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Vis-active TiO₂ – g-C₃N₄ photocatalytic coatings for advanced wastewater treatment and self-cleaning applications

IOANA TISMANAR¹, ANCA DUTA^{1,2*}

¹Transilvania University of Brasov, Renewable Energy Systems and Recycling R&D Center, 29 Eroilor Street, 500036, Brasov, Romania

²Romanian Academy of Technical Sciences, 26 Dacia Blvd., 030167 Bucharest, Romania

Abstract. Nowadays, the photocatalysts developed for the advanced wastewater treatment and self-cleaning applications are investigated targeting an up-scaled implementation. This paper reports on Vis-active TiO₂ – g-C₃N₄ composite thin films obtained *in-situ* using a precursor system deposited by the low-cost spray pyrolysis deposition technique followed by annealing. The films were characterized in terms of crystallinity, morphology, roughness, wettability and transmittance and the results are correlated with the methylene blue (10 ppm) removal efficiency under simulated solar radiation, at low irradiance value. Vis-activation was outlined along with a promising photocatalytic efficiency (~32%) and a good stability indicating that these films could be successfully implemented also as self-cleaning coatings.

Keywords: vis-active photocatalyst, TiO₂ – g-C₃N₄ composite film, composite stability.

1. Introduction

Various photocatalytic coatings are reported as suitable materials for the degradation of organic pollutants at (very) low concentration in wastewater or in air. Among these, the most often investigated is titanium dioxide (TiO₂) mainly because of its stability in aqueous systems, including at extreme pH values, [1]. The problem with the use of TiO₂ in large-scale applications is related to the type of radiation required to activate the photocatalyst, as TiO₂ is an UV-active material ($E_{g \text{ anatase}} = 3.2\text{eV}$, [2]) thus leading to high process costs. Therefore research is focused on the development of Vis- or solar-active photocatalytic materials that efficiently use low(er) cost radiation. A broad range of composites based on wide

*Correspondence address: a.duta@unitbv.ro

band gap *n*-type semiconductors (TiO₂, ZnO) and narrow band gap *p*-type semiconductors (Cu_xS, CuInS₂, Cu₂ZnSnS₄, graphene oxide GO, reduced graphene oxide rGO) are reported and various issues were outlined related to these composites as: their stability in the humid/wet working conditions, environmental issues, incorrect alignment of the energy bands, low thermal stability leading to a low crystallinity degree, [3, 4, 5]. A route to get VIS-active composite structures with high crystallinity degree involves coupling titanium dioxide with graphitic carbon nitride (g-C₃N₄), a narrower band gap *n*-type semiconductor ($E_g = 2.7\text{eV}$). The suitable energy bands alignment allows the Vis-activation of this tandem system along with a limited electron – hole recombination, leading to high efficiency in photocatalytic applications, [6].

This paper reports on TiO₂ – g-C₃N₄ photocatalytic thin films obtained by spray pyrolysis deposition (SPD) as a low cost, upscalable and efficient deposition method. The work focuses on a novel path to obtain *in-situ* the composite, at high temperature, using a precursor system consisting of titanium tetra-isopropoxide, acetylacetone and ethanol combined with urea as g-C₃N₄ precursor. After deposition the films were thermally treated to decompose urea forming g-C₃N₄ inserted in the TiO₂ matrix directly at the layer level. The films were characterized in terms of crystallinity, morphology, surface elemental composition, roughness, wettability and transmittance to investigate their properties as self-cleaning coatings and were tested in photocatalytic experiments using the standard methylene blue (MB) pollutant, [7] and simulated solar radiation at low irradiance value. Comparative experiments using only UV radiation were performed to outline the Vis-activation of the composite thin films. The stability in the working conditions was investigated following the variation of the surface properties (roughness and transmittance) recorded before and after the photocatalytic process.

2. Materials and Methods

The thin composite films were deposited on glass slides (1.5 cm x 1.5 cm) covered with fluorine doped tin oxide (FTO). The substrates were cleaned with detergent and water under sonication (Dekang, DK-600H), rinsed with deionized water and ethanol and were further dried in air.

An intermediate layer consisting only of TiO₂ was deposited by SPD using titanium tetra-isopropoxide (TTIP) as precursor, acetylacetone (AcAc) as complexing agent and ethanol (EtOH) as solvent in a TTIP:AcAc:EtOH = 1:1:15 volume ratio. This system was sprayed over the substrate at 400°C using 30 deposition sequences with 60s break between two pulses. This first layer was thermally treated at 450°C for 3 hours to increase its crystallinity and had the role to support the uniform deposition of the TiO₂ – g-C₃N₄ composite layer.

The second composite layer was further deposited at 400°C using a precursor system of TTIP, AcAc and EtOH in the same volume ratio as for the first layer and urea as g-C₃N₄ precursor (2.8 g of urea corresponding to 68 mL of precursor solution). 100 spraying sequences were employed with 60s break between

consecutive pulses. After deposition the double-layered thin films were thermally treated for 5 hours at high temperature (550 or 600°C) targeting the *in-situ* formation of g-C₃N₄. The final estimated content of g-C₃N₄ in the composite layer was 15%_w calculated based on the average yield of producing g-C₃N₄ powder using the urea precursor ($\eta \sim 12\%$) estimated by evaluating the amount of g-C₃N₄ powder obtained after urea calcination at 550°C and 600°C. Thus, two different composite thin films were deposited: TiO₂ / TiO₂ – g-C₃N₄ 550TT and TiO₂ / TiO₂ – g-C₃N₄ 600TT.

The characterization of the composite thin films employed X-ray diffraction (XRD, Bruker D8 Discover) and the Diffrac.EVA 5.0 software to evaluate the crystallinity degree; the surface morphology of the films was investigated using scanning electron microscopy (SEM, Hitachi model S-3400 N type II) and the average surface roughness (RMS) was estimated using atomic force microscopy (AFM, NT-MDT model BL222RNTE); the surface elemental composition was investigated using Energy Dispersive X-ray spectrometry (EDX, Thermo); the wetting behaviour of the composites was investigated by measuring the water contact angle (WCA) using a DataPhysics GmbH OCA 20 device with the water droplet volume of 10 μ L; the transmittance of the films was evaluated using an UV–VIS–NIR spectrophotometer (Perkin Elmer Lambda 950).

The composite thin films were tested in photocatalytic processes using the standard methylene blue (MB) aqueous solution with 10 ppm concentration, [7]. The films were immersed in 20 mL of MB solution (using 50 mL quartz beakers). The samples were left for 1h in dark to reach the adsorption/desorption equilibrium, then they were irradiated with a mixed UV+VIS radiation for 8h. This mix simulates the solar radiation at a much lower irradiance value, $G \sim 55 \text{ W/m}^2$, out of which 3 W/m^2 corresponds to the UV radiation. Comparative experiments were performed only using UV radiation ($G \sim 3 \text{ W/m}^2$) to outline the Vis-activation; tests in dark (9 hours) were also done to check the contribution of the adsorption. The absorbance of the MB solution at the maximum wavelength (665 nm) in the beginning and at the end of the process was measured using a spectrophotometer (UV-Vis-NIR Perkin Elmer Lambda 950) to calculate the process efficiency.

The stability of the composites was estimated observing the transmittance and the RMS variations in the thin films before and after the photocatalytic process.

3. Results and discussions

The XRD patterns of the composite double-layers are inserted in Fig. 1 where slightly visible peaks can be noticed at $2\theta = 28^\circ$ and 29° that, according to literature, can be attributed to g-C₃N₄, [8]. As expected, due to the high treatment temperature, peaks characteristic to the rutile TiO₂ polymorph can be noticed in the diffractogram at $2\theta = 43.3^\circ$, but these could also be peaks overlapping with those corresponding to the FTO substrate at $2\theta = 26.5^\circ$ and at $2\theta = 37.8^\circ$. The relatively high crystallinity degree (almost similar for both films) indicate that the films may

prove good efficiencies in photocatalytic processes, supporting a limited electron-hole recombination.

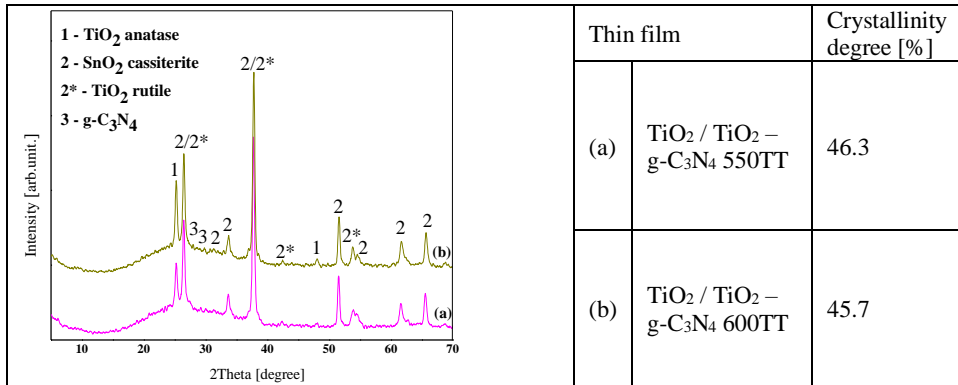


Fig. 1. XRD pattern of the films thermally treated at 550°C (a) and 600°C (b).

The SEM images in Fig. 2 outline the characteristic morphology of the TiO₂ film SPD deposited using TTIP as precursor, with a rather uniform aspect with small agglomerates of TiO₂ as previously presented, [5], and with additional rounded shapes that may correspond to the irregularly formed g-C₃N₄ at the films surface.

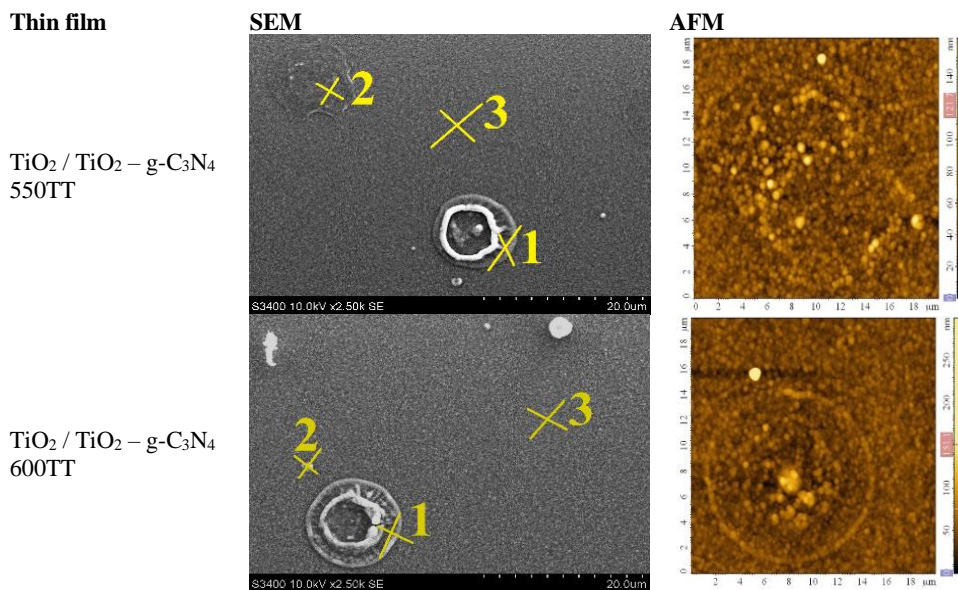


Fig. 2. SEM and AFM images of the composite double-layers.

The AFM images in Fig. 2 confirm the surface structure with aggregates indicating the presence of the filler.

The EDX results in Table 1 outline a slightly higher carbon (C) percentage near the rounded formations at the surface of the film. However, the nitrogen content (N) is

much too high compared to the carbon content (C) and to that of titanium (Ti) considering the concentration of 15%_w g-C₃N₄ in the composite film. This may be the consequence of an incomplete transformation of urea into g-C₃N₄ which would lead to other residual nitrogen containing compounds at the surface of the film.

Table 1 Elemental average surface composition of the composite thin films

Thin film sample		Element [%]				
		C	N	Ti	O	SE*
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 550TT	Point 1	10.57	20.75	18.87	48.69	1.12
	Point 2	10.37	20.53	18.05	49.17	1.88
	Point 3	5.27	14.60	23.41	53.37	3.35
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 600TT	Point 1	5.36	18.88	22.16	52.13	1.46
	Point 2	6.19	19.93	19.61	53.04	1.23
	Point 3	5.50	14.88	22.38	54.66	2.59

*SE: substrate elements (Sn, F, Si)

The relatively low RMS values and the rather high water contact angle inserted in Table 2 indicate that these films may not work very well in the adsorption step of the photocatalytic process.

The transmittance value, higher than 80%, indicate that these layers can be used as self-cleaning coatings on glazings, besides their use on opaque outdoor or indoor walls, for example.

Table 2 Roughness values of the composite thin film before and after photocatalysis, WCA and transmittance before and after photocatalysis

Thin film sample	RMS [nm]		WCA [°]	Transmittance at maximum of 631 nm [%]	
	Before process	After UV+VIS process		Before process	After UV+VIS process
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 550TT	13.7	12.2	33.6	81.1	80.0
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 600TT	14.8	10.4	38.9	82.8	80.4

Table 3. Photocatalytic efficiency under UV+VIS and UV irradiation and in dark on the composite thin films after 9h of contact with the MB 10 ppm solution

Thin film sample	Photocatalytic efficiency, η [%]		Adsorption [%]
	UV+VIS	UV	
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 550TT	31.30	18.09	8.48
TiO ₂ / TiO ₂ – g-C ₃ N ₄ 600TT	28.82	18.72	7.69

Beside the low RMS values, the photodegradation efficiencies in Table 3 for the MB removal show promising results that can be the consequence of the limited electron – hole recombination because of the rather high crystallinity degree. Vis-activation is confirmed by the higher photocatalytic efficiency recorded when using

UV+VIS radiation compared to the values recorded when using UV. The slightly lower photocatalytic efficiency recorded when using the sample thermally treated at 600°C may be correlated with the lower stability in the working conditions as the results in Table 2 show, but the RMS and transmittance results observed after the photocatalytic experiments using UV+VIS irradiation, have only small variations outlining the good stability of the composites. However, a higher variation could be noticed when using the films thermally treated at 600°C in good agreement with the lower photocatalytic efficiency.

4. Conclusions

The TiO₂ – g-C₃N₄ composite layers were deposited using SPD followed by high temperature thermal treatment to get graphitic carbon nitride directly at film level. The stability experiments in the working conditions indicate a higher variation in the roughness and transmittance for the sample thermally treated at 600°C, thus the thermal treatment at 550°C is recommended for preparing these composites. The results in the photocatalytic experiments outline the Vis-activation indicating the formation of the composite with a reduced electron-hole recombination. Further work will focus on the point of zero charge of the layers correlated with the process optimum conditions supporting the attraction between the pollutant and the photocatalyst targeting an increase in the process efficiency.

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