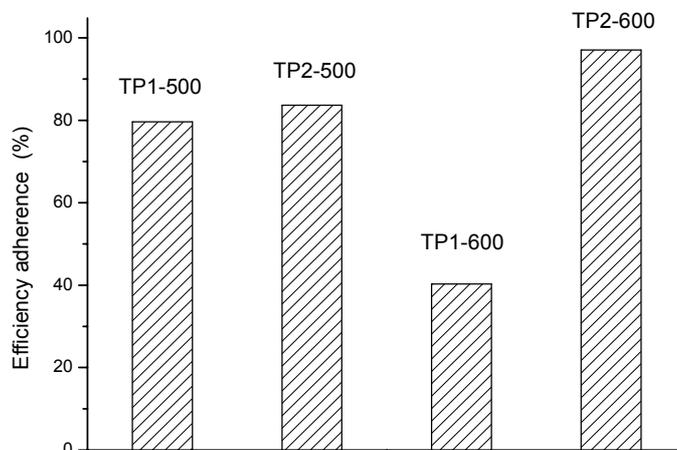


Fig. 7 – Adhesion efficiency of TiO<sub>2</sub> layers prepared with PPG or PEG and treated at 500°C and 600°C.

## CONCLUSIONS

The results of these experiments allowed the selection of PEG which determines a better dispersion and adhesion on substrates of TiO<sub>2</sub> particles. It was accepted that the heating temperature of 500°C for TiO<sub>2</sub> photoanodes enhanced their photocatalytic activity due to optimum anatase/rutile ratio in TiO<sub>2</sub> powders. Also, the annealing at 500°C establishes a good electrical contact among the nanoparticles and leads to formation of a TiO<sub>2</sub>/ITO nanostructured film. The FT/IR spectrum does not show absorption peaks due to additives used to prepare the TiO<sub>2</sub> samples, which indicates that the organic compounds decompose until the temperature of 500°C.

More aggregated average size of TiO<sub>2</sub> nanocrystals (20nm-40nm) for the TiO<sub>2</sub>-based layers prepared with PPG have been obtained. The lattice microstrain  $\langle \epsilon^2 \rangle_{hkl}^{1/2}$  for TiO<sub>2</sub>/PEG layers shows an increased value in the intercrystallite zones suggesting a higher TiO<sub>2</sub> nanoparticles - additive interaction.

The obtained titania-based layers can be used in photoelectrochemical cells (PECs) for hydrogen production.

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