

INTERDISCIPLINARY DOCTORAL SCHOOL

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## Composite materials with metal oxide matrix and filler of carbonic compounds with VIS- and solaractive photocatalytic properties

SUMMARY

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### Introduction

Currently, through the application of conventional wastewater treatment processes, the water is brought to the permissible limit concentrations for discharge into the emissary, according to NTPA-001, [1]. But in order to meet the European targets for water reuse, it is necessary to introduce an additional step to ensure water quality conditions for important uses.

The additional step or advanced treatment is usually applied after biological treatment and is efficiency at low concentrations of (organic) pollutants, when conventional treatment steps are no longer feasible. The application of advanced oxidation processes (AOP - Advanced Oxidation Processes) based on semiconductor photocatalytic materials appeared as a new approach in the degradation of organic pollutants in low concentrations in pre-treated wastewater, [2, 3]. An advanced oxidation process that has attracted the attention of researchers is heterogeneous photocatalysis, efficiency in the degradation of organic pollutants in water at low concentrations with the formation of non-toxic inorganic compounds, but its implementation on an industrial scale, in advanced wastewater treatment, is not possible (yet) due to the activation costs of stable and efficient photocatalytic materials.

Titanium dioxide TiO<sub>2</sub>, is among the most used semiconductors in advanced oxidation processes. However, its use on an industrial scale in photocatalytic processes is limited due to its activation with radiation from the ultraviolet (UV) spectral range, [2, 3]. For low-cost photocatalytic processes, VIS-activation of stable and efficient semiconductors is aimed, using the technique of doping or coupling two different semiconductors.

This work, entitled " Composite materials with metal oxide matrix and carbonic compound fillers with VIS- and solar-active photocatalytic properties" falls within the context of these concerns and follows to the development of new solar- and VIS-active photocatalytic composite materials based on titanium dioxide (TiO<sub>2</sub>) and graphitic carbon nitride filler ( $g-C_3N_4$ ) mainly investigating the properties of interest:improvement of photocatalytic activity, VIS-activation, stability and durability in the aqueous environment for use in photocatalytic processes, in advanced wastewater treatment aiming at recirculation and/or reuse.

### CHAPTER I. Composite materials with metal oxide matrix and carbonic compound fillers with VIS- and solar-active photocatalytic properties. Current state of the art

In addition to the VIS-activation, the use of photocatalytic materials in the process of heterogeneous photocatalysis, in applications such as advanced wastewater treatment or as self-cleaning surfaces, aims at improving the photodegradation efficiency of pollutants in low concentrations (ppm and ppb) and investigating thermal stability and chemical stability in the aqueous environment (over a wide pH range), [4, 5].

Following this properties, the PhD work aims to obtain solar- and VIS-active photocatalytic materials, stable in the working environment (in the pH range =  $7 \dots 8.50$ ), for use in advanced

oxidation processes in heterogeneous photocatalysis. The potential for scaling up the process of heterogeneous photocatalysis at an industrial level, for the advanced treatment wastewater targeting water reuse.

#### I.1. Semiconductor materials with photocatalytic properties. Titanium dioxide

Photocatalytic materials are usually semiconductors, which by exposure to visible (VIS) or UV radiation generate electron-hols pairs that participate in redox reactions to form reactive species, especially hydroxyl radicals, responsible for the degradation of organic compounds, [6, 7].

Semiconductors are materials whose main characteristic is the energy of the band gap; by exposure to light radiation, only the part of the incident radiation (those with energy  $hv \ge Eg$ ) is used by the material, when electrons are promoted from the valence band (BV) to the conduction band (BC), generating electron- hole pairs, [8, 9].

Semiconductors are of two categories:

*a) Wide band gap semiconductors* ( $E_g > 3,1 \text{ eV}$ ,  $\lambda_{activation} = 10 \dots 400 \text{ nm}$ ), active under irradiation with UV radiation.

b) Semiconductors with a narrow bandgap (Eg < 3.1 eV,  $\lambda_{activation}$  = 400 ... 800 nm), active under irradiation with VIS radiation.

Titanium dioxide,  $TiO_2$ , is an n-type semiconductor and prezent properties such as long-term corrosion/erosion resistance, very good stability in the aqueous environment over a wide pH range, non-toxicity and acceptable production cost, [3, 10]. Considering that  $TiO_2$  is a wide band gap semiconductor, Eg = 3.2 eV, thus it can be activated only using UV radiation. For an efficient process, the use of artificial radiation sources is required, which involves high costs, and the introduction of the process on an industrial scale, with a view to advanced wastewater treatment, can not be carried out under feasible conditions, [11].

In order to reduce the costs of the photocatalytic process, it is necessary to find solutions to extend the activation of stable and efficient semiconductors to the VIS spectral range, thus using a large part of the solar radiation. Different strategies for VIS-activation of TiO<sub>2</sub> photocatalyst have been development using doping or coupling processes with semiconductors active in the VIS spectral range.

### I.2. Vis-active semiconductor materials with photocatalytic properties

Due to stable and efficient semiconductors in photocatalysis are limited by activation under UV irradiation, it was chosen the doping them or coupling two semiconductors to extend the activation of the structures obtained using radiation in the VIS spectral range. In the latter case, with the VIS-activation also appears the advantage represented by the reduction of the electron-hole recombination process.

### I.2.1. Doped semiconductor photocatalysts

*Doping* – is a process by which some of the ions of the basic crystal lattice are replaced by other ions with the same sign of charge, but with a different charge value. By doping, additional energy levels are created in the bandgap of the semiconductor, so that activation occurs at (much) lower energy values, [12]. Although doping improves the VIS spectral response of wide band gap semiconductors it has been concluded that cation doping is detrimental to photocatalytic efficiency (and toxic) and anion doping is a difficult phenomenon to control, [12].

### I.2.2. Semiconductor photocatalysts coupled in diode or tandem structures

Coupling can be made between two n-type (n - n) or p-type (p - p) semiconductors in tandem systems, or between an n-type semiconductor and a p-type (n-p) semiconductor in diode-type systems / n - p heterojunctions. The n-p diode type composites are most used, being known in the field of electronic components, photovoltaic cells, etc..

By coupling wide band gap semiconductors (eg. TiO<sub>2</sub>, ZnO) with suitably positioned narrow band gap semiconductors (eg. metal sulphides, graphene derivatives or  $g-C_3N_4$ ), the band gap of the formed composite is significantly narrowed making it VIS – active, [13, 14].

The resulting diode / tandem structure, by the adequate positioning of BV and BC of the 2 semiconductors, Fig. 1, separated routes for charge carriers' migration are supported of the electrons and holes by provides enough time for the valence band holes in the narrow band gap semiconductor to react with water and/or with the hydroxide anions (HO-) to form oxidizing species (the hydroxyl radical, HO•), which contributes to decreasing the electron-hole recombination and therefore increasing the photocatalytic efficiency.



Semiconductor de tip "n"

Fig. 1 The alignment of the energy bands in the n-p junction, [13]

### I.2.3. Vis-active composite materials with titanium dioxide matrix and graphitic carbon nitride filler used in heterogeneous photocatalytic processes

An alternative for obtaining VIS-active structures with high crystallinity is graphitic carbon nitride,  $g - C_3N_4$ . Graphitic carbon nitride was mentioned for the first time in 2009, being used for the production of H<sub>2</sub> (and O<sub>2</sub>), [14], through photocatalytic processes. g-C<sub>3</sub>N<sub>4</sub> can be synthesized in two structures: s-triazine and tri-s-triazine, Fig. 2.



Fig. 2 The structure g-C<sub>3</sub>N<sub>4</sub> (a) s-triazine and(b) tri-s-triazine [15, 16]

Graphitic carbon nitride, g-C<sub>3</sub>N<sub>4</sub>, can be easily synthesized by polymerizing various nitrogen rich solid organic precursors such as urea  $(NH_2)_2C=O$ , thiourea  $(NH_2)_2C=S$ , cyanamide  $CH_2N_2$ , dicyandiamide  $C_2H_4N_4$ , melamine  $C_3H_6N_6$ , etc in air, [9], or in inert atmosphere (e.g. N<sub>2</sub> or Ar atmosphere), usually at temperatures ranging between 450°C and 600°C, [17]. Due to the N - bridges, the two-dimensional tri-s-triazine structure of g-C<sub>3</sub>N<sub>4</sub> shows high thermal stability up to 600°C, at temperatures higher than 700 – 750°C, g-C<sub>3</sub>N<sub>4</sub> completely decomposes, [17, 18].

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is an n-type semiconductor and has a narrow band gap (Eg = 2.7 eV,  $\lambda_{activation} = 459.25$  nm) being activated under VIS radiation, [15, 19]. The high chemical and thermal stability make the g-C<sub>3</sub>N<sub>4</sub> one of the most promising semiconductor materials, its use as individual semiconductor in photocatalytic processes is limited due to the high electron-hole recombination rate that leads to low efficiencies in the photocatalytic processes.

A good strategy for improving the photocatalytic efficiency by avoiding/reducing the electron-hole recombination is to couping  $g-C_3N_4$  with the semiconductor (TiO<sub>2</sub>) to develop tandem n - n heterojunctions.

According to the diagram in Fig. 3, VIS radiation is directly absorbed by  $g-C_3N_4$  (with a narrow band gap) generating electron-hole pairs; electrons move from the valence band of  $g-C_3N_4$  to the conduction band leaving behind a gap. Since  $g-C_3N_4$  has a higher negative potential in absolute value of the conduction band (-1.19 eV) compared to TiO<sub>2</sub> (-0.35 eV), [20, 21], electrons from the BC of  $g-C_3N_4$  can migrate readily in BC of TiO<sub>2</sub>. The tandem structure resulting from the adecvate positioning of the BV and BC of the 2 semiconductors allows separate circuits for the movement of electrons (and holes) and also allows sufficient time for the holes produced in the BV of  $g-C_3N_4$ 

(and/or TiO<sub>2</sub>) to react with water and with hydroxide anions (HO-) to form oxidizing species (the hydroxyl radicals, HO•), that contributes to the limiting of electron-hole recombination, thus improving the photocatalytic efficiency.



Fig. 3 Alignment of the energy bands in the  $TiO_2 - g-C_3N_4$  composite structures [21]

### I.3. Obtaining methods for the photocatalytic materials

In photocatalytic processes, semiconductor materials can be used in the form of powders or in the form of thin layers. These materials are used in heterogeneous photocatalysis in applications such as advanced wastewater treatment or as self-cleaning surfaces. Different methods have been developed and investigated mainly following the cost of obtaining photocatalytic materials with clearly formulated properties.

#### I.3.1. Obtaining methods for the photocatalytic powders

Among the most used methods for obtaining powders can be mentioned: the sol-gel method and the hydrothermal/solvothermal synthesis.

The sol-gel method is one of the most widely used methods of chemical synthesis, as it can be applied to a wide variety of compositions, offering the ability to control the shape, size and dimensional distribution of the product particles, [22, 23]. By this method, (micro)-powders and micro-fibers can be easily obtained. In addition to these, thin layers can also be obtained by spraying the sol (diluted/undiluted).

Although the use of powders is more efficient in photocatalytic applications due to the higher specific surface area, their use in advanced wastewater treatment raises significant technological problems when moving to an industrial level. It is necessary to introduce an advanced filtration step in the purification process to separate the powders for reuse, which is time, expensive and also involves the inevitable loss of photocatalyst powders, [23, 24]. To eliminate these costs, one usually opting for the using materials in the form of thin photocatalytic layers (films).

#### 1.3.2. Obtaining methods for thin photocatalytic layers

Thin photocatalytic layers can be obtained by physical or chemical deposition techniques, among which can be: chemical vapor deposition (Chemical Vapor Deposition - CVD), deposition of layers

with atomic size units (Atomic Layer Deposition - ALD), "doctor blade" method, deposition by spraying with pyrolysis (Spray Pyrolysis Deposition - SPD), deposition by spraying suspensions at ambient temperature, etc, [7, 24, 25, 26].

The spray pyrolysis deposition (SPD) technique is among the most effective and used methods due to the possibility of controlling the deposition parameters: deposition substrate temperature, carrier gas pressure, layer thickness (through the number of spraying sequences), etc. This consists in obtaining thin films starting from an aerosol (containing small precursor droplets dispersed in the air) driven towards a heated surface where, following the pyrolysis process, the formation of the thin layer takes place, [7].

Photocatalytic materials (powders or thin layers) are mainly investigated for their use in heterogeneous photocatalysis processes, with applications both in advanced wastewater treatment for reuse and that self-cleaning surfaces.

### I.4. Wastewater treatment for targeting reuse

Wastewater treatment is a complex process of retaining and neutralizing pollutants present in water after its use for various purposes. Discharge of these insufficiently treated waters can cause serious environmental consequences. This aspect must be strictly controlled through adequat wastewater treatment, according to the increasingly severe restrictions imposed on the quality conditions of wastewater treatment for discharge into the emissary, [27]. After wastewater treatment by conventional processes, the water is brought to limit concentrations allowed for discharge into to emissary. Thus, in order to meet European water reuse targets, it is necessary to introduce an additional step of advanced wastewater treatment to ensure water quality conditions.

In the last time (25 ... 30 years) wastewater processes through advanced oxidation (Advanced Oxidation Processes - AOP) represented a new approach in the degradation of organic pollutants in low concentrations up to mineralization (water and carbon dioxide), [24, 27]. Due to the current pressure on natural waters, in the future it is expected that these methods will be used extensively for the advanced treatment of wastewater for reuse.

### I.5. Advanced oxidation processes for pollutants degradation from wastewater. Heterogeneous photocatalysis

Advanced oxidation processes are used in wastewater treatment in addition to traditional methods because they are effective in degrading organic and biological pollutants, found in very low concentrations (ppm, ppb), thus bringing the water into the optimal parameters for reuse and/or recirculation. These processes take place under normal conditions of temperature and pressure, and involve the generation of highly reactive species, especially hydroxyl radicals (HO•), in sufficient quantities for pollutant degradation, [22, 24].

The most studied advanced oxidation processes are photolytic processes, processes activated by radiation: photolysis, homogeneous photocatalysis and heterogeneous photocatalysis.

Heterogeneous photocatalysis is an advanced oxidation process in which the catalyst is not in the same state of aggregation as the reactants. This process has been widely investigated because it represents the most efficient alternative to degrade organic pollutants present in wastewater in low concentrations, resulting in non-toxic inorganic compounds, [24].

In addition to being used in advanced wastewater treatment processes, heterogeneous photocatalysis is also found in applications in the field of architecture and construction (as self-cleaning surfaces) or in the sanitary field (as antibacterial surfaces), [28].

Like any catalytic process carried out in a heterogeneous system (S-L), the mechanism of the photocatalytic process proceeds through the following stages, [3]:

1. Adsorption of the pollutant on the photocatalyst surface.

2. Irradiation of the semiconductor photocatalyst with radiation having energy greater than or at least equal to that of the band gap ( $h_V \ge Eg$ ), equation 1.

 $photocatalyst + h\nu \rightarrow e_{(BC)} + h_{(BV)}^{+}$ (1)

A process that occurs in parallel during the unfolding of the photocatalytic mechanism is the electron-hole recombination process that leads to the (partial) deactivation of the photocatalyst, [29].

$$(e_{BC}^{-} + h_{BV}^{+}) \rightarrow \text{photocatalyst} + hv$$
 (2)

3. Oxidizing species generation and pollutant oxidation, equations (3) and (4):

$h^+ + H_2O \rightarrow HO \bullet + H^+$	oxidation reactions	(3)

 $h^+ + HO^- \rightarrow HO^-$  neutralization reaction (4)

Radical species (HO•) generated according to equations (3) or (4) are oxidants that can decompose pollutants adsorbed on the semiconductor surface to carbon dioxide and water (mineralization) and/or intermediate products, [30]:

 $HO \cdot + pollutant \rightarrow intermediate oxidation products \rightarrow CO_2 + H_2O + other mineralization products$  (5)

Photogenerated electrons can react with oxygen adsorbed on the surface of the photocatalyst forming superoxide anion radicals (•O2-), as oxidizing agents, [31]:

 $(0=0)O_2 + e^- \rightarrow \bullet O - O^- \qquad \text{reduction reaction} \tag{6}$ 

#### 4. Desorption of photodegradation products adsorbed on the catalyst surface.

In addition to the recombination process, the efficiency of the photocatalytic process also depends on the light absorption coefficient by the photocatalyst and the speed of the reduction or oxidation processes induced by the electron-hole pairs on the surface, [31]. Adsorption of the pollutant on the surface of the photocatalyst is another aspect that can limit the efficiency of photocatalytic processes, therefore for the successful implementation of photocatalytic processes it is necessary to create favorable conditions for pollutant adsorption by ensuring the optimal surface charge of the photocatalytic material.

Because the scale-up of photocatalytic technology using photocatalyst powders involves high process costs and may lead to loss of photocatalytic material, the use of thin layers is preferable, [32, 33].

### **Conclusions of Chapter I**

For the integration of wastewater in optimal reuse/recirculation parameters, after conventional process, it is necessary to introduce an additional stage of advanced wastewater treatment. Among the most studied advanced wastewater treatment processes for the removal of organic pollutants from water is the heterogeneous photocatalysis process, which is effective even at low concentrations of pollutants, ppm and ppb. Because it is a non-toxic process and uses photocatalysts with acceptable costs, heterogeneous photocatalysis can be widely applied after conventional methods.

Photocatalytic materials such as  $TiO_2$  and ZnO have been most reported due to their stability in aqueous environment, but the wide band gap (Eg = 3.2 eV) allows their activation only under irradiation with radiation in the UV spectral range, limiting their wide scale use. Radiation in the UV spectral range represents a small percentage of the solar spectrum, so for efficient processes it is necessary to use artificial radiation that greatly increases the costs of the process.

An alternative to using TiO<sub>2</sub> or ZnO on a large scale is to couple them with a narrow-bandgap semiconductor, with the formation of diode-type systems (n – p) or tandem-type systems (n – n) thus leading to VIS – activation, aiming at the same time to obtain structures that meet all the conditions for the efficiency of the photocatalytic process. Also, the high thermal stability of  $g-C_3N_4$  and TiO<sub>2</sub> represents an advantage in obtaining composites with high crystallinity, a property that favors photocatalytic efficiency, limits electron-hole recombination and ensures good stability in the aqueous environment of the obtained materials.

Taking into account these aspects, the **Aim and objectives of the doctoral PhD** were formulated:

The aim of the PhD program: Conception, realization and optimization of semiconductor metal oxide matrix (TiO2) and carbon compound filler (g-C3N4) composite materials with solar- and VIS- active photocatalytic properties used in heterogeneous photocatalysis for advanced wastewater treatmnet

### **Objectives of the PhD program**

01. Composite material design;

O2. Obtaining, characterizing and optimizing thin layers of small dimensions (1.5 x 1.5 cm<sup>2</sup>) and testing them in static photocatalytic processes;

O3. Obtaining, characterizing and optimizing thin films of larger dimensions (20 x 30 cm<sup>2</sup>) and testing them in photocatalytic processes at demonstrator level, in dynamic regime;

OS.1. Drafting of the doctoral thesis

OS.2. Dissemination of results

### CHAPTER II. Experimental techniques for obtaining and characterizing the thin photocatalytic layers used in organic pollutants removal from wastewater through advanced oxidation processes

### II.1. Materials, reagents and equipment used for the deposition and characterization of photocatalytic thin film

### a) Materials and reagents

- precursor: titanium tetraisopropoxide (TTIP, Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Sigma Aldrich, 97%)
- complexing agent: acetylacetone (AcAc, C5H8O2, Scharlau, 99%)
- solvent: ethanol (EtOH, C₂H₅OH Chimreactiv, 99%);
- pH corrector: acid acetic (HAc, CH<sub>3</sub>COOH, Scharlau, 99,8%);

- the ethanolic dispersion of g-C<sub>3</sub>N<sub>4</sub> at concentration, c = 70 mg/mL p prepared in the laboratory of the Transilvania University Research and Development Institute, Braşov (ICDT) using g-C<sub>3</sub>N<sub>4</sub> powder obtained by calcining the precursors urea (CH<sub>4</sub>N<sub>2</sub>O, 99%, Scharlau) and respectively melamine (C3H6N6 99%, Acros);

- distilled water;

- 0.1 N HCl solution, prepared using 37% HCl, Scharlau used for isoelectric point (PZC);
- sodium hydroxide solution (NaOH), 0.1 N solution prepared using NaOH (98% solid, Scharlau) – used for working pH adjustment and isoelectric point assessment;
- o methylene blue (MB, Scharlau C.I. 52015), diluted solution of MB, concentration 10 ppm;
- imidacloprid (IMD, 99.8%, Dr. Ehrenstorfer GmbH) diluted solution of IMD, concentration 10 ppm;
- substrate glass plates (dimensions 1.5 x 1.5 cm<sup>2</sup>) and glass/FTO (dimensions 1.5 x 1.5 cm<sup>2</sup> and 20 x 30 cm<sup>2</sup> divided as follows: 5 plates of 2 x 2 cm<sup>2</sup>, 1 plate of 8 x 10 cm<sup>2</sup> and 5 10 x 10 cm<sup>2</sup> plates), Pilkington TEC15 where: FTO fluorine-doped tin dioxide layer covering the glass substrate.

### b) Equipment used for the deposition of thin layers

- laboratory vessels and utensils: crucibles, pestle and mortar, Erlenmayer beakers, 50 mL Berzelius quartz beakers, magnets, nozzles, spatula, watch glass;

- electric hotplate with heating and stirring, LHG Ceran 500 22EB-C and electric hotplate with heating, LHG Ceran 500 44EB-R;

- microwave Nabertherm, LE14/11/B15, T<sub>max</sub> = 1100 °C;

- ultrasonic bath, Ultrasonic Cleaner, DEKANG ;

- industrial spraying robot type ABB IRB 140 for the deposition of thin layers of small dimensions (1.5 x 1.5 cm<sup>2</sup>) and industrial spraying robot type ABB IRB 2400 for the deposition of thin layers of large dimensions  $20 \times 30 \text{ cm}^2$ ;

- analytical balance, Kern, Als 120-4.

### c) Equipment used for the characterization of photocatalytic thin films

- X-ray diffractometer, Bruker D8 Discover - used to investigate crystalline phases and determine the degree of crystallinity using Diffrac.Eva V1.4 software - X-ray Diffraction technique;

- Scanning electron microscope, SEM S-3400N Hitachi - used to investigate the morphology of the layers - SEM Scanning Electron Microscopy technique;

-Energy Dispersive X-ray Spectroscope, EDX Thermo - used for the evaluation of surface elemental composition, equipment coupled to the Scanning Electron Microscope (SEM) technique Energy Dispersive X-ray Spectroscopy, EDX;

- Atomic Force Microscop, AFM Ntegra Spectra, NT-MDT - used to investigate layer morphology and roughness (RMS) - technique Atomic Force Microscopy, AFM;

- titrator SI Analytics Titroline 6000 - used for the evaluation of the isoelectric point (PZC).

### d) Equipment used for testing thin layers in photocatalytic processes:

- laboratory photoreactor equipped with 7 tubes for simulating solar radiation: tubes for radiation in the UV spectral range (F18W/T8, Philips,  $\lambda = 340 - 400$  nm,  $\lambda_{max} = 365$  nm) and tubes for VIS radiation (Philips, TL-D Super 80 18W/865,  $\lambda = 400 - 700$  nm,  $\lambda_{max} = 565$  nm) used to perform tests in static regime;

- demonstrator photoreactor for performing photocatalytic tests in dynamic regime using a large photocatalyst (20 x 30 cm<sup>2</sup>), with the possibility of regulating the flow rate of the pollutant solution*;* 

- vertical solar simulator with 20 UV lamps of the Osram type, Ultra-Vitalux 300 W and 52 VIS lamps of the Osram type, HaloparALU 100W, with the simulated solar radiation intensity of ~ 800 W/m<sup>2</sup> of which 19 W/m2 correspond to UV radiation;

- pyranometer type BF3, Delta-T used to measure radiation intensity (irradiance);

- pH - meter, Consort multi-parameter analyzer – used to measure the pH of pollutant solutions.

### II.2. Obtaining and characterization of graphitic carbon nitride powder

Graphitic carbon nitride was obtained by calcining urea and melamine precursors at two temperatures, respectively 550°C and 600°C.

### II.2.1. Graphitic carbon nitride powder obtained by calcination of the urea precursor

Starting from the recipe, [34], in the first stage, the graphitic carbon nitride powder was obtained by calcining the urea precursor (CH<sub>4</sub>N<sub>2</sub>O) at two different temperatures,  $T = 550^{\circ}$ C, respectively  $T = 600^{\circ}$ C.

### II.2.2. Graphitic carbon nitride powder obtained by calcination of the melamine precursor

The second stage consisted in obtaining the graphitic carbon nitride powder by calcining the melamine precursor ( $C_3H_6N_6$ ) also at temperatures of T = 550°C, respectively T = 600°C, [35]. The g- $C_3N_4$  powders were characterized structurally (XRD), morphologically (SEM, AFM) and surface elemental composition (EDX). In order to be used in the sol-gel synthesis, g- $C_3N_4$  powders were dispersed in ethanol, thus obtaining dispersions with the concentration, 70 mg/mL.

#### II.3. Deposition of the photocatalytic thin films

It was aimed to obtain VIS-active photocatalytic thin layers by integrating graphitic carbon nitride in the titanium dioxide matrix, using two of the most feasible techniques: (a) spray pyrolysis deposition (SPD) and (b) sol–gel synthesis followed by spray deposition of diluted sol in the volume ratio, sol:EtOH1:5<sub>(v)</sub>. Using the two techniques, both mono-layer thin films (spray deposition of diluted TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> sol on glass/FTO substrate (small size 1.5 x 1.5 cm<sup>2</sup>)) and double-layer thin films (small size 1.5 x 1.5 cm<sup>2</sup> and large size 20 x 30 cm<sup>2</sup> by depositing an intermediate TiO<sub>2</sub> layer of using the SPD tehnique over which a layer 2 of TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> was deposited by spraying the diluted sol).

### II.3.1. Spray pyrolysis deposition (SPD) for the deposition of the TiO2 interlayer

Spray pyrolysis deposition (SPD) was employed to deposit the first titanium dioxide (TiO<sub>2</sub>) layer on the FTO substrate (1.5 x 1.5 cm<sup>2</sup>) at a temperature of 400°C with a number of 30 spraying sequences with 60 second break between two consecutive spraying pulses. After deposition, this layer was annealed at 450°C, for 3 hours (glass/FTO/TiO<sub>2</sub>\_SPD). The precursor system used: solvent – ethanol, precursor titanium tetraisopropoxide and the complexing agent acetylacetone in the volume ratio TTIP : AcAc : EtOH = 1 : 1 : 15(V).

Before deposition, the substrates were cleaned with water and detergent in the ultrasonic bath for 10 minutes; they were rinsed first with distilled water and then with ethanol and air-dried.

### II.3.2. Obtaining of the TiO₂\_SG thin layer and the TiO₂ – g-C₃N₄\_SG composite layer by sol-gel (SG) method

 $TiO_2$  thin films and  $TiO_2-g-C_3N_4$  composites were obtained using sol-gel synthesis followed by spraying dilute sol. In the sol-gel synthesis of the composite layer, used TTIP as precursor, ethanolic dispersion of  $g-C_3N_4$ , c = 70 mg/mL (the  $g-C_3N_4$  ethanolic dispersion, will partially or totally replace

the continuous medium, ethanol, equired in the sol-gel synthesis), complexing agent acetylacetone, acetic acid to ensure the reaction pH (pH = 5) and with distilled water subsequently used as hydrolysis reactant, in volume ratio TTIP:g-C<sub>3</sub>N<sub>4</sub>:EtOH:AcAc:HAc:H<sub>2</sub>O 1 = :0.52:0.27:0.04:0.009:0.12(v). The sol was ultra-sonicated for 1.5 hours, t and was afterwards diluted in a volume ratio, sol:ethanol =  $1:5_{(v)}$  and ultra-sonicated before deposition for 0.5 hours. The sprying of TiO<sub>2</sub> and TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> diluted sol respectively on the glass/FTO substrate (1.5 x1.5 cm<sup>2</sup>) was done at the temperature of 100°C using 15 spraying sequences; the break between two consecutive pulses was 60 seconds. After deposition, the layers were thermally treated at 450°C for 2 hours.

Evaluating the results obtained, using the mono-layer composites, the research continued with the deposition of the double-layer type composites, by coupling the SPD and the SG techniques, focusing mainly on the properties of interest of the photocatalysts: VIS-activation, improvement of efficiency in photocatalytic processes and stability in the environment aqueous.

### II.3.3. Obtaining of the TiO₂\_SPD / TiO₂ – g-C₃N₄\_SG double-layer composites using SPD method coupled with sprying of the composite sol

Double-layer composites with TiO<sub>2</sub> matrix and g-C<sub>3</sub>N<sub>4</sub> filler were deposited by spraying a diluted composite sol using the sol-gel tehnique, the g-C<sub>3</sub>N<sub>4</sub> powder obtained by calcining the precursor urea at T = 550°C and T = 600°C. Initially, the aim was to optimize the temperature of the thermal treatment applied to the final composite, these being thermally treated at three different temperatures: at T = 150°C, T = 450°C and T = 480°C for 2 hours. The influence of the intermediate layer of TiO<sub>2</sub>\_SPD and the optimization of the content of g-C<sub>3</sub>N<sub>4</sub> in the composite 1% ... 20% were followed.

### II.3.3.1. Obtaining composite thin layers using g-C3N4 powder obtained by calcining of the urea precursor

Starting from the recipe, [34], in the first stage, the graphitic carbon nitride powder was synthesized using urea precursor calcined (CH<sub>4</sub>N<sub>2</sub>O) at two different temperatures, T = 550°C, respectively T = 600°C.

## II.3.3.2. Obtaining composite thin layers using g-C₃N₄ powder obtained by calcining of the melamine precursor

Comparatively, double-layer composites were also obtained in which the g-C<sub>3</sub>N<sub>4</sub> powder used was synthesized using melamine precursor calcined, according to Chap. II.2.2.

### II.4. Characterization of the photocatalytic thin films

The thin layers obtained were characterized using the following techniques: X-ray Diffraction (XRD), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy EDX, UV-VIS Spectroscopy.

### II.5. Testing the photocatalytic activity of the composite thin layers, at the laboratory level, in a static regime under UV radiation and UV+VIS radiation

After characterization, the composite thin layers were tested in photocatalytic processes. The photocatalytic activity of the composite thin films (plates of size  $1.5 \times 1.5 \text{ cm}^2$ ) was investigated by the photodegradation of the standard methylene blue (MB) pollutant using a diluted solution with, c = 10 ppm (STAS:ISO 10678; 2010, [36]), in static regime. To evaluate the VIS-activation of the composites following the integration of g-C<sub>3</sub>N<sub>4</sub> in the TiO<sub>2</sub> matrix, photocatalytic experiments were also performed in the photodegradation of the colorless imidacloprid (IMD) pollutant, c = 10 ppm.

In the static experiments, the composite thin layers were immersed in 20 mL of methylene blue (MB) solution of 10 ppm, at natural pH, (pH  $_{MB \text{ solution}} = 6.98$ ) and were kept in the dark for 1 hour to reach the adsorption-desorption equilibrium. It was then subjected to irradiation for 8 hours in a laboratory photoreactor, using:

- (a) UV+VIS simulated solar radiation (2 UV lamps + 5 VIS lamps), with irradiance G = 55 W/m<sup>2</sup>
- (b) UV radiation (2 UV lamps), with irradiance  $G = 3 W/m^2$ .

In parallel, adsorption tests were also run for 9 hours, in dark, to observe the contribution of adsorption to the overall photo-degradation efficiency. Photocatalytic experiments were also performed at an optimized pH value of the dilute solution of MB or IMD (pH <sub>MB/IMD solution</sub> = 8.50) following the PZC value of the photocatalytic films; the experiments were run out under conditions similar to those used in the tests carried out at natural pH.

The process efficiency was calculated, based on the initial absorbance and the absorbance measured after each hour of photocatalytic testing using the UV-VIS spectrophotometer (Perkin Elmer Lambda 950) at the maximum absorption wavelength of methylene blue ( $\lambda_{max MB} = 664$  nm) respectively, of imidacloprid ( $\lambda_{max IMD} = 269$  nm).

$$\eta = \frac{A_i - A_t}{A_i} \cdot 100 \quad [\%] \tag{7}$$

were:  $\eta$  – process efficiency;

A<sub>i</sub> – absorbance of the initial MB/IMD solution;

A<sub>t</sub> – absorbance of MB/IMD solution at fixed time points.

### II.6. Testing the photocatalytic activity of composite thin films in dynamic regime at the demonstrator level

The laboratory optimized composite was deposited on large surfaces (total surface of 600 cm<sup>2</sup>). In the photocatalytic experiments, 5 liters of methylene blue solution, 10 ppm, at pH <sub>MB solution</sub> = 8.50 were used. The experiment was carried out in continuous flow, ranging the flow rate of the pollutant

solution, D = 0.5; 1 and 1.5 L/min in three different experiments. The duration of the process was 1 hour of adsorption (in the dark) followed by 8 hours of irradiation under simulated solar radiation UV+VIS, with irradiance,  $G_{UV+VIS}$  = 800 W/m<sup>2</sup>, out of which  $G_{UV}$  = 19 W/m<sup>2</sup>. The methylene blue photodegradation efficiency using the composite layers and the stability of these layers were tested by performing 3 successive cycles of photocatalysis with the specification that, after each cycle, the photocatalyst was regenerated by washing with distilled water (5 liters) in continuous flow, for 30 minutes, at a flow rate of 0.5 L/min, 1 L/min, respectively 1.5 L/min.

To highlight the VIS-sensitization due to methylene blue dye under VIS-radiation irradiation and at the same time to investigate the VIS-activation of the composite, photocatalysis tests were performed using the colorless pollutant imidacloprid (IMD), at 10 ppm.

#### II.7. Evaluation of the stability of the photocatalytic thin films in aqueous media

The stability of the photocatalytic layers was investigated based on the transmittance spectra (VIS spectral range  $\lambda$  = 400 ... 800 nm, using UV – Vis – NIR Spectrophotometer, Perkin Elmer 950, by investigating the morphology (SEM, S-3400N-Hitachi and AFM, Ntegra Spectra, NT-MDT) and roughness evaluation (RMS - AFM) of the photocatalyst before and after the photocatalysis process.

### CHAPTER III. TiO<sub>2</sub>\_SPD and TiO<sub>2</sub>\_SG photocatalytic thin films used for the photodegradation of the methylene blue standard pollutant

The photocatalytic thin layers with small surface 1.5 x 1.5 cm<sup>2</sup>) obtained by the spray pyrolysis deposition (SPD) method, respectively, by the sol-gel (SG) technique followed by the spray deposition of TiO<sub>2</sub> diluted sol, were characterized in terms: crystallinity (XRD), morphology (SEM and AFM), roughness (RMS) and superficial elemental composition (EDX), being then investigated in photocatalysis tests carried out in static regime, using a methylene blue (MB, 10 ppm) diluted solution at natural pH and optimized pH.

### III.1. Structural, morphological, elemental composition and roughness characterization of the TiO<sub>2</sub>\_SPD and TiO<sub>2</sub>\_SG layers

The X-ray diffraction spectra for samples show the characteristic peaks of the crystalline phase anatase –  $TiO_2$ , peaks with higher intensity in the case of the thin layer obtained by spraying the  $TiO_2$  sol, and therefore higher degree of crystallinity . In addition to the peaks characteristic of the crystalline phase of  $TiO_2$  anatase, the characteristic peaks of  $SnO_2$  cassiterite corresponding to the substrate used, glass/FTO, confirmed the deposition of thin layers.

In the morphology of the TiO<sub>2</sub> layer deposited by spray pyrolysis, shows the uniform deposition with only a few small TiO<sub>2</sub> aggregates individually attached to the surface, thus indicating a good adhesion/compatibility of the layer deposited on the glass/FTO substrate. Comparatively, the thin layer of TiO<sub>2</sub> deposited by spraying the diluted sol shows a morphology with numerous aggregates

of  $TiO_2$  on the surface; micro-cracks were also present on this layer, due to obtaining a thick layer or due to the reduced compatibility between the  $TiO_2$  layer deposited by spraying sol and the substrate.

#### III.2. The selection of the working pH

The the point(s) of zero charge (PZC) of the thin films, used were evaluated to optimize the working pH. The evaluation shows 2 inflection point(s) corresponding to the glass/FTO substrate used, PZC FTO 1 =  $3.80 \dots 4.27$  and PZC FTO 2 =  $8.26 \dots 8.43$  and a PZC inflection point corresponding to titanium dioxide PZC =  $4.34 \dots 5.34$ ,. To cover all the inflection points and to favor the attraction between the photocatalytic surface and the pollutant, taking into account that methylene blue is positively charged at pH > 3.8, [37] and the thin layer surface is negatively charged after the PZC value maximum, therefore the photocatalysis tests should be performed at pH <sub>MB solution</sub> = 8.50 and, at the natural pH (pH ~ 6.98) of the dye solution.

### III.3. Photodegradation efficiency of the methylene blue standard pollutant using TiO2\_SPD and TiO2\_SG layers

Higher methylene blue photodegradation efficiencies were obtained using the glass/FTO/TiO<sub>2</sub>\_SG thin layer. These results are due to the properties of this material: higher degree of crystallinity and significantly RMS values. Higher photodegradation efficiencies were obtained at pH = 8.50, in the case of both types of thin layers, which confirms that the pH must be carefully optimized to support the pollutant-photocatalyst electrostatic attraction. The photocatalysis results under UV+VIS irradiation were found to be similar to those obtained under UV irradiation, confirming the activity of the TiO<sub>2</sub> photocatalyst under UV irradiation alone.

### III.4. Evaluation of the stability of the TiO2\_SPD and TiO2\_SG layers in aqueous media

The stability of the thin layers was evaluated by analysis of morphology, roughness and by evaluating the transmittance spectra of the layers before and after the photocatalysis process. Small changes in morphology, slight increase in roughness, and small variations in transmittance spectra ( $\Delta T = 3\%$ ) before and after photocatalysis/adsorption indicated a good stability of these layers in the aqueous environment.

### **Conclusions of chapter 3**

Thin layers of  $TiO_2$  type obtained by the SPD method and by spraying the diluted  $TiO_2$  sol (sol-gel synthesis), were investigated at the laboratory level in photocatalytic processes, using the methylene blue pollutant in a dilute solution, 10 ppm. Higher methylene blue photodegradation efficiencies were obtained on the glass/FTO/TiO<sub>2</sub>\_SG thin films, which were correlated with the material properties. Performing the photocatalysis tests at pH = 8.50 led to higher pollutant photodegradation efficiencies in the case of both types of thin layers due to higher adsorption efficiencies (after one hour of darkness), confirming the need to optimize the working pH.

The good stability in the aqueous environment of the thin layers was demonstrated by the small variations in transmittance spectra and roughness and by the small changes in morphology at pH values between 7 – 8.50, pH values needed/used in wastewater treatment.

Considering that the obtained results confirm the activation of TiO<sub>2</sub> exclusively under UV radiation irradiation, to improve the photocatalytic activity it is necessary to use artificial energy sources, which raises the cost of the process. In order to have as low process costs as possible, but also good photocatalytic activity, the best solution is to activate the photocatalyst under VIS radiation, thus using a greater proportion of the solar radiation.

In this work, it was proposed to obtain VIS-/solar-active composite thin layers by integrating graphitic carbon nitride in the TiO<sub>2</sub> matrix and investigating them in photocatalytic processes.

## CAPITOLUL IV. Double-layer TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG composites used in the photodegradation of organic pollutants in water. Photocatalytic experiments in static mode

Composites with  $TiO_2$  matrix and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) filler were obtained. The photodegradation efficiency of the methylene blue and imidacloprid pollutants, VIS-activation and stability of the composites in the aqueous environment were studied, following: the optimization of the thermall treatment temperature applied to the final composite, the influence of the intermediate layer of  $TiO_2$ \_SPD and the influence of the content of  $g-C_3N_4$  in the composite.

### IV.1. Structural, morphological and surface elemental composition characterization of g-C₃N₄ powders

The X-ray diffraction, Fig. 4, demonstrating the obtaining of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) by the presence of characteristic peaks at  $2\theta = 13^{\circ}$  and  $2\theta = 27$  ...  $28^{\circ}$  for all four types of powders that have a degree of crystallinity of 46 ... 55 %. The obtaining of graphitic carbon nitride was also supported by the surface elemental composition results.



Fig. 4 X-ray diffraction for the four  $g-C_3N_4$  powders obtained from urea precursor (u) and melamine precursor (m) at  $T = 550^\circ$ C respectively at  $T = 600^\circ$ C

# VI.2. The influence of the thermal treatment temperature applied on the TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG double layer composites on the stability of the layers and on the photodegradation efficiency of the methylene blue standard pollutant

Glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG double-layer composites with 5% g-C<sub>3</sub>N<sub>4</sub> content in the composite layer were obtained. Graphitic carbon nitride used in the sol-gel synthesis of these composites was obtained from urea precursor at T = 550°C and T = 600°C. The composite layers were thermally treated at three different temperatures: TTT = 150°C; TTT = 450°C, respectively TTT = 480°C thus following the influence of the temperature of the thermal treatment applied to the double-layer composite on the stability in the aqueous environment and on the photodegradation efficiency of the methylene blue pollutant from a diluted solution with c = 10 ppm. Characterizations of structure and morphology were performed, respectively roughness and transmittance spectra of the double-layer composites.

X-ray diffraction spectra indicated the presence of peaks characteristic of the crystalline phase of the anatase TiO<sub>2</sub> polymorph, peaks with higher intensity in the case of composites thermally treated at T = 450°C and T = 480°C, compared to composites thermally treated at T = 150°C, where the intensity of the peaks was much lower. In addition to these, the SnO<sub>2</sub> cassiterite peaks were also highlighted, being due to the substrate used. The crystalline phase of the TiO<sub>2</sub>-anatase polymorph at T > 450°C leads to an increase in the degree of crystallinity, and the relatively insignificant difference in crystallinity between the composites thermally treated at T = 450°C and T = 480°C is due to the small temperature variation.

The composite thin films shows a morphology with platelets of  $g-C_3N_4$  well covered with TiO<sub>2</sub> aggregates distributed all over the film surface. In the case of the composites thermally treated at T = 150°C and T = 450°C, a more uniform distribution of the aggregates on the film surface is observed compared to the composite thermally treated at T = 480°C, when a reorganization of the aggregates takes place.



Fig. 5 SEM images for composite thin layers  $glass/FTO/TiO_2 SPD/TiO_2 - g-C_3N_4 550 SG;$  (a)  $TT_{composite} = 150°C;$  (b)  $TT_{composite} = 450°C;$  (c)  $TT_{composite} = 480°C$ 



Fig. 6 SEM images for composite thin layers  $glass /FTO/TiO_2 - g-C_3N_4 - 600 - SG;$  (a)  $TT_{composite} = 150^{\circ}C$ , (b)  $TT_{composite} = 450^{\circ}C;$  (c)  $TT_{composite} = 480^{\circ}C$ 

The roughness values of the thin layers are also similar for the two types of powders used in obtaining the composites, but it should be noted that the roughness increases with the increase in the thermal treatment temperature, Table 1. Although, the roughness variations between the composites are small, they can influence the photocatalytic efficiency by favoring the adsorption step.

Sample	TT <sub>composite</sub>	RMS value [nm]
<i>The roughness of the composites</i> glass/ FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _ <b>550_</b> SG		
(a) glass/FTO/TiO2_SPD/TiO2 – g-C3N4_550_ SG	150	265
(b) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _550_SG	450	273
(c) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _550_SG	480	301
<i>The roughness of the composites</i> glass/FT0/Ti0 <sub>2</sub> _SPD/Ti0 <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _ <b>600_</b> SG		
(a) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _600_SG	150	270
(b) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _600_SG	450	267
(c) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _600_SG	480	297

Table 1 Roughness values of the double-layer composites

Higher MB photodegradation efficiencies, Fig. 7 were recorded using the composites annealed at a higher temperature of 450°C compared to T = 150°C. At temperatures higher than 450°C, the process proceeds with reduced efficiency, these results can be correlated with the lower values of the degree of crystallinity and the RMS values of the thin layers. Also the lower photodegradation efficiencies recorded under UV irradiation compared to those MB photodegradation efficiencies recorded under UV+VIS radiation ( $\eta$ UV+VIS >  $\eta$  UV) demonstrate the VIS - activation of the composites following the integration of g-C<sub>3</sub>N<sub>4</sub> as a filler. The photocatalytic experiments performed at pH <sub>MB solution</sub> = 8.50 they recorded the photodegradation efficiencies of MB approximately 10% higher, indicating that the selection of the working pH is an important step that must be carefully performed.



Fig. 7 Photodegradation efficiencies of MB under UV+VIS irradiation on composites as a function of thermal treatment temperature and working pH: glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_550\_SG: (a)  $pH_{MB solution} = 6,98$  and (a`)  $pH_{MB solution} = 8,50$ and glass /FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_600\_SG: (b)  $pH_{MB solution} = 6,98 \neq i$  (b`)  $pH_{MB solution} = 8,50$ 

The results demonstrated that the temperature of the thermal treatment applied to the final composite influences the photodegradation efficiency of MB and the stability in the aqueous environment of the composite thin layers. For the following investigations it was recommended to thermal treated the final composite at T = 450°C for 2 hours and using the g-C<sub>3</sub>N<sub>4</sub> powder obtained from the urea precursor at T = 550°C. The research continued with obtaining mono-layer and double-layer composites following the influence of the interlayer of TiO<sub>2</sub>\_SPD.

### IV.3. Influence of the TiO<sub>2</sub>\_SPD interlayer on the photodegradation efficiency of the methylene blue standard pollutant

Next, the influence of the  $TiO_2$ \_SPD interlayer in the double-layer composite structure on the photodegradation efficiency of the methylene blue pollutant was investigated.

X-ray diffraction spectra, Fig. 8, indicated the presence of characteristic peaks of the TiO<sub>2</sub> anatase polymorph and SnO<sub>2</sub> corresponding to the FTO layer (glass/FTO) with a stronger intensity of the TiO<sub>2</sub> anatase peak in the double-layer composite, an aspect also confirmed by the higher degree of crystallinity, Table 2. The higher degree of crystallinity on the double-layer composite is due to the high adhesion of layer 2 to the similar substrate (TiO<sub>2</sub> film) which favors the ordering of layer 2 (TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG) on a glass/FTO/TiO<sub>2</sub>\_SPD substrate compared to the development of the composite layer on a substrate with which the similarities are less (glass/FTO substrate).



Fig. 8 X-ray diffractogram of composite thin films: (a) glass/FTO/TiO2\_SPD/TiO2 – g-C3N4\_SG\_5% and (b) glass/FTO/TiO2 – g-C3N4\_SG\_5%

Sample Degree of crystallinit	
(a) glass/FTO/TiO₂ – g-C₃N₄_SG_5%	44,5
(b) glass/FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> - g-C <sub>3</sub> N <sub>4</sub> _SG_5%	47,5

Table 2 The degree of crystallinity of the composite thin films

Compared to double-layer thin films where the morphology shows more uniformly distributed agglomerations on the film surface, the composite thin films without TiO<sub>2</sub> interlayer have a multi-agglomeration morphology. These may be due to the agglomeration of g-C<sub>3</sub>N<sub>4</sub> in certain areas, thus concluding that the deposition of the composite layer 2 on a glass/FTO/TiO<sub>2</sub>\_SPD type substrate favors obtaining a layer with a higher degree of uniformity, Fig. 9.



Fig. 9 SEM and AFM images of the composite thin layers (a) glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>SG\_5%; (b) glass/FTO/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG\_5%

The promising results in the photodegradation process of methylene blue were obtained using the double-layer composite thin films. These values is due to both the structural properties and the more uniform morphology. The results recorded in the investigation of the influence of the intermediate layer on the photocatalytic activity recommend the use of double-layer composites in further studies.

Aiming to obtain materials with good photocatalytic properties (photocatalytic activity, stability in the aqueous medium and VIS-activation), but also low cost of the photocatalytic process, the use

of g-C<sub>3</sub>N<sub>4</sub> in the composite was further investigated, aiming to optimize its content in the TiO<sub>2</sub> - g - C<sub>3</sub>N<sub>4</sub> structures.

## IV.4. The influence of the content of g-C₃N₄ in the composite layer (1 ... 20%) on the photodegradation efficiency of methylene blue and on the stability of the photocatalytic film under UV and UV+VIS irradiation

Double layer composites were obtained by varying the content of  $g-C_3N_4$  (1%; 3%; 5%; 10%; 15% and 20%). The influence of the content of  $g-C_3N_4$  (obtained from urea precursor) in the composite layer on the photodegradation efficiency of the methylene blue pollutant and on the stability of the film in photocatalytic processes carried out in a static regime, at the laboratory level, was followed.

The diffraction spectra shown in Fig. 10 indicated the presence of peaks characteristic of the TiO<sup>2</sup> anatase polymorph and SnO<sub>2</sub> cassiterite peaks for all double-layer composites. The characteristic peak of g-C<sub>3</sub>N<sub>4</sub> at 2 $\theta$  = 27...28° was present only for the double-layer composite with 20% g-C<sub>3</sub>N<sub>4</sub> Fig. 10 (A) diffractogram (g), but it can be seen more clearly in Fig. 10 (B) when the composite with 20% g-C<sub>3</sub>N<sub>4</sub> was deposited on glass without FTO layer (thus eliminating the SnO<sub>2</sub> peak present at 2 $\theta$  = 26.7°); the absence of the g-C<sub>3</sub>N<sub>4</sub> peak for the other composites is (the result of) the low content of g-C<sub>3</sub>N<sub>4</sub> and its uniform distribution in the composite.



Fig. 10 XRD characterization results: (A) double-layer composites: (a) glass/FT0/TiO<sub>2</sub>\_SPD; (b) glass /FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_1%; (c) glass /FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_3%; (d) glass / FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_5%; (e) glass /FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_10%; (f) glass FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_15%; (g) glass /FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_10%; (f) glass FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_15%; (g) glass /FT0/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_20% și (B) double-layer composites glass/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>SG\_20% deposited on a glass substrate (without FTO)

The results of the XRD characterization in Table 3 show an increase in the degree of crystallinity for the double-layer composites investigated, with the increase in the content of  $g-C_3N_4$  in the

composite up to a content of 10%; at higher g-C₃N₄ content, the degree of crystallinity remains constant probably due to the agglomeration of graphitic carbon nitride.

Sample	Degree of crystallinity, DG [%]
(a) glass/FTO/TiO2_SPD	39,5
(b) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _SG_1%	44,7
(c) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _SG_3%	46,3
(d) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> - g-C <sub>3</sub> N <sub>4</sub> _SG_5%	47,3
(e) glass /FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> - g-C <sub>3</sub> N <sub>4</sub> _SG_10%	49,8
(f) glass FTO/TiO <sub>2</sub> _SPD/TiO <sub>2</sub> – g-C <sub>3</sub> N <sub>4</sub> _SG_15%	49,6
(g) glass /FTO/TiO2_SPD/TiO2 – g-C3N4_SG_20%	50,2

Table 3 Degree of crystallinity of the interlayer TiO<sub>2</sub> SPD and of the double-layer composites TiO<sub>2</sub> SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> SG

SEM images showed that the morphology of the composites varies with  $g-C_3N_4$  content, with an increase in  $g-C_3N_4$  content resulting in more  $g-C_3N_4$  platelets cover with TiO<sub>2</sub> aggregates. Moreover, at a higher content of  $g-C_3N_4$  in the composite (15% and 20%), significant agglomerations of the filler appear at the surface of the film, confirmed by the results of the surface elemental composition.

Small changes in the morphology of the composites were observed after the photocatalysis process (partial passage of  $TiO_2$  aggregates in the solution), but performing the tests at optimized pH (pH = 8.50) does not seem to influence the stability of the composites. The small morphological changes were correlated with the small roughness variations and transmittance variations demonstrating the obtaining of stable photocatalytic materials in the investigated pH range (6.98 – 8.50).

The photocatalysis results indicated VIS-activation of the composites even at low g-C<sub>3</sub>N<sub>4</sub> content when using the tandem system, with lower photodegradation efficiencies recorded under UV irradiation compared to photodegradation efficiencies recorded under irradiation with UV + VIS radiation. The photodegradation efficiency of methylene blue at pH  $_{MB \text{ solution}} = 8.50$  indicated higher values by about 13% than the results recorded at natural pH, again confirming the positive effect of pollutant-photocatalyst electrostatic attraction. The best results in MB photodegradation were obtained on composites with 5% g-C<sub>3</sub>N<sub>4</sub> content, suggesting that this is the optimal content in TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> composites.



Fig. 11 Photodegradation efficiencies of MB under UV + VIS irradiation recorded during static regime, on the TiO<sub>2</sub>\_SPD interlayer and on the TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub> 1 ... 20%\_SG double-layer composites at: (a) pH <sub>MB solution</sub> = 6.98 and (b) pH <sub>MB solution</sub> = 8.50

The most promising results in terms of photocatalytic activity and stability in the working conditions were recorded using the glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub>\_SG double-layer composite with 5% g-C<sub>3</sub>N<sub>4</sub> content, recommending its use in further studies of research. Also the VIS-activation of the optimal composite was demonstrated by the photodegradation of the colorless imidacloprid (IMD) pollutant. These results, recommended that the composite with 5% g-C<sub>3</sub>N<sub>4</sub> content in a glass/FTO/TiO<sub>2</sub>\_g-C<sub>3</sub>N<sub>4</sub>\_SG\_5% structure be tested at demonstrator level, and the g-C<sub>3</sub>N<sub>4</sub> used be obtained by calcination of urea at T = 550°C.

#### **Conclusions of chapter 4**

Mono- and double-layer composites with  $TiO_2$  matrix and  $g-C_3N_4$  filler were deposited by combining spray pyrolysis deposition (SPD) technique and sol-gel (SG) synthesis followed by  $TiO_2 - g-C_3N_4$  sol spraying, using small (1.5 x 1.5 cm<sup>2</sup>) glass and glass/FTO substrates. The photocatalytic activity and the stability of the composites were investigated aiming at the optimization of the temperature of the thermal treatment applied to the composite layer, the optimization of the structure of the mono- or double-layer composites and the optimization of the content of  $g-C_3N_4$  in the composites (1% ... 20%).

The obtained results demonstrated that the temperature of the thermal treatment applied to the final composite influences the photodegradation efficiency of MB and also the stability in the aqueous environment of the composite thin layers. The optimal temperature and duration of thermal treatment of the composite were  $T = 450^{\circ}$ C, for 2 hours.

It has been demonstrated that the use of an intermediate layer of  $TiO_2$  deposited between the glass/FTO substrate and the  $TiO_2 - g-C_3N_4$  composite layer improves the photocatalytic activity of the composites, and the stability in the working environment is not negatively affected.

Investigating the influence of the content of  $g-C_3N_4$  in the composite on the photocatalytic activity, the results recorded in the static regime, at laboratory scale, suggested an optimal content of 5%  $g-C_3N_4$  in the composite layer, when the photodegradation efficiency of MB is up to 41% after nine hours of experiment.

The lower photodegradation efficiencies under UV irradiation compared to MB photodegradation efficiencies recorded under UV+VIS irradiation outlining VIS - activation of the composites following the integration of  $g-C_3N_4$  as a filler in the TiO<sub>2</sub> matrix, even at low  $g-C_3N_4$  content. The VIS-activation of the composites was also confirmed by the results of photocatalytic experiments using the (colorless) pesticide imidacloprid (IMD) as pollutant.

The results, recirded using glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG composite thin layers with 5% g-C<sub>3</sub>N<sub>4</sub> content (g-C<sub>3</sub>N<sub>4</sub> obtained from urea precursor) were recommended for use in advanced wastewater treatment, in the next step, on the demonstrator photoreactor.

## **CAPITOLUL V.** Investigation of the optimized TiO<sub>2</sub>\_SPD / TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG double-layer composite, in dynamic regime, at demonstrator level

The double-layer composite selected as optimal having the structure glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> –  $g-C_3N_4\_SG\_5\%$  was deposited on larger surfaces (20 x 30 cm<sup>2</sup>) under similar conditions to those for obtaining the composite on small surfaces (1 .5 x 1.5 cm<sup>2</sup>) and was investigated by performing photocatalysis tests in the demonstrator photoreactor, in dynamic regime.

### V.1. Structural and morphological characterization of the double-layer composite used in the demonstrator photoreactor

The structure and morphology of the composite selected to be deposited on large surfaces were similar to those recorded on the double-layer composite deposited on small surfaces.

## V.2. Photodegradation efficiency of the methylene blue standard pollutant using TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG double-layer composite in the demonstrator photoreactor under dynamic regime and under simulated solar irradiation

In the photocatalytic experiment carried out at the demonstrator level, 5 liters of diluted solution (10 ppm) of methylene blue were used at  $pH_{MB \text{ solution}} = 8.50$ . The experiment was carried out in continuous flow, at three different values of the flow rate of the pollutant solution: 0.5 L/min, 1 L/min and 1.5 L/min. The duration of the photocatalysis process was similar to that used in the laboratory experiment: 1 hour of adsorption (in the dark) followed by 8 hours under irradiation with simulated solar radiation with  $G_{UV+VIS} = 800 \text{ W/m}^2$  and  $GUV=19 \text{ W/m}^2$ . The photocatalytic activity and the stability of the photocatalysis, after optimizing the flow rate of the pollutant solution.

### V.3. Influence of pollutant solution flow rate on the photodegradation efficiency and double-layer composite stability at demonstrator level

Testing of the composite with 5% g-C<sub>3</sub>N<sub>4</sub> at the demonstrator level, in the dynamic regime, led to significantly higher MB pollutant, photodegradation efficiencies compared to the efficiencies recorded at the laboratory level in the static regime. A continuous and relatively constant increase in the photodegradation efficiency of MB was observed throughout the tests, regardless of the flow rate of the pollutant solution used in the process, confirming that the photocatalyst still works after 9 hours of the process. It was found that the flow rate of the pollutant solution used in the photocatalyst. The higher adsorption results after one hour in the dark, supported the higher photodegradation efficiency, with the best results recorded at a flow rate of 1 L/min.

After the photocatalysis tests performed at flow rates of 0.5 L/min and 1.5 L/min in the SEM images, microcracks could be identified on the surface of the composite, Fig 12b and Fig. 12 d. Also, the slight increase in roughness after the photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min indicates a possible loading of the photocatalyst. A slight decrease in the transmittance of the layers was also observed, confirming the loading of the photocatalyst with MB photodegradation products or MB molecules adsorbed on the surface that were not degraded, more pronounced after the photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min and 1.5 L/min and 1.5 L/min photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min and 1.5 L/min photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min and 1.5 L/min photocatalysis processes carried out at a flow rate of 0.5 L/min and 1.5 L/min.



Fig. 12 SEM images of the glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG\_5% before and after the photocatalysis process, recorded in dynamic regime: a) before photocatalysis; and after photocatalysis at a flow rate of b) 0.5 L/min; c) 1 L/min and d) 1.5 L/min

The most results in terms of photodegradation efficiency and stability of the composite under working conditions at the demonstrator level ranging the flow rate of the pollutant solution were

recorded in the tests performed at a flow rate of 1 L/min; thus, the research continued with the investigation of the stability and durability of the selected composite, used in the demonstrator photoreactor, in dynamic regime by performing 3 successive cycles of photocatalysis, at a flow rate of 1 L/min.

### V.4. Stability of the double-layer composite in photocatalytic processes at the demonstrator level, in the dynamic regime, during three successive cycles of photocatalytic process

The SEM and AFM images recorded before and after each of the three photocatalysis cycles, indicate a good stability of the composite film in the aqueous environment, well supported only small changes recorded in morphology after the 3 photocatalysis cycles, the presence of initial agglomerates being less pronounced, with more aggregates, distributed due to a possible (partial) washing of TiO<sub>2</sub> particles, more evident in AFM image. The stability of the composite was also supported by the small variations of roughness and transmittance, a more obvious decrease can be notice only after Cycle III; this decrease may be due to the (partial) washing of the particles from the film surface and their passage into the MB solution. A decrease in MB photodegradation efficiency of about 4% was observed after the 3<sup>rd</sup> cycle of photocatalysis, but can be considered acceptable, demonstrating that the photocatalyst thin film is efficient after 27 hours of processing.

The MB photodegradation results and the stability and durability in the aqueous environment for the two types of composites, investigated at the laboratory level, in static regime and at demonstrator level in dynamic regime, recommend the glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C3N4\_SG\_5% structure for the photocatalytic degradation processes of MB pollutant in wastewater treatment, and further experiments were designed to also investigate the removal of other pollutants using the demonstrator photoreactor.

### V.5. Investigation of the VIS-activation of the composite thin films; photodegradation efficiency using the imidacloprid pollutant at demonstrator scale with simulated solar irradiation

Morphology investigation by SEM and AFM before and after the photocatalysis process using the MB and IMD pollutants indicated a good stability of the composite in the aqueous environment, as insignificant changes in morphology were outlining. Also, the transmittance variations before and after the 3 cycles of photocatalysis are very small; using imidacloprid as a test pollutant, only a slight increase in transmittance was observed ( $\Delta T = 1 \dots 2\%$ ) due to the partial passing of several TiO<sub>2</sub> aggregates from the thin film surface into the IMD solution, an aspect also supported by the decrease in the roughness of the composite. At the same time, the small variations in transmittance and roughness indicate the good stability of the composite in the aqueous environment and in working conditions, regardless of the type of pollutant. The wash out effect (partial passind of TiO<sub>2</sub> aggregates from the thin film surface into the IMD solution) was also be observed when using the IMD solution when a RMS reduction can be noticed even after each cycle. IMD pollutant may be more difficult to degrade due to the flexibility of its molecule that may limit its adsorption efficiency. However, the overall decrease in the photodegradation efficiency after the 3<sup>rd</sup> cycle of

photocatalysis (~4% for MB and ~7% for IMD) can be considered acceptable, demonstrating that the photocatalyst is efficient even after 27 h of the processing.

Considering the results recorded in the photodegradation processes of MB and IMD in terms of photodegradation efficiency, aqueous stability and photocatalyst durability, the glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub>\_SG\_5% composite is recommended in advanced wastewater treatment, through photocatalytic processes and can be selected for next-stage process scaling to pilot scale.

### **Conclusions of chapter 5**

The photocatalytic experiments using the demonstrator photoreactor were carried out at 3 different values of the flow rate of the pollutant solution: 0.5 L/min, 1 L/min, 1.5 L/min. The best results in terms of stability in the aqueous envinorement and photodegradation efficiency of methylene blue were recorded at a flow rate of 1 L/min ( $\eta_{MB} = 63\%$  after 8 hours of irradiation UV+VIS, G = 800 W/m<sup>2</sup>), thus indicating the optimal value of flow rate for operation in the demonstrator photoreactor. The experiments demonstrated an increase in the photodegradation efficiency of MB of about 23% compared to the results obtained at the laboratory level due mainly to the irradiance of the radiation used, of approx. 15 times higher.

The investigation of the photodegradation efficiency, stability and durability of the selected composite continued by performing three successive photocatalysis cycles (with a total duration of 27 hours); the relatively small decrease in methylene blue photodegradation efficiency after Cycle II and Cycle III (about 4%) indicated a "partial" clogging/loading of the photocatalyst surface with MB photodegradation products incompletely removed by regeneration. But the small variations of transmittance and roughness values (RMS) before and after the photocatalytic process, indicated a good stability of the composite in the aqueous environment, in a dynamic regime.

The lower photodegradation efficiency after 8 h of irradiation of imidacloprid (IMD,  $\eta_{IMD}$  = 56%) compared to MB ( $\eta_{MB}$  = 63%) highlights the dye-sensitization effect under VIS radiation.

The good stability and durability of the composite in the working environment was outlining by morphology investigations, by small variations in transmittance and roughness. These results are promising and considering the industrial up-scaling of the photocatalytic process, using the glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG\_5% composite in advanced wastewater treatment for reuse.

### **Final conclusions**

Currently, through the application of conventional processes, the water is brought to the limit concentrations admissible for discharge into natural effluents, but in order to meet the reuse requirements, it is necessary to introduce an additional step to ensure the minimum quality conditions of the treated waters for their use in different applications. In recent years, various approaches have emerged to treat wastewater for reuse, including ion exchange adsorption, ultrafiltration/nanofiltration, membrane separation, and advanced oxidation processes.

Advanced oxidation processes are recommended in wastewater treatment, in addition to traditional methods, because they are efficient in degrading organic pollutants in very low concentrations (concentrations of the order of ppm, ppb).

Among the most studied advanced oxidation processes is the heterogeneous photocatalysis process. For the industrial implementation of the heterogeneous photocatalysis process, as a potential additional step in the treated wastewater for reuse, it is necessary to use photocatalytic materials with low cost of production and activation, especially under VIS irradiation.

The most using of the photocatalytic materials are  $TiO_2$  and ZnO due to their stability in aqueous environment, but the wide band gap (Eg ~ 3.2 eV) allows their activation only under irradiation with radiation in the UV spectral range, limiting their using in the process of photocatalysis introduced as an additional step in advanced wastewater treatment. Radiation from the UV spectral range represents 5-10% of the solar spectrum, so for efficient processes it is necessary to use artificial radiation that greatly increases process costs.

Alternative methods of large-scale use of stable and efficient metal oxides in photocatalytic processes are their doping (with cations or anions) or their coupling with a semiconductor with a narrow bandgap, with the formation of diode-type systems (n - p) or systems of tandem type (n - n or p-p) thus leading to VIS – activation.

VIS-active structures (n-p) are found by coupling graphene derivatives (r)GO semiconductors (p-type semiconductors) with  $TiO_2$  (n-type) semiconductors.

The disadvantage of graphene derivatives is the reduced thermal stability that limits the use of methods for obtaining structures with high crystallinity.

To obtain structures with high crystallinity, a semiconductor that has attracted the attention of researchers recently is graphitic carbon nitride,  $g-C_3N_4$ , an n-type semiconductor active in the VIS range. The coupling of the semiconductor TiO<sub>2</sub> (Eg = 3.2 eV) with the semiconductor  $g-C_3N_4$  (Eg = 2.7 eV), forms tandem n-n structures, VIS – active.

Starting from the current state of knowledge, through the work "Composite materials with metal oxide matrix and filler of carbon compounds with solar- and VIS-active photocatalytic properties" thin composite layers with  $TiO_2$  matrix and filler of  $g-C_3N_4$  were developed. Composite thin layers were investigated following the main properties of photocatalytic materials: photodegradation efficiency, VIS-activation and stability in aqueous envinoremnet which were correlated with the results obtained in the investigation of crystallinity, morphology, roughness and transmittance spectra aiming at their use in photocatalytic processes for treated advanced wastewater treatment targeting the euse.

**1.** Initially, TiO<sub>2</sub>\_SPD thin layers deposited by spray pyrolysis deposition (SPD) at the temperature of 400°C followed by annealead at 450°C for 3 hours and TiO<sub>2</sub>\_SG thin layers deposited using the sol-gel technique followed by spraying a diluted TiO<sub>2</sub> sol at the temperature of 100°C followed by thermal treatment at 450°C for 2 hours; the deposition substrate chosen was glass/FTO, with small surfaces 1.5 x 1.5 cm<sup>2</sup>.

The thin layers were investigated in photocatalytic processes, in static regime, using a methylene blue solution, 10 ppm and irradiation with simulated solar radiation UV+VIS, respectively UV radiation with  $G = 55 \text{ W/m}^2$ ; adsorption tests (in dark) were also performed.

Promising methylene blue photodegradation efficiencies were obtained using glass/FTO/TiO<sub>2</sub>\_SG thin layers, being correlated with higher crystallinity and roughness properties compared to glass/FTO/TiO<sub>2</sub>\_SPD layer values confirming the importance of these properties in pollutant photodegradation.

Selecting the optimal pH (pH  $_{MB \text{ solution}}$  = 8.50) led to higher methylene blue photodegradation efficiencies compared to the results obtained at natural pH, for both layers; the small variations of the transmittance and the morphology of the thin layers before/after photocatalysis, indicated their good stability in the aqueous environment.

The photodegradation efficiencies of MB under UV + VIS irradiation are similar to the efficiencies recorded under UV irradiation, thus demonstrating that the TiO<sub>2</sub> photocatalyst is activated only by the UV radiation.

Aiming at VIS-activation, improvement of photocatalytic efficiency and reduction of process costs, the development of new composite materials with TiO<sub>2</sub> matrix and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) filler was further proposed followed by their testing in photocatalytic processes.

**2.** The research continued with obtaining mono- and double-layer composites based on  $TiO_2 - g-C_3N_4$ , deposited on glass/FTO of small surfaces (1.5 x 1.5 cm<sup>2</sup>). The double-layer composites were obtaining by coupling the two techniques: SPD and sol-gel; initially an interlayer (layer 1) of  $TiO_2$  was obtained using the SPD technique over which a layer 2 was deposited by spraying a diluted sol of  $TiO_2 - g-C_3N_4$ . The objective was to obtain VIS-active composite materials, with good stability in the aqueous environment and low production cost, aiming to optimize the thermal treatment temperature applied to the final composite, the influence of the interlayer, the influence of the content of  $g-C_3N_4$  in the composite and the influence of the type of  $g-C_3N_4$  used, depending on the obtaining precursor; graphitic carbon nitride, was synthesized by calcining urea and melamine precursors at temperatures of 500°C and 600°C.

- X-ray diffraction and surface elemental composition (EDX) confirmed the obtaining of g-C<sub>3</sub>N<sub>4</sub>; in order to be used in sol-gel synthesis, g-C<sub>3</sub>N<sub>4</sub> powder was dispersed in ethanol, obtaining a dispersion of 70 mg/mL.

**2.1.** In the first stage, glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub>\_SG double-layer composites with a content of 5% g-C<sub>3</sub>N<sub>4</sub> were obtained; g-C<sub>3</sub>N<sub>4</sub> used was obtained from urea precursor at T = 550°C and T = 600°C; the composites were thermally treated at T = 150°C, 450°C and 480°C, for 2 hours.

- the influence of the thermal treatment temperature applied to the final composite on the photodegradation efficiency of MB was investigated at pH  $_{\rm MB\,solution}$  = 6.98 (the natural pH of the MB solution) and at a pH value optimized following the evaluation of the PZC (pH  $_{\rm MB\,solution}$  = 8.50); the influence of the thermal treatment temperature on the stability of the composite in the aqueous environment was also investigated;

- the structure (degree of crystallinity), morphology and roughness (RMS values) results demonstrated that the thermal treatment temperature influences both the photodegradation efficiency of MB and the stability of the composites in the aqueous environment;

- the best results were recorded using the double-layer composites thermal treated at T = 450 °C for 2 hours and g-C<sub>3</sub>N<sub>4</sub> obtained by calcining urea at T = 550 °C;

**2.2.** Following the optimization of the thermal treatment temperature applied to the final composite, the research continued with the investigation of the effect of the deposition of an interlayer of TiO<sub>2</sub>\_SPD on the photocatalytic activity and stability in the working environment.

- it was found that the use of the TiO<sub>2</sub>\_SPD interlayer improves the properties of interest of the photocatalytic materials by raising the degree of crystallinity and roughness, which is why the MB photodegradation efficiencies were higher using the double-layer composites; stability in aqueous environment was found to be good for both types of composites, demonstrated by small variations in transmittance and roughness of the composites.

- following the interesting properties of photocatalytic materials, in the continuation of the studies it is recommended to use double-layer composites.

**2.3.** Photolysis tests confirmed dye-sensitization effect under UV + VIS irradiation as the concentration of MB decreases by about 5.5% within 8 hours of irradiation in the absence of the photocatalyst.

**2.4.** Starting from the optimization of the conditions for obtaining the double-layer composites, the influence of the  $g-C_3N_4$  content ( $g-C_3N_4$  obtained from urea precursor, at T = 550°C) in the composite layer (1% ... 20%) was further investigated;

- the diffraction spectra of the investigated photocatalytic materials confirmed the presence of the corresponding g-C<sub>3</sub>N<sub>4</sub> peak only for the 20% composite; in the case of the other composites, the absence of the g-C<sub>3</sub>N<sub>4</sub> peak is a consequence of the low content of g-C<sub>3</sub>N<sub>4</sub>, well uniform distributed in the composite, also supported by the EDX results.

- SEM image and EDX rezults confirmed that with increasing  $g-C_3N_4$  content in the composite it agglomerates, an aspect confirmed by the presence of  $g-C_3N_4$  plates covered with TiO<sub>2</sub> particles, distributed on the surface.

- photocatalytic activity testing indicates a continuous increase in MB photodegradation efficiency with increasing g-C<sub>3</sub>N<sub>4</sub> content up to 5%; at higher g-C<sub>3</sub>N<sub>4</sub> content (10%, 15% and 20%) the photodegradation efficiency are lower, possibly due to the agglomeration of g-C<sub>3</sub>N<sub>4</sub> flakes in the composites (according to the SEM and EDX), when the interfaces between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are possibly fewer and/or and weaker.;

- the lower photodegradation efficiencies recorded under UV irradiation compared to MB photodegradation efficiencies obtained under UV+VIS irradiation ( $\eta$ UV+VIS >  $\eta$ UV) demonstrate VIS - activation of the composites following the integration of g-C<sub>3</sub>N<sub>4</sub> as a filler, even at low g-C<sub>3</sub>N<sub>4</sub> contents;

- photocatalytic experiments using imidacloprid (IMD) as a colorless pollutant, confirmed the VIS-activation of the composites;

- significantly higher MB photodegradation efficiencies were recorded in the photocatalytic experiments performed at an optimized pH (8.50) compared to the experiments performed at the natural pH of the MB solution (6.98), confirming that adsorption is a key step in the photocatalytic mechanism;

- the results regarding the stability in the aqueous environment of the double-layer composites obtained by investigating the transmittance, by morphological and by roughness variations before and after the photocatalysis process indicated good stability of these materials regardless of the content of  $g-C_3N_4$ ;

- according to the results recorded in the static regime, at the laboratory level, the optimal content of 5% g-C<sub>3</sub>N<sub>4</sub> in the composite layer was suggested, when the photodegradation efficiency of MB is up to 41% after nine hours of process.

**2.5.** Comparatively, under similar conditions, double layer composites were obtained using  $g-C_3N_4$  syntetized from melamine precursor. The photocatalysis process using these composites proceeded with lower efficiencies (by ~10%) compared to the results obtained using the composites in which  $g-C_3N_4$  obtained from the urea precursor, due to the lower roughness values that determined significant adsorption efficiencies more reduced.

- double-layer glass/FTO/TiO<sub>2</sub> \_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>\_SG composites with 5% g-C<sub>3</sub>N<sub>4</sub> content obtained from urea precursor thermal treated at 450°C are recommended for testing in advanced wastewater treatment processes in the next step, using the demonstrator photoreactor and simulated solar radiation.

**3.** The selected double-layer composite glass/FTO/TiO<sub>2</sub> \_SPD/TiO<sub>2</sub> - g-C<sub>3</sub>N<sub>4</sub>\_SG\_5% was deposited on large surfaces (the total surface of the deposited composite was 600 cm<sup>2</sup>, surface composed of: 5 plates of 10 x10 cm<sup>2</sup>, one plate 10 x 8 cm<sup>2</sup> and 5 plates 2 x 2 cm<sup>2</sup>), for investigating photocatalytic processes at the demonstrator level, in dynamic regime, using simulated solar radiation.

- the photocatalytic efficiency, the stability of the composite in the aqueous environment and the VIS-activation of the composite were investigated, in dynamic regime, using a methylene blue and imidacloprid solution ,10 ppm.

- the structural and morphology results demonstrated the successful transposition of the selected composite, deposited on large surfaces (20 x 30  $cm^2$ ), used on the demonstrator photoreactor.

- the flow rate of the pollutant solution was found to influence the photodegradation efficiency of MB, the best results were recorded at a flow rate = 1 L/min ( $\eta_{MB}$  = 63%), thus indicating the optimal flow rate value for testing in the demonstrator photoreactor. Also, the use of UV + VIS radiation at an irradiance G = 800 W/m<sup>2</sup> (value close to solar irradiance) led to an increase in the photodegradation efficiency of MB (approximately 23%) compared to the results obtained at laboratory level (G = 55 W /m<sup>2</sup>).

- the evaluation of the morphology and roughness of the composites after the photocatalytic process, indicated a lower stability of the composites subjected to the tests carried

out at flow rates of 0.5 L/min and 1.5 L/min, confirming the optimal value of the flow rate recommended in the photocatalytic tests at the level of demonstrator of 1 L/min.

**3.1.** The photodegradation efficiency, stability and durability of the selected composite were further investigated, by performing three successive cycles of photocatalysis, with a total duration of the 3 cycles of 27 hours; in the photocatalytic experiments the pollutant solution flow rate used was 1 L/min.

- after each photocatalysis cycle (before being used in the next cycle), the photocatalyst was regenerated by washing with distilled water, in dynamic regime, for 30 minutes.

- a freshly prepared methylene blue (c = 10 ppm) solution, was used for each cycle of photocatalysis.

- a relatively small decrease in the photodegradation efficiency of methylene blue, after Cycle II and Cycle III (about 4%), indicated the relatively insignificant clogging with MB photodegradation products of the photocatalyst surface, confirming its optimal operation even after 27 hours of process.

- the reduced changes in morphology, small variations in transmittance and roughness of the composite after the 3 cycles of photocatalysis demonstrated a good stability in the aqueous environment under continuous flow.

**3.2.** Demonstrator level photocatalytic experiments were performed in dynamic regime using composites with 10% g-C<sub>3</sub>N<sub>4</sub> in the composite to see to what extent the results obtained at the laboratory level are also relevant in demonstrator level experiments:

- Demonstrator level investigation of the photocatalytic activity, stability, and durability of the 10% g-C<sub>3</sub>N<sub>4</sub> composite was performed through 3 successive photocatalysis cycles using a methylene blue solution (10 ppm) and a flow rate 1 L / min. The photodegradation efficiency of MB about 4% lower even after the first cycle of photocatalysis and with a significant decrease after Cycle II and Cycle III (about 10%) compared to the results obtained using the composite with 5% g-C<sub>3</sub>N<sub>4</sub> filler, confirmed correctly designating the composite with 5% g-C<sub>3</sub>N<sub>4</sub> as optimal. Also, the decrease in transmittance ( $\Delta T = 10\%$ ) and the significant decrease in roughness values after the 3 photocatalysis cycles indicate a lower stability of this composite.

This set of results recommends the use of glass/FTO/TiO\_  $_2$  \_SPD/TiO\_ - g-C\_3N\_4\_SG\_5% composite, further in research.

**3.3.** VIS – activation of the selected composite was investigated by tests at demonstrator level also using the imidacloprid colorless pollutant (10 ppm) solution. The photocatalysis tests were performed under the previously optimized conditions, using the pollutant MB.

- the lower photodegradation efficiency of imidacloprid (IMD,  $\eta_{IMD} = 56\%$ ) compared to MB ( $\eta_{MB} = 63\%$ ) highlights the dye-sensitization effect under VIS radiation, and the values more of the photodegradation efficiency of IMD may be due to the more complex structure of the molecule of this pollutant. However, its remarcable the stability and durability of the composite in the work environment, regardless of the type of pollutant.

These results are promising considering the industrial up-scaling of the photocatalytic process using the composite glass/FTO/TiO<sub>2</sub>\_SPD/TiO<sub>2</sub> –  $g-C_3N_4\_SG_5\%$ , for the advanced treatment of wastewater targeting the reuse.

#### **ORIGINAL CONTRIBUTIONS**

Starting from the current state of knowledge, new solar- and VIS-active composite materials have been developed in the form of thin films (monolayer and double-layer) with titanium dioxide  $(TiO_2)$ matrix and graphitic carbon nitride filler (g-C<sub>3</sub>N<sub>4</sub>). Mono- and double-layer composites have been investigated *for use in the removal of organic pollutants from wastewater by advanced treatment methods, with a view to their reuse in non-potable applications.* The photocatalytic materials were made and gradually optimized so as to meet the conditions for improving the photodegradation efficiency of organic pollutants in low concentrations, especially by activating in the VIS spectral range and by ensuring stability and durability in working conditions.

For the development of VIS-active composites with TiO<sub>2</sub> matrix and g-C<sub>3</sub>N<sub>4</sub> filler, two easily scalable techniques were used:

- (1) spray pyrolysis deposition (SPD) to deposited an interlayer of TiO<sub>2</sub> on the glass/FTO substrate at 400°C (layer 1) followed by:
- (2) sol-gel (SG) technique for deposited a composite layer (layer 2) over layer 1 by spraying the  $TiO_2 g-C_3N_4$  sol, diluted 1:5 with ethanol.

The development of composite materials based on  $TiO_2 - g-C_3N_4$  in the form of thin layers deposited on small substrates (1.5 x 1.5 cm<sup>2</sup>) and at demonstrator level (total surface of 600 cm<sup>2</sup>) by combining the two methods of deposition, presents a certain degree of novelty in the development of VIS-active photocatalytic materials.

In order to obtain materials with low production cost and good photocatalytic properties, the optimization of two parameters was aimed at: the thermal treatment temperature applied to the final composite and the content of  $g-C_3N_4$  in the composite. Additionally, the rol of a TiO<sub>2</sub> interlayer to increase the crystallinity and stability of the composite layer was investigated.

The optimal variant for obtaining composites, with an advanced degree of novelty, was:

- deposition of double-layer composites: a first layer (layer 1) of TiO<sub>2</sub> using the SPD method over which a composite layer (layer 2) of TiO<sub>2</sub> –  $g-C_3N_4$  was deposited by spraying diluted sol, followed by thermaly treated of the final composite at a temperature of 450°C for 2 hours. In these composites the  $g-C_3N_4$  used was obtained starting from urea as a precursor, calcined at 550 °C.

- in order to identify the optimal content of  $g-C_3N_4$  in the composite, a wide range was tried (1% ... 20%) and the properties of interest of the photocatalytic materials were followed: the photodegradation efficiency of the standard methylene blue pollutant, (10 ppm) under irradiation with simulated solar radiation, at low irradiance values in conjunction with VIS-activation of the

composite; the influence of the  $g-C_3N_4$  content on the stability of the composites in the aqueous environment. Following these aspects during laboratory experiments, the best results were obtained using the duble-layer composites with 5%  $g-C_3N_4$  content, recommending the use of this composite in the next stage, at the demonstrator scale.

The laboratory optimized composite was deposited on larger surfaces for dynamic demonstratorlevel experiments using simulated solar radiation (UV + VIS), with irradiance close to natural solar radiation. The properties of interest were: photocatalytic efficiency (improved) and VIS-activation, stability and durability in the working environment (aqueous); these were highlighted at the demonstrator level by performing 3 successive cycles of photocatalysis, with a total process duration of 27 hours, using a dye (MB) and a colorless pollutant (IMD), using the double-layer composite containing 5% g-C<sub>3</sub>N<sub>4</sub>.

The geometry of the photocatalyst in the demonstrator photoreactor allows industrial scale-up of the advanced wastewater treatment process through advanced oxidation processes. Thus, the achievement of the proposed objectives recommends the use of this type of material, in photocatalytic processes at an industrial level, a result with an advanced degree of novelty.

### List of published works

The results obtained during the doctoral program were capitalized through the following publications:

- Tismanar I., Gheorghita S., Bogatu C., Covei M., Duta A., *Ceramic-based coatings for photocatalysts,* in *Advanced Ceramic Coatings for Energy Applications*, Gupta K. R., Motallebzadeh A., Kakooei S., Nguyen T. A., Behera A. (Eds.), Elsevier, Amsterdam, The Netherlands, 2024, pp. 249 271, DOI:10.1016/B978-0-323-99620-4.00011-7
- Tismanar I., Bogatu C., Gheorghita S., Duta A., Visible- and solar-active photocatalytic ceramic coatings, in Advanced Ceramic Coatings: Fundamentals, manufacturing and classification, Gupta K. R., Motallebzadeh A., Kakooei S., Nguyen T. A., Behera A. (Eds.), Elsevier, Amsterdam, The Netherlands, 2023, pp. 233 254, https://doi.org/10.1016/B978-0-323-99659-4.00016-4
- 3. **Gheorghita S.**, Bogatu C., Duta A.,  $TiO_2 g C_3N_4$  thin film photocatalyst on large substrates for advanced wastewater treatment, Journal of Sol-Gel Science and Technology, Noiembrie 2023, DOI:10.1007/s10971-023-06263-y, (IF = 2,3)
- 4. **Gheorghita S.**, Bogatu C., Duta A., *Self-cleaning surfaces based on TiO*<sub>2</sub> g- $C_3N_4$ , Proceeding of the IEEE of the International Semiconductor Conference, CAS 2023, Sinaia, Romania, Noiembrie 2023, DOI: 10.1109/CAS59036.2023.10303656
- 5. Covei, M., Bogatu, C., **Gheorghita, S.,** Duta, A., Stroescu, H., Nicolescu, M., Calderon Moreno, J. M., Atkinson, I., Bratan, V., Gartner, M., *Influence of the deposition parameters on the*

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- Bogatu C., Gheorghita S., Perniu D., Obreja C., Buiu O., Duta A., *Photocatalytic activity and stability of the ZnO-GO composite thin films*, Proceeding of the IEEE of the International Semiconductor Conference, CAS 2021, DOI: 10.1109/CAS52836.2021.9604130
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- Tismanar I., Bogatu C., Gheorghita S., Obreja A. C., Buiu O., Duta A., Stability of the composite thin films MO<sub>x</sub> GO in photocatalytic processes, Proceeding of the IEEE of the International Semiconductor Conference CAS 2020, Sinaia, România, 7-9 Octombrie 2020, DOI: 10.1109/CAS50358.2020.9268013

Papers in positions 1 and 2 are ISI indexed and papers 3 and 5 are ISI rated.

Papers related to positions 4, 6, 7, 8 and 9 are published in conference volumes:

- 1. International Semiconductor Conference, (CAS, 2020/2021/2023 Sinaia and CAS 2022 Brașov) pozițiile 4, 6,7 și 9
- 2. Conference for Sustainable Energy (CSE, 2020) pozițion 8

### Conference:

- Gheorghita S., Bogatu C., Duta A., Stability of photocatalytic thin film TiO<sub>2</sub> g-C<sub>3</sub>N<sub>4</sub>, 12<sup>th</sup> International Conference on Environmental Engineering and Management, ICEEM2023, Iași, Romania, 12 – 16 September 2023 – poster
- Gheorghita S., Bogatu C., Duta A., Effect of the thermal treatment on the photocatalytic TiO<sub>2</sub> – g-C<sub>3</sub>N<sub>4</sub> composites, International Semiconductor Conference, CAS 2022 – prezentare orală
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The author who presented the work is highlighted with "**bold type**"

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#### Abstract

### Composite materials with metal oxide matrix and filler of carbonic compounds with VIS- and solar-active photocatalytic properties

The aims of PhD thesis is to develop novel solar- and VIS-active photocatalytic materials of a double-layer composite based on titanium dioxide (TiO<sub>2</sub>) and graphitic carbon nitride filler ( $g-C_3N_4$ ). The innovative double-layer structure was obtained using the easily scalable spray pyrolysis deposition technique to obtain a TiO<sub>2</sub> interlayer deposited on a glass/FTO substrate at 400°C and thermal treated after deposition at 450°C. The role of the interlayer was to increase the compatibility between the substrate and the composite layer. A composite layer 2 was deposited over the intermediate layer using the sol-gel (SG) technique, by spraying the sol diluted with  $TiO_2 - g-C_3N_4$  at a temperature of 100°C. Considering the high thermal stability of  $g-C_3N_4$  (up to 600°C) and obtaining the crystalline phases of the  $TiO_2$  matrix (>400°C), the double-layer composites were thermal treated at 450°C for 2 hours to increase the degree of crystallinity and by default the photodegradation efficiency of pollutants (the high degree of crystallinity increases the mobility of charge carriers and therefore decreases electron-hole recombination). The main aim was to improve the photocatalytic activity and the stability of the materials obtained in the aqueous environment. Thus, the double-layer composites were investigated by photocatalytic tests performed at laboratory level (static regime) and photocatalytic tests at demonstrator level (dynamic regime) using simulated solar irradiation similar with the solar radiation. The promising photodegradation efficiencies and good stability in aqueous medium for 27 hours led to the selection of the optimal  $TiO_2$ -g-C<sub>3</sub>N<sub>4</sub> type material (5% g-C<sub>3</sub>N<sub>4</sub> content in the composite) and the proposal of its use on an industrial scale. Also this composite material proved to be VIS-active following the integration of  $g-C_3N_4$  as a filler in the TiO<sub>2</sub> matrix.