Vis (solar) – active TiO_2 - Graphene Oxide Composite Thin Films for Continuous Flow Photocatalytic Wastewater Treatment

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The photocatalytic processes are widely investigated because of their effectiveness in the organic pollutants removal at low concentrations in applications such as wastewater treatement, air purification, self-cleaning, antibacterial and antifogging coatings. Among the materials used as photocatalysts, the most studied is titanium dioxide (TiO_2) but the major problems that limit its implementation are the UV-activation (Eg = 3.0...3.2 eV) and the fast recombination of the photo-generated electrons and holes. Recently, carbon based materials (mainly, graphene oxide, GO or reduced graphene oxide, rGO) were used as fillers in composites with metal oxide matrix for such applications activated by VIS or solar radiation. Due to their unique electrical properties given by the 2D structure, the main role of the GO or rGO is as collector for the photo-generated electrons, thus limiting/avoiding recombination. Moreover, because of the p-type behavior of these fillers (Eg = 2.2...2.7 eV, depending on the functionalisation) and the propper band gap aligniament, Vis (solar)-active n-p junction can be developed.

Wastewater treatement applications ask for a continuous flow operation mainly when targeting water re-use. However, few studies report on such continuous flow photocatalytic systems. This paper reports on a TiO_2/TiO_2-GO two-layered thin composite film obtained by spray pyrolysis deposition (SPD) coupled with sol-gel spraying deposited on 10 x 10 cm^2 FTO substrates. The first TiO_2 layer was deposited by SPD on FTO glass, at 400°C (30 spraying sequences, 60s break between pulses) from titanium tetra-isopropoxide (TTIP) precursor, mixed with acetylacetone (AcAc) and ethanol (EtOH) in a 1:1:15 volume ratio. This first layer was annealed at 450°C for 3 hours to get a crystalline film that well suport the TiO_2-GO second layer deposited by robotic spraying at 100ºC (15 sequences, 60s break), using a sol-gel dispersion of TTIP, EtOH, AcAc, acetic acid (HAc) and aqueous GO dispersion (30 mg/mL, obtained using the Hummers method) in the volume ratio: TTIP:EtOH:AcAc:HAc:GO = 1:0.800:0.044:0.009:0.120. After deposition, the composite thin film was thermally treated for 1 hour at 150°C to decompose/remove the by-products without degrading GO. The final content of GO in the composite was 1.4 $\%_w$. Six of these samples, were placed at the bottom of a pilot photoreactor to form a 30 x 20 cm^2 photocatalytic surface. Moreover, one of these samples was cut in small plates to allow characterization. The photoreactor was sealed with an upper side of a quartz plate. The photodegradatin tests used methylene blue (MB) standard pollutant (c_{MB} = 10ppm) and the flow rate of the pollutant solution was fixed at 1.0 L/min. Simulated solar radiation was used during tests (G = 800 W/m^2, out of which 10% corresponded to the UV radiation) to evaluate the efficiency of the photocatalyst and the GO contribution to the composite‘s Vis-activation (parallel experiments were also run using only UV radiation). The results show promising efficiencies (η > 50%) when using simulated solar radiation compared with UV radiation (G = 80 W/m^2) confirming the Vis-activation of the composite.

***Acknowledgements*:** This work was supported by the grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0619, contract no. 42 PCCDI/2018 within PNCDI.