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VIS-ACTIVE PHOTOCATALYTIC COMPOSITES FOR ADVANCED WASTEWATER TREATEMENT

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Abstract. Advanced wastewater treatment targeting water reuse is currently an important research topic and the heterogeneous photocatalysis processes represent potential candidates. Most of the photocatalysts are aqueously stable metal oxides as TiO_2 or ZnO; however, their use is limited due to the processes costs as these oxides are wide bandgap semiconductors that are activated only by UV radiation. Many alternatives are investigated to develop VIS- or solar-active photocatalysts among which most effective proved to be the diode type composites that associate the n-type semiconductor (TiO_2) with a p-type semiconductor with lower band gap as CZTS or CIS. The challenges raised in developing thin films photocatalysts of diode type are discussed considering the advanced treatment under VIS and simulated solar radiation of a wastewater polluted with methylene blue (standard pollutant). Further on, new composites of TiO_2 – Graphene oxide are presented considering the same application.

Keywords: advanced wastewater treatment, diode type photocatalyst, TiO_2 – CZTS composite, TiO_2 - $CuInS_2$ composite, TiO_2 - graphene oxide composite

1. Introduction

The 6th Sustainable Development Goal aims at clean water and sanitation. This is an important target formulated by the United Nations, as currently over 40% of the world population is affected by water scarcity and over 1.7 billion people are living in river basins where water use exceeds the recharge [1].
Advanced wastewater treatment targeting water reuse (without intermediary discharge in the environment) represents a concrete goal, that is considered as a next step in the already existing wastewater treatment processes that run according

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to certain discharge limits. These limits have to be reformulated, mitigating the pollutants concentrations, to allow the reuse of water in industrial processes and in agriculture. Moreover, water reuse can represent a reliable water supply source that is almost independent from the seasonal variation of the water sources and is thus able to cover the peak demand. This is why, in May 2018, at EU level a legal document was formulated: *Proposal for a Regulation of the European Parliament and of the Council on minimum requirements for water reuse,* [2].

Water reuse represents the use of treated wastewater for various applications among which the most common are the non-potable ones, as for industrial processes or in agriculture, for irrigation during periods of drought. Specifically, the reused water is already used in several cities all over the world for flashing the toilets, for watering the parks and the loans, for washing cars and streets, in decorative fountains, in hydrants, etc. When implementing such systems different pipe lines have to be designed two for the non-potable and for the potable water that are clearly signalized, [3].

Reused water can also be employed for potable use, as drinking water, but the treatment conditions and the results are, as expected, stricter in this case. However, in communities with water shortage, water reuse may represent a viable solution for expanding the water resources.

The process of treating the wastewater prior its reuse is usually called *water reclamation*. According to the 2008 estimations, the United States of America reuses a larger volume of water than any other country (about 2 billion gallons per day), followed by Saudi Arabia, Egypt, Israel, Spain, Mexico, China with 0.3 ...0.5 billion gallons per day in each country, [4].

2. Heterogeneous photocatalysis for advanced wastewater treatment

Water reuse involves the removal of certain pollutants, at low concentrations (ppm or ppb) and hereby the traditional processes are not well suited, especially considering organic pollutants as dyes, pesticides, nutrients, etc. This type of pollutants can be efficiently oxidized through heterogeneous photocatalysis that was firstly reported by Fujishima and Honda, [5], for obtaining hydrogen through water splitting in a photoelectrochemical cell using TiO_2 and Pt as electrodes.

The main steps in the heterogeneous photocatalytic process for oxidizing the pollutants from wastewater are:

1) The pollutants adsorption on the photocatalytic surface. To have an efficient process, a high specific surface and an appropriate surface charge, opposite to the pollutant (partial) charge, are required for the catalyst. This is why the process conditions should be well optimized by selecting the appropriate working pH that supports the pollutant adsorption on the photocatalyst surface;

2) The photocatalyst irradiation with a radiation that has the energy at least as high as the semiconductor photocatalyst bandgap. During irradiation, the electrons use the energy to migrate from the filled valence band to the empty conduction band, leaving behind a hole (Eq.1). The holes from the photogenerated electron-hole

pairs can react with the hydroxide ions or with water to produce the hydroxile radical (Eq. 2) that is an active specie able to oxidize the pollutants. Moreover, the electrons can react with the oxygen dissolved in water forming the superoxide radical (Eq. 3) that can further react with H^+ to produce the hydroperoxide radical (Eq. 4).

$$Photocatalyst + h\nu \rightarrow h_{VB}^{+} + e_{CB}^{-} \quad (1)$$

$$H_2O + h_{VB}^{+} \rightarrow HO^{\cdot} + H^{+} \quad (2)$$

$$O_2 + e_{CB}^{-} \rightarrow O_2^{-\cdot} \quad (3)$$

$$O_2^{-\cdot} + H^{+} \rightarrow HOO^{\cdot} \quad (4)$$

Obviously, the electrons and the holes can recombine thus limiting the generation of oxidation species. This is why the electron-hole photo-generation should be accompanied by alternative processes that involve one of these charge carriers (preferably, the electrons), leaving the other ready for the photocatalytic mechanism;

3) The pollutants oxidation that occurs based on the reactions of the oxidative species, (e.g. $HO^{\cdot}$), with the adsorbed pollutant molecules. The process can advance up to pollutant's mineralization, forming gaseous species (CO_2, nitrogen oxides) and water.

4) The last step in the process is the by-product(s) desorption, leaving the photocatalyst surface empty to re-start the processes. According to the process evolution, the desorption involves gases or liquid by-products.

Although TiO_2 has a very good aqueous stability, its use is limited by its wide bandgap (3.15 ... 3.2 eV) that allows only UV activation, thus raising the costs of the photocatalytic process.

This is why for feasible, up-scalable advanced wastewater treatment processes, VIS-active, aqueously stable, non-toxic photocatalysts have to be developed. More recently, Vis- and solar-active photocatalytic processes were considered in the treatment of contaminants of emergent concern (CEC) in wastewater and this requires the development of photocatalytic structures that are not relying (only) on TiO_2 or other wide bandgap semiconductors as those already considered state of the art.

3. VIS-active photocatalytic thin films for advanced wastewater treatment

Research on identifying solutions to get VIS- and solar active photocatalysts is intense and covers doping TiO_2 with metallic or non-metallic (C, S or N) species, [6] or developing composite structures consisting of TiO_2 (n-type semiconductor) and low bandgap p-type semiconductors, mimicking aqueously stable photovoltaic structures.

Metal doping is outlined to have several significant drawbacks as the dopant insolubility, the surface aggregation of the doping species instead of substitution, changing the usual balance among the titania polymorphs, etc. [7]. Further on, the non-metal doping can lead to extending the activation range towards VIS if doping is well controlled, i.e. if the non-metal substitutionally replaces oxygen in the

lattice and is not inserted in the lattice interstices. These doping methods represent thus a possible but highly sensitive path for developing solar-active photocatalysts. This is why the concept of developing composite photocatalysts, of tandem type (n-n) or of diode type (n-p) was investigated in our group through various photocatalytic composites.

Although the use of photocatalytic dispersions is more efficient because the entire surface of each powder grain is available to the process, the advanced wastewater treatment processes using dispersions are not highly recommended because they have to involve additional steps for the photocatalyst separation and its reconditioning before re-used. Moreover, the results recorded in the photocatalytic test for advanced wastewater treatment can be further extended in developing self-cleaning coatings. This is why the use of photocatalytic thin films is highly investigated and additional pre-requisites are considered for the thin films stability under irradiation and various flow rates.

Tandem photocatalysts that couple two n-type semiconductors are often employed considering the active photocatalyst (e.g. TiO_2) deposited as thin film on FTO ($F:SnO_2$) coated glass. The use of these type of composites allows a better morphology control and may reduce the electron-hole recombination but VIS-activation is not the direct result of coupling.

Diode type photocatalysts were developed by associating a narrow bandgap, p-type semiconductor with TiO_2 in multilayered thin films, as in the examples included in Table 1:

Table 1. Diode-type VIS-active thin film photocatalysts

Photocatalytic thin film	Tested pollutant	Radiation type and intensity	Photocatalytic efficiency [%]	Reference
$CuInS_2/TiO_2/SnO_2$	Methylene Blue (MB) 0.0125 mM	UV (15%) + VIS (85%): 10 W/m^2	92.3%	[8]
$SnO_2/Cu_xS(Cu_xO)/TiO_2$	Phenol: 4;10;20 ppm	UV (15%) + VIS (85%): 10 W/m^2	Max.: 9%	[9]
$CuInS_2/TiO_2/SnO_2$	MB 0.0125 mM (4ppm)	VIS: 32 W/m^2 UV: 9 W/m^2 UV+VIS: 10 W/m^2	90...92% 75...78% 90...92%	[10]
Cu_2ZnSnS_4/TiO_2	MB 0.0125 mM	UV (3%) + VIS (97%): 34 W/m^2 VIS: 33 W/m^2	43.5% 25%	[11]
Cu_2ZnSnS_4/TiO_2	Imidacloprid (IMD): 10ppm Phenol:10 ppm	UV (3%) + VIS (97%): 34 W/m^2	IMD: 12% Phenol 20%	[12]

The results show that the diode type thin films involving $CuInS_2$ support a very good photocatalytic efficiency under simulated solar radiation (even at very low irradiance values) in the photodegradation of the standard dye, methylene blue (ISO 10678:2010). Also these thin films have a good aqueous stability and experiments proved that the best working pH is 7 for all the investigated pollutant concentrations. Moreover, the VIS-activation is clearly proved as the

photodegradation efficiency under UV+VIS irradiation is higher than those recorded under UV radiation. It is to notice that the irradiation duration proved to be important as experimental test done for 3 hours of irradiation lead to efficiencies about half as compared to the experimental tests done under 6 hours of irradiation. In all the experiments a contact time (in dark) was designed in the beginning to leave the pollutant to adsorb on the thin film surface, before irradiation.

Using $CuInS_2$ is effective but it involves a scarce element (In) therefore, the concept was further investigated using as p-type semiconductor copper sulphide (partially oxidized at copper oxide). Copper sulphide and TiO_2 have not a complete well alignment of the band gaps and, because of the uneven composition of the composite and its lack of stability, the efficiency recorded in phenol photodegradation was rather low, and mainly due to the UV component of the radiation.

Bi-layered composites of Cu_2ZnSnS_4 (CZTS) and TiO_2 were further investigated as containing common elements, thus being with significant lower cost as compared with the composite involving $CuInS_2$. The results show acceptable photocatalytic efficiencies in methylene blue photodegradation (43.5%). The bands alignment between the narrow and the wide bandgap semiconductors is important for supporting the charge carriers flow: the valence band and the conduction band in the narrow band gap semiconductor should be higher than the valence band and the conduction band in the wide band gap semiconductor. The thin films were obtained using spray pyrolysis deposition thus when depositing Cu_2ZnSnS_4 it was also obtained Cu_2SnS_3 (as outlined by the XRD analysis) that limits the correct bands alignment. However, this can be tuned by TiO_2 doping. The experiments showed that the stability of the photocatalytic films after 72 hours of irradiation is mainly influenced by the sulfide potential leaching, thus the thickness of the upper TiO_2 layer is important and has to be optimized because a thicker titania layer, with a protective role, may limit the access of light to the p-type semiconductor.

Multi-layered VIS-active photocatalysts including TiO_2 (anatase) were further considered using graphene oxide (GO). As graphene and its derivatives start to decompose in air at temperatures higher than 180˚C, the composite had as first layer TiO_2 deposited using spray pyrolysis, followed by annealing at 450ºC and on this crystalline substrate a composite TiO_2 – GO, obtained through sol-gel synthesis was sprayed at 100ºC followed by annealing at 150ºC. The crystallinity degree of this composite is good (36%) and the thin film proved to be VIS active with the photodegradation efficiency of a MB 10ppm solution of 14.7% under UV irradiation and of 25.2% under UV (3%) + VIS (97%) irradiation at an overall irradiance value of 55 W/m^2.

4. Conclusions

Photocatalysis can be employed as an advanced wastewater treatment process targeting water reuse. For upscaling, the process has to be efficient and acceptable in terms of costs, being activated using VIS- or solar radiation.

The paper outlines a synthesis of the results obtained in developing aqueously stable photocatalytic thin films with composite structure based on TiO_2, currently considered the most performant photocatalytic material (activated under UV radiation). Various photocatalytic composites are discussed with a focus on those of diode type associating the n-type TiO_2 with p-type semiconductors that can be activated under VIS or solar radiation. It was outlined that, although $CuInS_2$ develops highly efficient photocatalysts when combined with titania (anatase), due to the indium scarcity, the use of such a composite is not fully feasible. Further on, the use of Cu_2ZnSnS_4 is discussed outlining that the CZTS p-type semiconductor meets all the requirements for being part of the photocatalytic composite but its deposition usually runs along with other by-products. In the end, the use of graphene derivatives (graphene oxide) is presented along with the deposition conditions of the photocatalytic multi-layer obtained while preventing the GO decomposition.

These types of photocatalytic composites represent viable alternatives that allow the organic pollutants decomposition at very low concentration using solar radiation.

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