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THE INFLUENCE OF TiO_2 CONTENT IN PREPARATION OF TiO_2/ITO NANOSTRUCTURED FILMS

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Commercial TiO_2 powder (P-25, Degussa) was added in different mass proportions in order to obtain various colloidal suspensions. Three different TiO_2-based films with various mass proportion of composition were prepared and comparatively, their photoelectrochemical properties were studied. An adherence test has been proposed and showed that with the increase of TiO_2 amount, a better adherence of films on substrate was obtained. The thickness of the TiO_2/ITO films and the values of TiO_2 band gap energy are determined. Optoelectronic characteristics, the structural and morphological properties of TiO_2/ITO films were evaluated.

INTRODUCTION

Titanium dioxide (TiO_2) films are widely used in sensors, solar cells, electrochromic devices, photoelectrochemical cells (PECs) and photodegradation of organic pollutants from wastewater.[1-2] TiO_2 has received attention as a popular photocatalyst and it has been widely studied due to its optical-electronic properties, chemical stability, high resistance to corrosion and photocorrosion, non-toxicity and low-cost.[3-4]

The TiO_2 powder Degussa P-25 contains anatase and rutile phases in a ratio of about 4 : 1 and it is considered a standard material in the field of photocatalytic processes due to optimum ratio between the two phases with higher photocatalytic efficiency, non-toxicity, chemical stability, corrosion resistance.[5-6]

In this work, the commercial TiO_2 powder (P-25, Degussa) was used in different amounts in order to form TiO_2/ITO nanostructured films and their optoelectronic characteristics, structural and morphological properties of TiO_2/ITO films were evaluated.

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EXPERIMENTAL

TiO_2 films were prepared on going from commercial P25 TiO_2 powder (ca. 80% anatase and 20% rutile) of about 30 nm in diameter particles, kindly supplied by Degussa AG, Germany. The method for obtaining the TiO_2 colloidal suspensions mainly followed the method described by Myung Soon Lee *et al.*[7] Three colloidal suspensions were prepared via wet-chemical techniques using different TiO_2 amounts (1:2:3 ratio). As additives bi-distilled water, acetylacetone (Merck, Germany), polyethylene glycol (Machery-Nagel, Germany) and Triton X-100 (Fluka, Switzerland) were used and the ingredients were mixed in an ultrasonication bath for 45 min at 30°C. All additives were used without any further purification.

Each sample (name samples: TG-3, TG-6, respectively, TG-9) was deposited on a conductive indium tin oxide glass (ITO, 30 Ω/square) by spin-coating (1000 rpm, 60 sec). The samples were dried in normal conditions for 48 h and then annealed at 500°C in air for 60 min (temperature increasing rate of 10°C/min) in order to establish the electrical contact among the nanoparticles and to form an TiO_2/ITO nanostructured film with enhance resistance and better crystallinity.

The thickness of the TiO_2 layers were evaluated by weighting method using Analytical Balance Radwag, Poland, with an accuracy of 0.00001 g. Optoelectronic characteristics of TiO_2/ITO films were examined by using UV–VIS spectrophotometry (JASCO V-550 spectrometer) and spectrofluorimetry (ABL&E JASCO V 6500 spectrofluorimeter). The structural and morphological study of the TiO_2-based films was performed by FT/IR spectroscopy (JASCO FT/IR – 6100 Fourier Transform Infrared Spectrometer) using KBr pellet technique, FT/IR microscopy (JASCO IRT – 3000 Irtron Infrared Microscope in reflectance mode) and X-ray diffraction (BRUKER D8 Advance X-ray diffractometer). The $Cu_{K\alpha}$ radiation was collimated with Soller slits and a germanium monochromator was used.

RESULTS AND DISCUSSION

The film thickness was determined by weighting method approximation. The thickness of the TiO_2/ITO films and the values of TiO_2 band gap energy are presented in the Table 1. Obviously, the film thicknesses increase with the increase of the TiO_2 amount content. Also, the band gap energy widens with increasing film thickness. The values of band gap energies of TiO_2/ITO films are slightly larger than the known value of anatase TiO_2 (3.2 eV).[8]

The value of band gap energy (E_g) can be found by extrapolation from the UV-VIS spectra using Tauc's formula:[9]

$$(\alpha h\nu)^2 = A\,(h\nu - E_g),$$

where, α is the absorption coefficient (cm^{-1}), A - the constant, $h\nu$ - the photon energy (eV) and E_g is the band gap energy.

The plot of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ indicates the direct type of the predominant electronic transition.[10]

The adherence method was used for quantitative measurements aim to evaluate the weight loss after the immersion the TiO_2/ITO films into a solution of Triton X 1% as surfactant and ultrasonicated for 60 min at 30°C. During this process, some Triton-X molecules adsorb on TiO_2 particles and it is necessary to dry films at 220°C for 1 h in order to remove them. The quantities of titanium dioxide remained on ITO glasses was approximated by weighing method with an average deviation order of 10^{-5}. The efficiency of test adherence is the percentage expressing the amount of titanium dioxide remained adherent on ITO glass substrate after test.

The results of adherence test (Fig. 1) showed that with the increase of TiO_2 amount, a better adherence of films on substrate was obtained.

Table 1

TiO_2 samples properties

Samples name	TiO_2 mass (g)	Film thickness (μm)	E_g (eV)
TG-3	0.3	0.092±13.43%	3.26
TG-6	0.6	0.154± 5.12%	3.39
TG-9	0.9	0.298± 1.51%	3.41

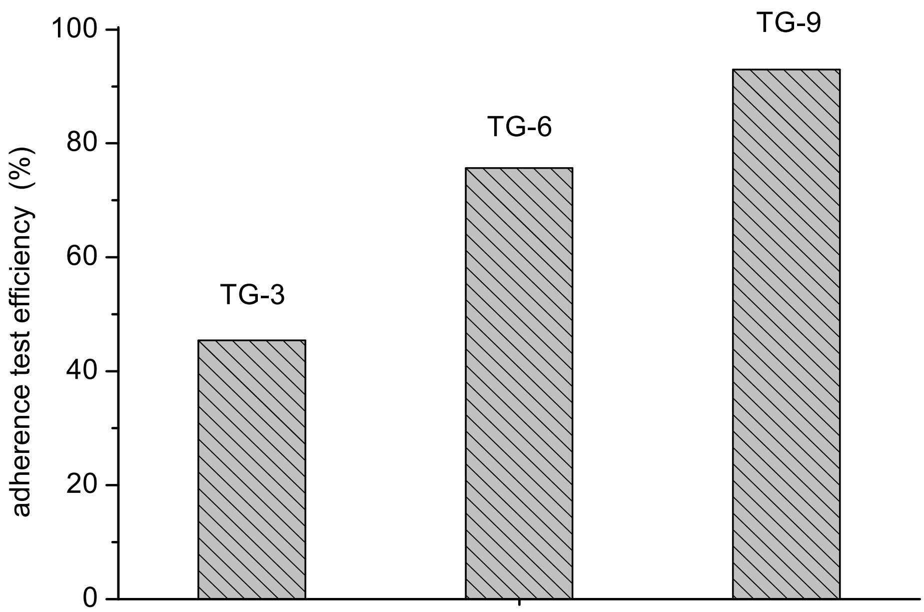


Fig. 1 – The adherence test efficiency for all three films (TG-3, TG-6 and TG-9).

Fig. 2 shows UV–VIS absorption spectra of the TiO_2 films. It can be seen that one absorbance peak (about 310 nm) appears for all of three TiO_2 films, in agreement to TiO_2 band gap energy. However, the intensities of UV-VIS absorption band decreases in the order: TG-9 > TG-6 > TG-3, by diminishing the amount of TiO_2 used in the wet-chemical technique.

Fig. 3 illustrates the fluorescence emission spectra of TiO_2 films measured in the range of 330–620 nm at the exciting wavelength of 320 nm. The maximum wavelength shifts from 350 to 480 nm for all films. However, the fluorescence maximum is almost constant at around 356 nm and it can be seen that all the films exhibit emission peak at the same wavelength. The wavelengths of emission peaks slightly depend on the film thickness.

Fig. 4 presents the FT/IR microscopy images of the TiO_2/ITO films in reflexion mode (square dimensions of 100x100 μm^2). It can be observed that the films have different dispersion grade of TiO_2 nanoparticles. Their size ranges in field 2-20 μm for TG-3, 10-25 μm for TG-6 and 10-40 μm for TG-9, respectively. The particle number increases with the addition of larger amounts of titania, being possible the appearance of some TiO_2 clusters.

FT/IR spectra of TiO_2/ITO films are shown in Fig. 5. The absorption bands at 3436 cm^{-1} and at 1636 cm^{-1} have been ascribed to the hydrogen-bonded surface species (hydroxyl and water) absorption. The first band corresponds to the O-H stretching vibration whereas the other one is assigned to the H-O-H bending vibration.[11-12] The presence of these peaks after annealing is due to residual hydroxyl groups of adsorbed water and/or to the end hydroxyl from polymers used in films preparation. At ~ 660 cm^{-1} a broad intense band due to Ti-O-Ti vibrations appears.[11-12]

XRD diffraction patterns (Fig. 6) illustrate the fact that all samples contain mainly TiO_2-anatase (PDF card no. 89-4921) crystalline phase.

The TiO_2-anatase unit cell volume V, effective crystallite mean size, D_{eff} (nm), and the mean root mean square (rms) of the microstrains, $<\varepsilon^2>^{1/2}_{hkl}$, determinated by Warren-Averbach Fourier analysis[13] are presented in Table 2.

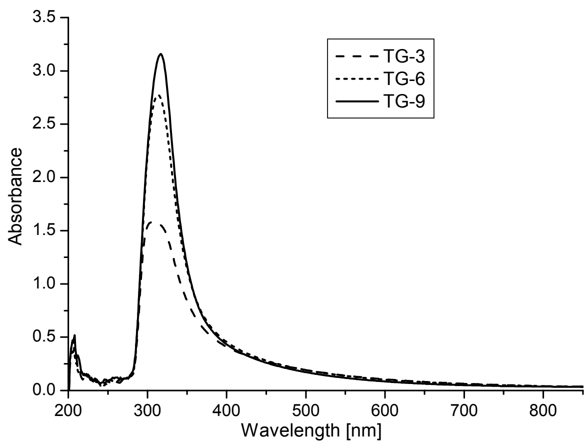


Fig. 2 – UV-VIS spectra of TiO_2/ITO films.

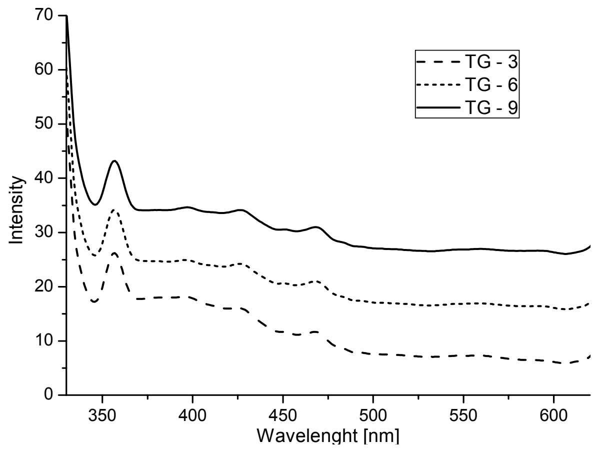
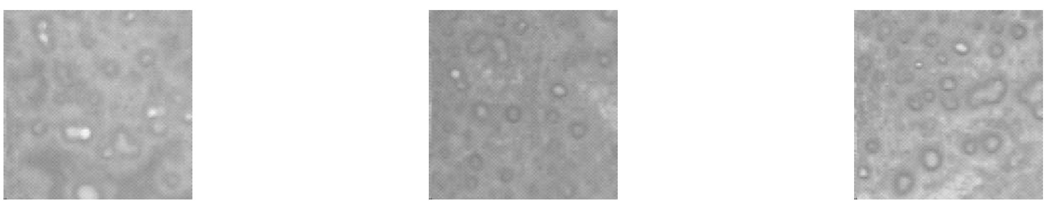


Fig. 3 – Fluorescence spectra of TiO_2/ITO films.



TG-3 TG-6 TG-9

Fig. 4 – FT/IR microscopy images of TiO_2/ITO films.

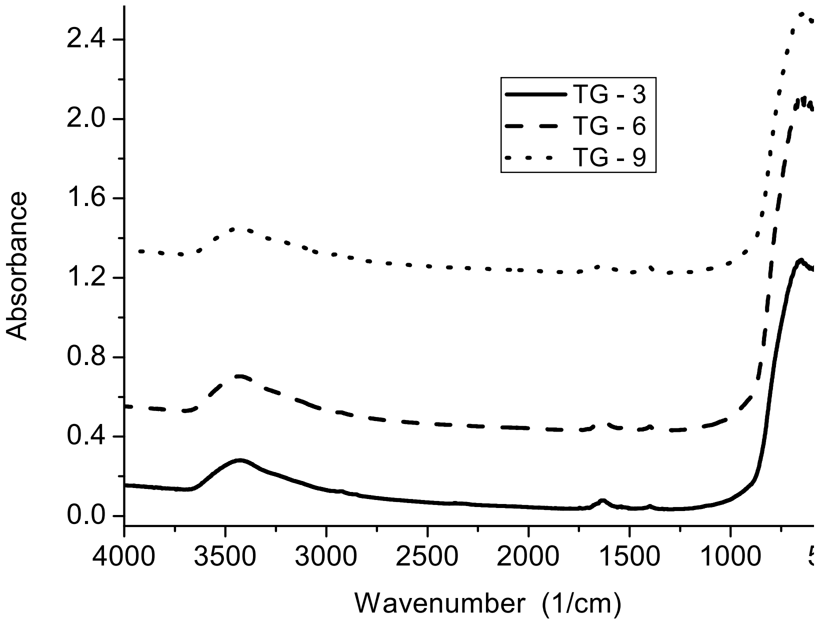


Fig. 5 – FT/IR spectra of TiO_2/ITO films.

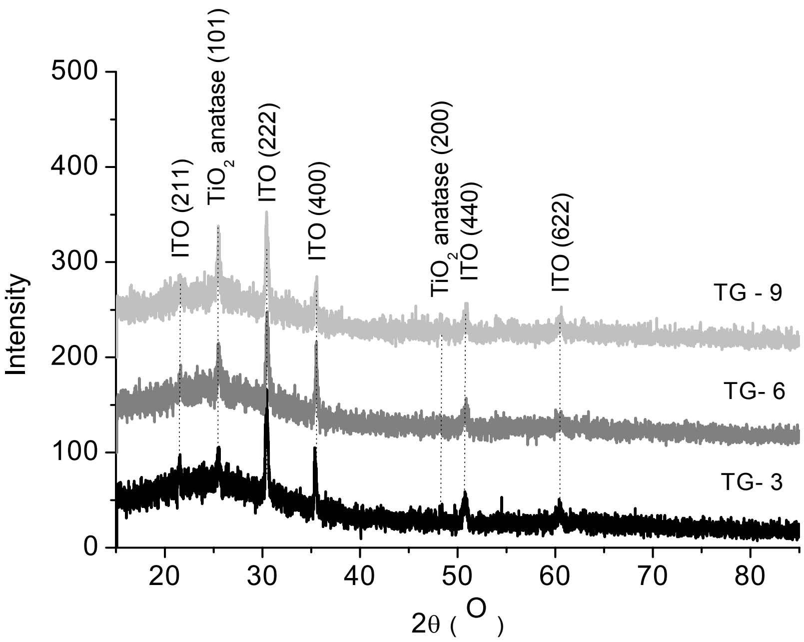


Fig. 6 – X-ray diffraction patterns of TiO_2/ITO films.

Table 2

Anatase unit cell volume V, effective crystallite means size, D_{eff}(nm), and the mean root mean square (rms) of the microstrains, $<\varepsilon^2>^{1/2}_{hkl}$ of TiO_2/ITO samples

Sample's name	Parameter		Anatase unit cell volume, V [Å^3]	D_{eff} [nm]	$<\varepsilon^2>^{1/2}_{hkl} \times 10^3$
	a [Å]	c [Å]			
TG-3	3.8027	9.5702	138.39	24.21	9.56
TG-6	3.7853	9.5620	137.01	31.42	7.24
TG-9	3.7840	9.5156	136.25	39.60	3.42

CONCLUSIONS

Three different TiO_2-based films with various mass proportion of composition were prepared and comparatively, their photoelectrochemical properties were studied.

The results of adhesion test described above showed that with the increase of TiO_2 amount, a better adhesion of films on substrate was obtained.

The increasing thickness of TiO_2 films enhances the UV absorption. A correlation between different TiO_2 mass proportions used in the TiO_2/ITO films preparation and the band gap energy was noticed: the increasing amount of TiO_2 enhances the value of energy band gap.

The XRD patterns of TiO_2/ITO films showed an anatase structure with [101] preferred orientation. The [101] TiO_2 anatase diffraction line becomes stronger with increasing film thickness, indicating a better crystallinity and a [101] crystallites orientation at the TiO_2 film/ITO substrate zone.

The photocatalytic activity of the TiO_2/ITO nanostructured films used in the photodegradation processes of some pollutants from wastewater is under progress.

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