

Synthesis and morpho-structural properties of TiO₂-based materials

V. PURCAR^{a,*}, V. RĂDIȚOIU^a, C.-A. NICOLAE^a, A. N. FRONE^a, A. RĂDIȚOIU^a, F. M. RADULY^a, R. ȘOMOGHI^a, R. A. GABOR^a, S. CĂPRĂRESCU^b

^aNational Research and Development Institute for Chemistry and Petrochemistry - ICECHIM, Spl. Independentei 202, 6th District, 060021 Bucharest, Romania

^bPolitehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, Inorganic Chemistry, Physical Chemistry and Electrochemistry Department, 1-7 Polizu Str., 011061, Bucharest, Romania

TiO₂-based materials modified with methyltriethoxysilane (MTES) have been synthesized by sol-gel method and deposited onto glass substrates in order to obtain TiO₂-SiO₂ thin films. The effect of MTES on formation of TiO₂-based materials was investigated by FTIR and UV-Vis spectroscopy, TGA analysis, TEM and contact angle. FT-IR spectra of obtained materials demonstrated that the silane reacts via a cross-link and covalently bond on the TiO₂ surface. The high contact angle values were obtained for coatings coverage layer with materials modified with MTES and indicate that the functional Si-CH₃ groups and TiO₂ nanoparticle form a protective layer at the coating's surface.

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1. Introduction

Titanium dioxide (TiO₂) is widely used in environmental applications due to its high photosensitivity, physical and chemical stability, low cost, non-toxicity, resistance to corrosion, versatile in the integration with different substrates, complete mineralization of organic pollutants [1-4]. Many efforts have been dedicated to the modification of TiO₂ materials from the point of view of their morphology and phase structures through the following methods: hydrothermal synthesis method, sol-gel, anodization and template method, supercritical carbon dioxide, and ultrasonic irradiation [5-8]. Sol-gel process was found to be a very useful tool to obtain TiO₂ products of various sizes, shapes and formats (e.g., fibers, films, monoliths, and nano-sized particles). These products can be utilized in a diverse range of scientific and engineering fields, such as the ceramic industry, nuclear field industry and electronics industry [9-13]. Investigation of physical and chemical property of TiO₂ is of interest to researchers because the TiO₂ is considered an ideal semiconductor for photocatalysis. N. Venkatachalam et al. [1] demonstrated that the sol-gel process coupled with ultrasonic treatment can be used to obtain different forms of nano TiO₂ particles. Sharma et al. [14] synthesized TiO₂ nanoparticles through the hydrolysis process of titanium (IV) iso-propoxide and prepared thin films by dip coating method. Recently, Zhou et al. [15] reveals that mixed metal oxides (TiO₂-SiO₂) enhance the photocatalytic performance due to improved surface adsorption and increasing surface hydroxyl group in the thin film. Guan [16] investigated the relationship between hydrophilicity, photocatalysis and the self-cleaning effect of TiO₂/SiO₂

surface. The authors found that these surfaces present more hydrophilic activity, but less photocatalytic activity. Jesus et al. [17] prepared the TiO₂/SiO₂ composites films by sol-gel dip-coating method in order to obtain super hydrophilic, adherent and transparent coatings. Fateh et al. [18] realized coating with transparent SiO₂/TiO₂ thin films by sol-gel method having photocatalytic activity and superhydrophobicity after exposure to UV light. S.A.Mayén-Hernández [19] demonstrated that the acid catalysts had an important effect on the morphology and photocatalytic activity of the TiO₂ thin films. Kajitvichyanukul et al. [20] shows that the properties of TiO₂ thin film were influenced by major parameters, such as molar ratio of alkoxide to alcohol, calcination temperature, and coating cycles.

The aim of the present paper was to study the effect of silane precursor on formation of TiO₂-based materials deposited on glass surface. Different dispersions of TiO₂ were prepared using two types of TiO₂ powders: TiO₂ without dye (blank) and TiO₂ sensitized with dye (iron phthalocyanine tetracarboxylic acids). These TiO₂ powders were dispersed in ethanol, HCl (0.1 N) and acetylacetone, and modified with silane precursor (methyltriethoxysilane, MTES). The resulted dispersions were deposited onto glass slides in order to analysis the reflectance and wettability of thin films. Optical and structural characteristics of the obtained TiO₂-based materials have been carried out by Fourier transform infrared (FTIR) and ultraviolet-visible (UV-Vis) spectroscopy techniques, thermal gravimetric analysis (TGA).

2. Experimental

2.1. Materials

TiO₂ powders as such (blank) and sensitized with dye (iron phthalocyanine tetracarboxylic acids) were prepared in a similar way to that previously reported [21]. Methyltriethoxysilane (99%, MTES, Aldrich) was used as modified agent. Ethanol (99.9%, EtOH), as a solvent, was obtained from Chimreactiv S.R.L. HCl (0.1N), as a catalyst, was purchased from Sigma-Aldrich. Acetylacetone (99%, Carlo Erba) was used as chelating agent. The chemicals were used as received.

2.2. Synthesis of modified TiO₂ materials

TiO₂ powders (0.01 g) as such (blank) and sensitized with dye (iron phthalocyanine tetracarboxylic acids) were

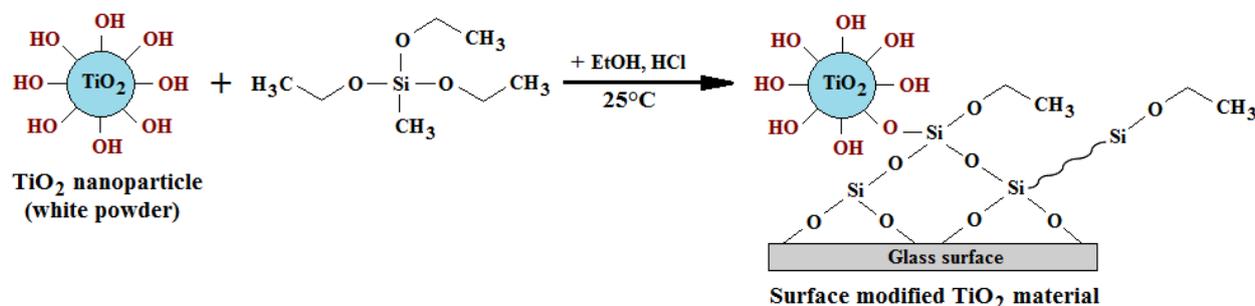


Fig. 1. Formation mechanism of TiO₂-SiO₂ materials and thin films deposited on glass surface

Table 1. The compositions of the final solutions used to produce different forms of TiO₂-SiO₂ materials and thin films

Sample	Stage 1 (1 h)					Stage 2 (1.5 h)	
	TiO ₂ (g)		EtOH (ml)	HCl (0.1 N) (ml)	MTES (ml)	Acetylacetone (ml)	HCl (0.1 N) (ml)
	Type of TiO ₂ powder	Amount (g)					
T5	TiO ₂ blank	0.01	12	0.2	0.8	0.4	0.4
T7	TiO ₂ sensitized	0.01	12	0.2	0.8	0.4	0.4
T9	TiO ₂ blank	0.01	12	0.2	-	0.4	0.4
T10	TiO ₂ sensitized	0.01	12	0.2	-	0.4	0.4

2.3. Characterization methods

Morphology and shape of the resulted TiO₂-based materials (0.05 mL samples diluted in 25 mL of ethanol and ultrasonicated for 5 min) were investigated via transmission electron microscopy (TEM) with a Tecnai™ G2 F20 TWIN Cryo-TEM instrument (FEI Company, Eindhoven, Netherlands) at 200 kV acceleration voltages. The samples were observed directly without further staining for improving contrast.

Fourier-transform infrared spectra of TiO₂-based materials were obtained through Jasco FT-IR 6300 instrument (JASCO Int. Co., Ltd., Tokyo, Japan), in the range 400–4000 cm⁻¹ (30 scans at a resolution of 4 cm⁻¹). Thermal analysis of the modified TiO₂ materials was performed in nitrogen atmosphere (10 °C/min), 40–700 °C

dispersed in ethanol (12 ml) through ultrasonically stirred for 10 min. Then, 0.2 ml of HCl (0.1 N) and 0.8 ml methyltriethoxysilane were added to the solutions under magnetically stirred for 1 h, 300 rpm, at room temperature (25°C). In the second step, 0.4 ml of acetylacetone and 0.4 ml of HCl (0.1 N) were added in the reaction and magnetically stirred for another 1.5 h. The final solutions were further used to produce different forms of TiO₂-SiO₂ materials and thin films (see Fig. 1). The compositions of the final solutions were summarized in Table 1.

The glass substrate, to ensure uniform wetting, was cleaned with soap, distilled water, and finally with ethanol. The sol-gel films were obtained by draw down sample coating with the manual applicator. All final materials were dried and kept (overnight) at room temperature (25°C) before being used for further investigations.

range, using a TA TGA Q5000 IR instrument (TA Instruments, New Castle, DE, USA).

The UV-VIS-NIR reflectance spectra were obtained with an UV-VIS-NIR-Jasco V-570 spectrophotometer (JASCO Int. Co., Ltd., Tokyo, Japan). Reflectance of coated samples was determinate by diffuse reflectance analysis, in the range 380–780 nm. Contact angles (CAs) measurements were determined using a CAM 200 Contact Angle Tensiometer (KSV instruments, Finland) equipped with a high resolution camera (Basler A602f) and an auto-dispenser. All CAs measurements were carried out in a static regime at room temperature with a drop volume of 6 μL. The reported contact angles were calculated from water drop images (average of ten liquid droplets placed in various regions of the film surface).

3. Results and discussion

The obtained TiO₂ solutions were characterized both as modified materials and as films deposited onto a glass slides.

The morphology and size of obtained TiO₂ solutions were examined by transmission electron microscopy (TEM). Fig. 2 shows the TEM images of sample without MTES (T10) and of sample with MTES (T7), characterized as dispersions. It can be seen that the sample T10 presents particles with an average diameter of ~ 10-20 nm. Sample with MTES (T7) exhibit larger particles than those measured for sample T10. This result shows that MTES can react on the different faces of TiO₂ nanoparticles and specific adsorption of silane precursor could reduce the surface energy of the forming nanoparticles [22]. The obtained results are in good agreement with previously published data by Innocenzi et al. [23], which demonstrate that, the particles have different size distribution as function of MTES contents.

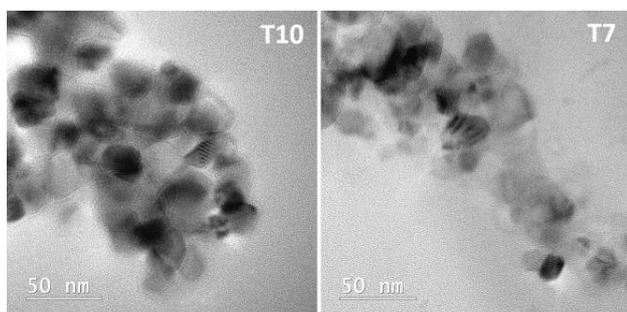


Fig. 2. TEM images of: TiO₂-based material without MTES (T10) and modified TiO₂-based materials with MTES (T7)

The FT-IR spectra of modified TiO₂-based materials are depicted in Fig. 3. The transmission band at ~3301 cm⁻¹ is due to O–H bond of H-bonded H₂O, hydroxyl terminals, H-bonded OH vibrations of alcohol and H-bonded Si–OH in chain, respectively [24]. The bands located in the 2960 and 2870 cm⁻¹ region are assigned to asymmetric and symmetric –CH₂– and –CH₃ modes of the functional groups from methyltriethoxysilane [25]. The peak at 1717 cm⁻¹ associated with the C=O stretching mode is observed in the spectra of modified TiO₂ materials [26]. The functional vibration modes of acetylacetone group are located at 1511 cm⁻¹ (C=C) and 1350 cm⁻¹ (C–C). The bands found at ~1030 and ~1100 cm⁻¹ (Si–O–Si stretching vibrations) and at 927 cm⁻¹ (Si–O–Ti linkage), confirming that the silane react via a cross-link and covalently bond on the TiO₂ surface. The characteristic band of Si–CH₃ group is found at 769 cm⁻¹ [27]. The spectrum of TiO₂- based material (T5), show the peak of Ti–O bond at 407 cm⁻¹ [28].

Compared to the sample T5, in the spectrum of TiO₂-based material sensitized with dye (T7) can be observed new peaks. The peak at 633 cm⁻¹ is due to the Fe–O symmetrical stretch, as it was found for goethite [29]. The occurrence of an intense peak at 497 cm⁻¹ is also due to Fe–O stretch, frequently found for different iron oxides [30]. The low wavenumber bands found between 410 cm⁻¹ and 460 cm⁻¹ spectral interval are attributed to rocking motions of the oxygen atoms perpendicular to the Si–O–Si plane according to Que et al. [31]. These results suggest that the TiO₂ sensitized with dye (T7) change the properties of materials, confirmed by the shift of some peaks (407 and 493 cm⁻¹) toward higher wavenumbers (419 and 497 cm⁻¹).

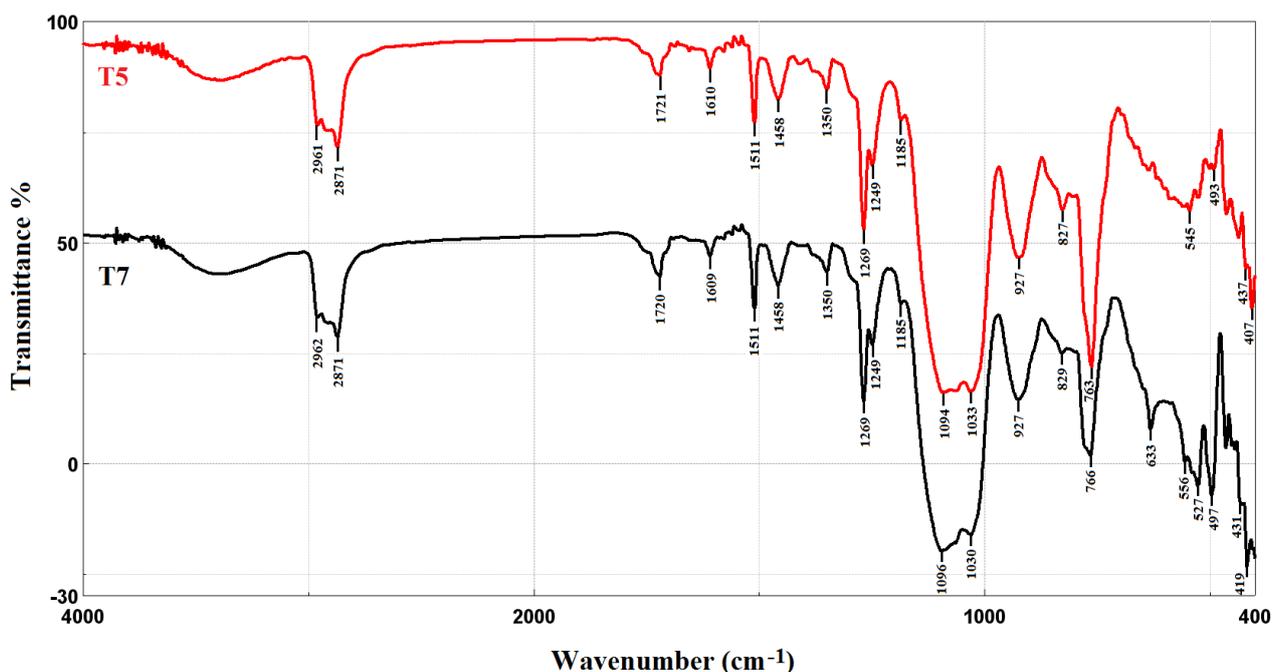


Fig. 3. FTIR spectra of modified TiO₂-based materials with silane precursor (MTES)

TGA analysis was performed on these TiO₂-based materials in order to establish the main thermal events and the thermal behavior is shown in Fig. 4. TGA thermographs reveal that the weight % of TiO₂-based materials without MTES (samples T9 and T10) decreases from 40 up to about 180 °C, and then sharply decreases from 275 to 450 °C (see Fig. 3 a and Table 2). The first zone corresponds mainly to the removal of physically adsorbed water and solvent [32-34]. For these samples, relatively slight weight loss after 450 °C can be attributed to water molecules formed from condensation of hydroxyl groups on the particle's surface (TiOH) [35].

As can be seen from Fig. 4 (b) and Table 3, the modified TiO₂-based materials with MTES (samples T5 and T7) show sharp weight loss, beginning at around 210 °C, continued till 510 °C. The weight loss can be associated with additional condensation reactions that take place at the surface of the inorganic skeleton, leading to further crosslinking and water release. In temperature ranging from 210 to 345 °C, weight loss can be caused mainly by degradation of Si-compounds on TiO₂ surface, and other organic intermediates.

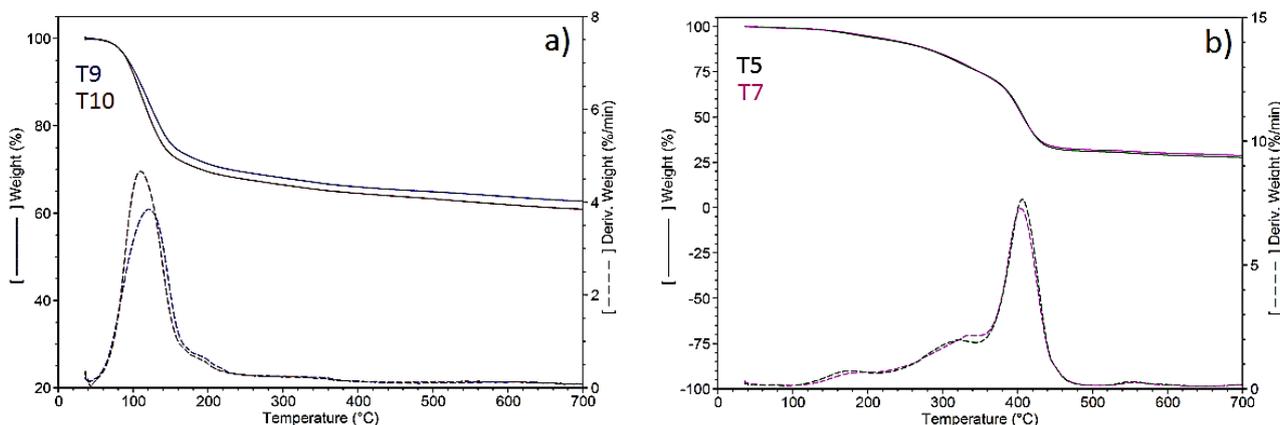


Fig. 4. Thermogravimetric analysis curves of obtained samples (see Table 1)

Table 2. Thermal degradation of TiO₂-based materials

Sample	40-180°C		180-275°C		275-450°C		450-700°C		Residue at 700 °C N ₂
	Wt. loss %	Tmax °C							
T9	27.38	120.8	3.94	195.9	3.30	347.2	2.67	611.2	62.71
T10	29.33	109.5	3.61	195.2	3.20	333.0	2.99	544.2	60.87

¹ T_{max} (°C) = T(da/dt)_{max}

Table 3. Thermal degradation of modified TiO₂-based materials with MTES

Sample	40-210°C		210-345°C		345-510°C		510-700°C		Residue at 700 °C N ₂
	Wt. loss %	Tmax °C							
T5	6.42	179.1	17.93	321.2	44.71	406.6	3.25	552.3	27.69
T7	5.91	196.9	18.31	333.6	43.99	404.5	2.99	555.1	28.80

¹ T_{max} (°C) = T(da/dt)_{max}

Diffuse reflectance analysis as a function of a wavelength of the visible light is presented in Fig. 5. This figure indicates the anti-reflective character of the TiO₂-SiO₂ films deposited on glass slides. The reflectance's at 550 nm of obtained films are about 15.5% for films covered with TiO₂-based materials with MTES (samples T5 and T7) and 16.2% for films covered with TiO₂-based

materials without MTES (samples T9 and T10). It can be seen that the glasses coated with samples T9 and T10 show a high reflectance compared with the films T5 and T7, which indicated that the addition of MTES can improve the transparency of the films.

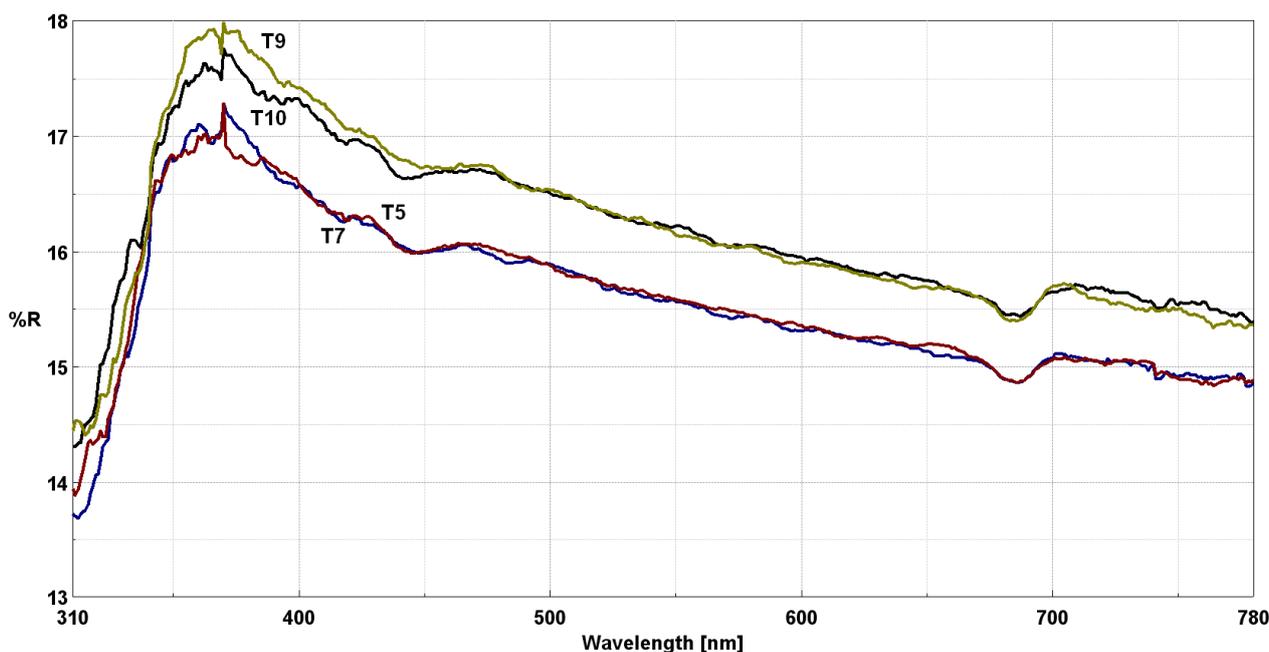


Fig. 5. Diffuse reflectance spectra of coatings covered with TiO₂-based materials: without MTES (T9 and T10) and with MTES (T5 and T7)

The wetting ability of obtained coatings is shown in Fig. 6 and evaluated by Contact Angle (CA) measurements. It can be seen that the contact angle of water on glass surfaces increased from 35° to 66° after the addition of MTES in the system. This result indicates that the nature of surfaces covered with TiO₂-based materials with MTES (samples T5 and T7) were changed due to the introduction of the organic groups into the silica network.

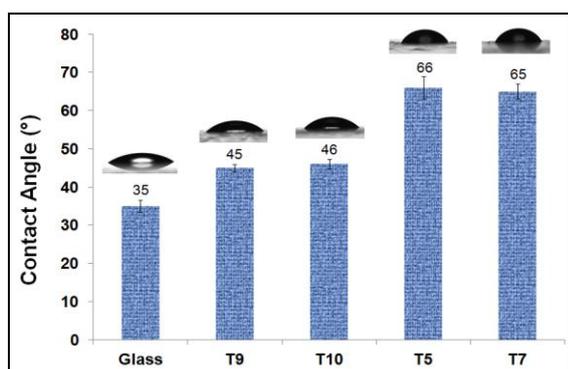


Fig. 6. Water contact angle of coatings covered with TiO₂-based materials: without MTES (T9 and T10) and with MTES (T5 and T7)

The functional Si-CH₃ groups and TiO₂ nanoparticle form a protective layer at the coating's surface, as a result of the silylating reactions between alkoxy groups and Ti atoms on the surface. These results indicate that the addition of organic groups into the TiO₂ material can reduce the wettability of these films. The property of films was enhanced due to the decrease of chemically adsorbed -OH groups at the surface. It was proved that the silanol

groups (Si-OH) made the film surface polar and reactive, allowing interaction with water molecules physically adsorbed or bounded by hydrogen bonds [36]. The obtained results are in good agreement with previously published data by Latthe et al. [37], which demonstrate, that the contact angle of the film increase when MTES is used as co-precursor.

4. Conclusions

This work reports the preparation and characterization of modified TiO₂-based materials. The obtained materials were characterized through TEM microscopy, FTIR and UV-VIS spectroscopy, TGA analysis, and CA measurements. The results revealed the effect of silane precursor (MTES) on formation of TiO₂-based materials. TEM images show that the sample with MTES exhibit larger particles. FTIR indicated that the MTES react via a cross-link and covalently bond on the TiO₂ surface. The difference between the total losses of the obtained materials was due to the organofunctional group. Diffuse reflectance analysis confirmed the anti-reflective character of the TiO₂-SiO₂ films deposited on glass slides. CA measurements showed that the nature of TiO₂-SiO₂ film surface can be changed using silane precursor with short alkyl chain. These obtained TiO₂-based materials can be used for developing a new kind of products applied in pigments industry.

Acknowledgements

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*Corresponding author: purcarvioleta@gmail.com