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Vis-active photocatalytic composite thin films for advanced wastewater treatment

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Abstract. Conventional wastewater treatment processes are preparing the water for discharge thus it still contains small amounts of pollutants. For re-use, advanced wastewater treatment is required and heterogeneous photocatalysis represent a viable path for removing organic pollutants at very low concentrations but still above the discharge limit. The mostly investigated photocatalyst is TiO_2 that is a wide band gap semiconductor that can be activated only using UV radiation. However, for large-scale implementation of advanced wastewater treatment, there are required efficient and affordable processes, thus Vis- or solar-activated photocatalysts. Attempts on extending the photocatalytic response towards Vis are under intensive research including the development of composite structures with TiO_2 matrix and various fillers that are discussed through this paper. The latest results involving carbon-based fillers are presented along with the extended use of the composites acting also as self-cleaning coatings.

Keywords: Vis-active photocatalytic composite thin film; TiO_2 – GO composite, TiO_2 – rGO composite

1. Introduction

Sustainable development requires to formulate production processes aiming at the preservation of the natural resources in a large extend and water represents the second mostly used resource (after the air) on the Earth thus, water re-use is one major target formulated for the near future to get a more sustainable distant one. Moreover, according to the EU Water Framework Directive (2000/60/EC), one third of the EU's territory is already facing the so-called "water stress" and, as estimated, by 2025 over 3.5 billion people at world level, [1], would face this stress as result of water scarcity, [1]. This is why advanced wastewater treatment is currently considered as a viable path for the water re-use and intense research and

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up-scaling activities are running for identifying novel processes and novel materials that are aimed to support large-scale processes to be implemented in the current wastewater treatment plants.

The removal of pollutant traces is difficult as low concentrated pollutants (at ppm or ppb level) are difficult trap or destroy using conventional, thus affordable, processes. One such type of processes are represented by the ion exchange that can be implemented for reducing, down to zero, the heavy metals concentrations as it is already done in the water treatment plants for de-hardening the water.

Traces of low bio-degradable organic pollutants, are very difficult to remove thus the depollution processes have to involve their breakup through advanced oxidation processes, as the photo-catalytic processes are. These type of processes are recommended for the removal of emergent organic pollutants such as phenolic compounds, various pharmaceutical compounds, pesticides or dyes at low concentrations.

The photocatalytic advanced oxidation processes are of two types: homogeneous photocatalysis and heterogeneous photocatalysis and for meeting the affordability conditions, the activation is targeted to be done using the natural irradiation source, the solar radiation.

Homogeneous photocatalytic processes are mostly reported using the Fenton type catalyst that was firstly formulated in 1894, [2], when the chemist Fenton discovered that ferrous salts can activate hydrogen peroxide for degrading the tartaric acid and in the late 1960s this process reached the up-scaling level for removing toxic organic pollutants. Despite its performance and simplicity, the Fenton process has significant drawbacks as the strong acid environment required during the process, the costs of the reagents and the large production of ferric sludge, [3]. This is why the research was extended towards the heterogeneous photocatalysis for being able to meet the targets set for up-scaled water re-use.

Heterogeneous photocatalysis was initially investigated by Fujishima and Honda, [4], to obtain hydrogen through water splitting, by using TiO_2 as photo-electrode. Further on, this process was investigated in detail and it was observed that radical intermediates, as the hydroxyl radical ($\text{HO}\cdot$), are formed and this type of intermediates may be used for oxidizing various recalcitrant organic pollutants up to mineralization.

Various solid state materials were investigated as photo-catalysts and several metal oxides proved to be active in the degradation of low concentrated organic pollutants in aqueous solutions. Among these, mostly mentioned are TiO_2 , ZnO and SnO_2 , [5], as these are abundant in nature and have a high stability in the aqueous environment. However, as wide band gap semiconductors ($E_g > 3.1$ eV, for all three above mentioned), their large-scale use is limited by the cost of the activation energy that has to be in the UV spectral range ($\lambda < 387.5$ nm) of the solar radiation and this is known to represent only maximum 12 % of the global solar radiation. Thus, intensive research is dedicated to extending the photocatalytic response towards the Vis- spectral range and various paths were proposed as cation- (iron, chromium, palladium, etc.), or anion- (boron, carbon,

nitrogen or sulphur) doping, [6]. The research proved only a limited extension, therefore knowledge coming from other type of applications was employed and one example is the knowledge coming from the solid state solar cells (SSSC) as the diode-type structure in these devices proved also to correspond to the Vis-active photocatalysts.

This paper presents a synthesis of the results recorded, particularly by our group, on Vis-active photocatalysts with diode-type structures involving titanium dioxide as n-type semiconductor coupled with p-type semiconductors of sulphide or graphene derivatives type.

2. Diode-type Vis-active photocatalytic structures

There are thousands of papers on heterogeneous photocatalysis. A comprehensive review, [7], outlines the progress and the unknowns focusing on the main candidate that was, from the very beginning TiO_2 , and its anion doping recognized as efficient in band gap engineering for VIS-activation, [8].

A different approach considers the suitable band gap alignment of two different semiconductors, when the activation energy represents the difference between the lowest conduction band and highest valence band in the assembly, as theoretically and experimentally firstly proved by Scanlon, [9].

2.1. TiO_2 – sulfides composite structures

Following the latest described concept, the research was extended considering that *an aqueously stable photovoltaic cell will be a Vis - active photocatalyst*. Moreover, for upscaling, the photocatalytic processes should be efficient and cost effective.

This concept was explored by developing thin films of Glass/ SnO_2 :F/CZTS/ TiO_2 (n-p-n type) heterojunctions. The choice of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is in line with the H2020 recommendation on critical materials as it only contains common metals and non-metals thus, also the associated costs to this p-type semiconductor are affordable.

The main issue related to the CZTS component is the control of the composition in the precursor system that supports the predominant deposition of this three metals sulphide using an up-scalable technique, as e.g. Spray Pyrolysis Deposition (SPD). The optimum atomic ratio in the precursor system was selected to be: Cu:Zn:Sn:S = 1.8:1.2:1:10 by solving the adequate metal chlorides and thiourea amounts in a water - ethanol mixture. The large excess of the Sulphur compound (thiourea) is required to compensate its sublimation during deposition and annealing. The deposition temperature was optimized at 300°C and further annealing at 400°C for one hour was found to improve the crystallinity, [10]. Following the experimental characterization results, it was noticed that CZTS was not the only sulphide formed in the thin layer and additional sulphides as Cu_2S , ZnS , SnS , oxides as ZnO , SnO_2

and ZnCuSnO_4 could be observed in the XRD spectra, depending on the water content in the water-ethanol mixture used to prepare the precursor system, Fig. 1.

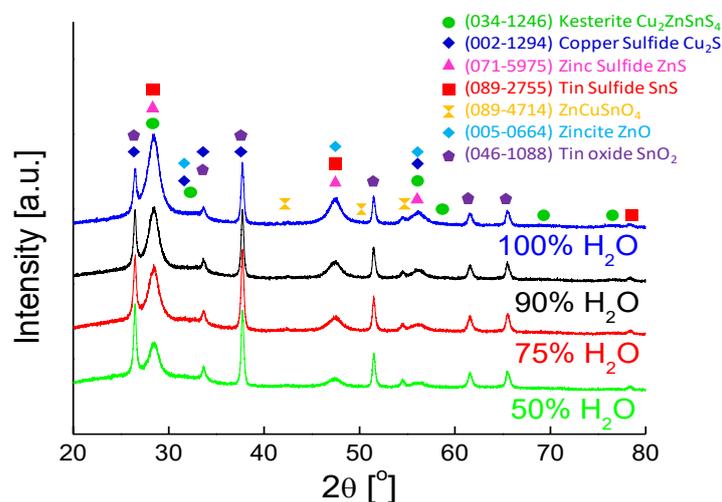


Fig. 1. XRD patterns of the CZTS samples obtained using precursor systems with 0, 10, 25 and 50% ethanol.

Following these results the water:ethanol ratio was optimized at 1:1 as having the mostly reduced (crystalline) impurities content. Moreover, the EDX analyses outlined additional Cu_2SnS_3 , [10], that may result in small amounts thus disturbing the suitable energy bands alignment, having as consequence the limited efficiency value at 50%.

The outer TiO_2 layer was deposited using also SPD and an ethanol precursor system with TiCl_4 dissolve to reach the concentration of 0.1M that proved to be optimum, as compared with the 0.05M, [10].

The stability of these thin films represents another topic of interest and it was found that the films have a good stability when the pesticide imidacloprid was the targeted pollutant as a variation of 15% in the transmittance of the thin film was recorded after 48 hours of process. However, the pollutant type is important as for phenol, in similar experimental conditions, the transmittance variation was up to 30%, [11, 12].

Following these results recorded using lab-scale thin films ($1.5 \times 1.5 \text{ cm}^2$), deposition was further done on larger plates ($10 \times 10 \text{ cm}^2$); these were inserted in a continuous flow demonstrator photo-reactor presented in Fig.5.

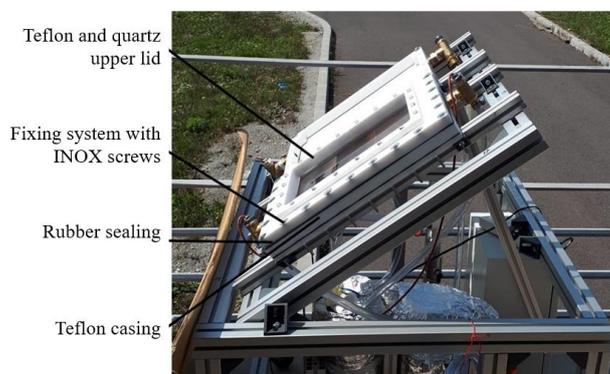


Fig. 2. Photo-catalytic demonstrator reactor for in- and out-door testing.

This equipment was designed and developed in the frame of the project PN-III-P2-2.1-PED-2016-0514 *Continuous flow laboratory technology based on photocatalysis and adsorption for simultaneous removal of toxic organic pollutants and heavy metals* (PhotocatFlow) and is currently used for testing the up-scaling conditions of the processes using all the photocatalytic materials developed and optimized at laboratory scale.

Diode-type photocatalytic structures were further investigated using different other types of p-type semiconductors associated with TiO_2 , as e.g. the association of fly ash (a mix of metal oxides) and/or Cu_xS , [13]. A significant problem that was observed is related to the relatively poor aqueous stability of most such photocatalysts, usually of sulfide type.

Therefore, diode type composites involving highly aqueously stable components were investigated as there are the TiO_2 - graphene derivatives composite thin films.

2.2. TiO_2 – graphene derivative composite structures

Vis-active composite structures were considered by matching the n-type semiconductor TiO_2 (or ZnO) with p-type semiconductor(s) as graphene oxide (GO) or reduced graphene oxide (rGO).

Graphene oxide was selected to obtain continuous interfaces between the ionic metal oxide and the polar GO as, when using the non-polar graphene, the composite films did not show enough stability even in no-flow conditions. The functional groups in GO are responsible for reducing the conduction of this material as GO with a functionalization degree of 50% has a band gap value of $E_g = 2.2$ eV while the increase of this degree at 75% leads to a band gap value of $E_g = 2.7$ eV, [14].

As the sketch in Fig. 3 shows, TiO_2 and GO have a suitable energy bands alignment that supports avoiding the charge carriers (electrons and holes) recombination. These charge carriers are involved in oxidation and reduction reactions that end up in producing oxidation species, mainly the hydroxyl radical

and the super-oxide radical ion (according to the reactions outlined in the figure); these species may interact with the organic pollutants in the wastewater that are further oxidized, up to mineralization.

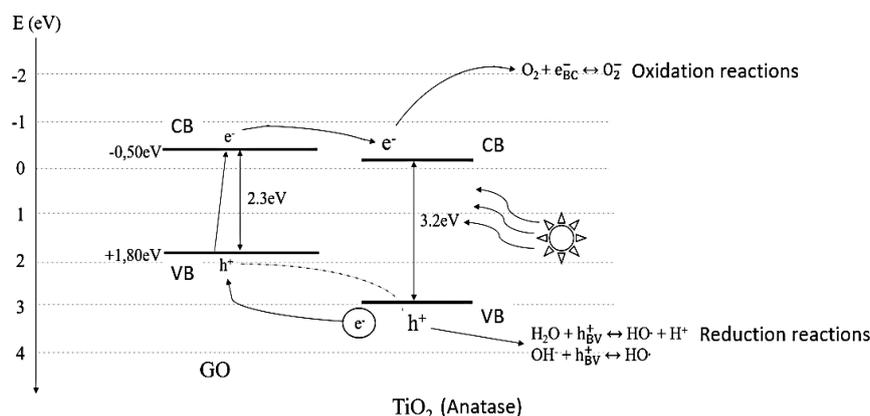


Fig. 3. Alignment of the energy bands in the TiO_2 – GO composite

The main issue related to this type of composites is the limited thermal stability of the graphene derivatives as GO is reported to be stable up to 170...180°C, [15].

The deposition of TiO_2 at such a low temperature has as direct effect a very low crystallinity degree, thus an increased recombination of the charge carriers. This is why a double layered thin film was proposed as photocatalyst, [16], having:

Layer 1: a TiO_2 thin film deposited on an FTO coated glass (where FTO is the acronym for *fluorine doped tin oxide*, $\text{SnO}_2:\text{F}$) using SPD, at 400°C, followed by annealing at 450°C for 3 hours to get an acceptable crystallinity degree (37%).

Layer 2: a TiO_2 -GO composite thin film obtained by spraying a diluted sol over the first layer. The sol was prepared using titanium tetra-isopropoxide (TTIP), ethanol, acetylacetone and acetic acid in a volume ratio of 1:0.8:0.04:0.009, [16]. An aqueous GO dispersion (30 mg/mL) was prepared using a modified method of the one originally suggested by Hummers and Offeman, [17]. The GO dispersion was slowly added under continuous stirring in the TiO_2 precursor system, to obtain the composite sol.

The double layered composite was in the end thermally treated at 150°C when roughnesses close to 95 nm were recorded for the composite with a GO overall content of 5%.

Parallel experiments were done using TiCl_4 as precursor and it was observed that the samples using TTIP have a lower roughness (up to 9 nm, compared to up to 19 nm for the film using TiCl_4), but a higher crystallinity (57.2%) thus had a better reduced recombination of the charge carriers leading to a higher photocatalytic efficiency. This proves that adsorption, strongly influenced by the surface roughness, being the first step in the photocatalytic mechanism is influential

however, a more significant effect on increasing the efficiency has an increased crystallinity that supports the reduction in the charge carriers recombination.

The photocatalytic efficiency in removing the standard methylene blue dye, [18], reached values of 24.8% under UV+Vis irradiation, as compared to 20,9% when using UV radiation, proving the Vis-activation of the photocatalyst. The highest efficiency was recorded for the sample containing 5% GO reaching 31.8% under UV+Vis radiation and 22.2% when using only UV. The influence of the pollutant molecule on the efficiency was investigated in a group of experiments run in similar conditions but using imidacloprid solutions and the recorded efficiency was significantly lower: 17% for UV+Vis and 12% under UV, although Vis- activation was also confirmed.

Similar experiments were run for thin films where the composite was developed using TiO_2 matrix and rGO as filler, [19], with slightly lower results, as the diagrams in Fig.4 show:

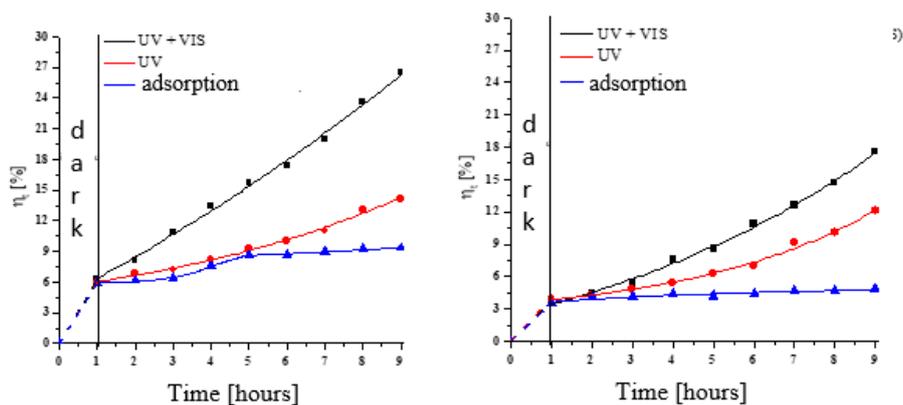


Fig. 4. Efficiency of the MB (left) and IMD (right) removal under UV + VIS and UV irradiation and in dark using the composite thin films $\text{TiO}_2 - \text{rGO}$ with 5% rGO.

The stability of the thin films was evaluated in continuous flow regime, using the photocatalytic demonstrator reactor operated during three cycles of 1 hour in dark + 8 hours under irradiation for each cycle. The films were characterized before and after each of the three cycles and it was observed that the crystallinity is not significantly affected but changes in the roughness values (up to 25%) were observed with a different tendency, depending on the pollutant: a surface roughness increase was observed when degrading methylene blue and a decrease was recorded when using imidacloprid.

These changes are more significant for the thin films with lower (r)GO content and occur mainly when degrading methylene blue as a possible consequence of the better adsorption efficiency of this pollutant and of the degradation intermediate products. It is also to notice that TiO_2 aggregates are resident on the surface of the

thin film(s) and that the immersion in imidacloprid has as result the removal of such aggregates in the pollutant solution, [16].

As GO and rGO have a limited thermal stability, further composites involving carbon- based fillers with a high thermal stability will be investigated in the future, as composites of $\text{TiO}_2 - \text{g-C}_3\text{N}_4$ type.

3. Self-cleaning applications

In the end, the composite thin films were investigated as potential self-cleaning coatings. As result of their rather low transmittance value ($T\% < 80\%$), these layers can only be used for protecting opaque surfaces as walls or ceramic surfaces, but not on glazing.

One important property in self-cleaning applications is the thin films hydrophilicity, estimated based on the water contact angle (WCA). The values of the WCA are inserted in Table 1 and outline that the thin films are hydrophilic and the UV radiation induces super-hydrophilicity ($\text{WCA} < 10^\circ$), confirming the effect also noted by Banerjee et al., [20], thus well supporting the self-cleaning properties.

Table 1. Water contact angle of the composite thin films before and after the photocatalytic (PC) process

Sample	Water contact angle [$^\circ$]				
	Before PC	After 1 h of UV conditioning	After the 1 st PC cycle	After the 2 nd PC cycle	After 2 nd cycle + 2 h of UV+VIS conditioning
Glass/FTO/ TiO_2 / TiO_2 -GO 1,4% _w	12.1	< 1	10.5	32.0	< 5
Glass/FTO/ TiO_2 / TiO_2 -GO 3% _w	7.2	< 1	8.2	9.0	< 1
Glass/FTO/ TiO_2 / TiO_2 -GO 5% _w	8.2	< 1	9.7	10.8	< 1
Glass/FTO/ TiO_2 / TiO_2 -GO 10% _w	6.8	< 1	6.6	7.2	< 1
Glass/FTO/ TiO_2 / TiO_2 -rGO 5% _w	19.5	6.3	10.1	7.2	4.0

As the results show, this effect is not permanent, thus the film reverses to the hydrophilic state, as this initially was. This may be the consequence of the water molecules loss, during UV irradiation of the thin films that are not immersed in the aqueous environment. This effect may lead to variation in the surface roughness thus also in the contact angle of the water droplets.

However, considering that in outdoor applications, the solar radiation (containing UV) is daily present, one may assume that these coatings are well-suited for self-cleaning applications, reaching the super-hydrophilic state during sunny days.

4. Conclusions

This paper contains a synthesis of the significant results recorded on Vis-active photocatalytic thin films, aiming at their use for advanced wastewater treatment or for self-cleaning coatings.

Composite multi-layered structures are discussed considering that Vis-activation can be directly linked to structures well mimicking those existing in photovoltaics with ceramic composition. Thus, diode type multi-junction thin films, using TiO_2 , as n-type semiconductor and various sulphides (CZTS, Cu_xS) as p-type component, are discussed correlated with their photocatalytic performance in degrading dyes and pesticides pollutants.

As the stability in the aqueous environment of this type of composites represents an issue that has to be carefully watched during their use, a novel type of composites is presented consisting of a double layered thin film of TiO_2 and $\text{TiO}_2 - (\text{r})\text{GO}$. The mostly influential factors on the photocatalytic efficiency are analyzed and conclusions on the recommended research paths to be followed in the future are outlined.

The use of these type of composites as self-cleaning coatings is analyzed based on the hydrophilic behavior of the thin films and it was outlined that super-hydrophilicity can be observed after UV irradiation; thus, in real time conditions, super-hydrophilicity can be expected during sunny days with positive consequences on the self-cleaning properties of the deposited layers on opaque surfaces.

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