Vis-Active Photocatalytic Composites for Advanced Wastewater Treatment

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The use of thin photocatalytic films is investigated for efficient and upscalable advanced wastewater treatment processes. TiO_2 is a wide band gap semiconductor (E_g = 3.2 eV), that can only be activated using UV radiation and this is one major barrier in the wider implementation of the photocatalytic processes. Various solutions were investigated to get VIS-active photocatalysts. One such solution is represented by the deposition of composite photocatalysts of TiO_2 (an "n" type semiconductor) and a "p" type semiconductor, mimicking a photovoltaic cell. As p-type semiconductor, $CuInS_2$ was firstly investigated in composite thin film structures of $CuInS_2/TiO_2/SnO_2$ type and the methylene blue (MB) removal efficiency was higher than 95%, under low intensity radiation (G = 55 W/m^2), consisting of 10% UV+ 90% VIS. However, $CuInS_2$ involves indium, a rather scarce material, thus its replacement has to be considered for large-scale applications. The concept was further extended by using Cu_2ZnSnS_4 (CZTS) as p-type semiconductor but its limited stability in the aqueous environment lead to its replacement with graphene oxide (GO).

Using these composite thin layers, a comparative discussion on the photocatalytic efficiency under UV+VIS irradiation (that mimics the solar radiation spectrum but at lower irradiance values) is presented considering the standard MB 20 ppm solution.

Spray Pyrolysis Deposition (SPD) was used to deposit the CZTS / TiO2 composite thin film on a FTO-coated glass substrate. The metal chlorides and thiourea were dissolved in ethanol forming the CZTS precursor system that was deposited at 300^{o}C, followed by annealing at 400^{o}C, for one hour. The titanium dioxide thin film was SPD deposited using an ethanol solution of $TiCl_4$ at 350^{o}C, followed by 3 hours annealing at 450^{o}C.

The TiO_2 – GO composite layer was prepared by SPD depositing a first TiO_2 thin film, using the same precursor system as for the CZTS-TiO_2 composite that was afterwards annealed. A second layer was sprayed consisting of a TiO_2-GO dispersion obtained through sol-gel synthesis, using titanium tetra-isopropoxide (TTIP), acetylacetone and acetic acid dissolved in ethanol. To prevent the GO decomposition, annealing was not employed for this second layer and the deposition temperature was kept bellow 180^{o}C.

The composite layers of CZTS-TiO_2 and TiO_2 – GO types were characterized in terms of crystallinity (XRD), morphology (SEM) and roughness (AFM). Further on their stability was investigated by measuring the transmittance of the thin films before and after the process and it was found that highly crystalline thin films have a better stability in the aqueous environment.
The composite thin layers were used to investigate the photocatalytic decomposition of Methylene Blue (ISO 10678:2010 standard). The results confirm that both composites are VIS-active and the removal efficiencies are promising, depending on the pollutant's concentration.

The mostly stable thin films in the aqueous working environment proved to be those of TiO_2 – GO type.

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