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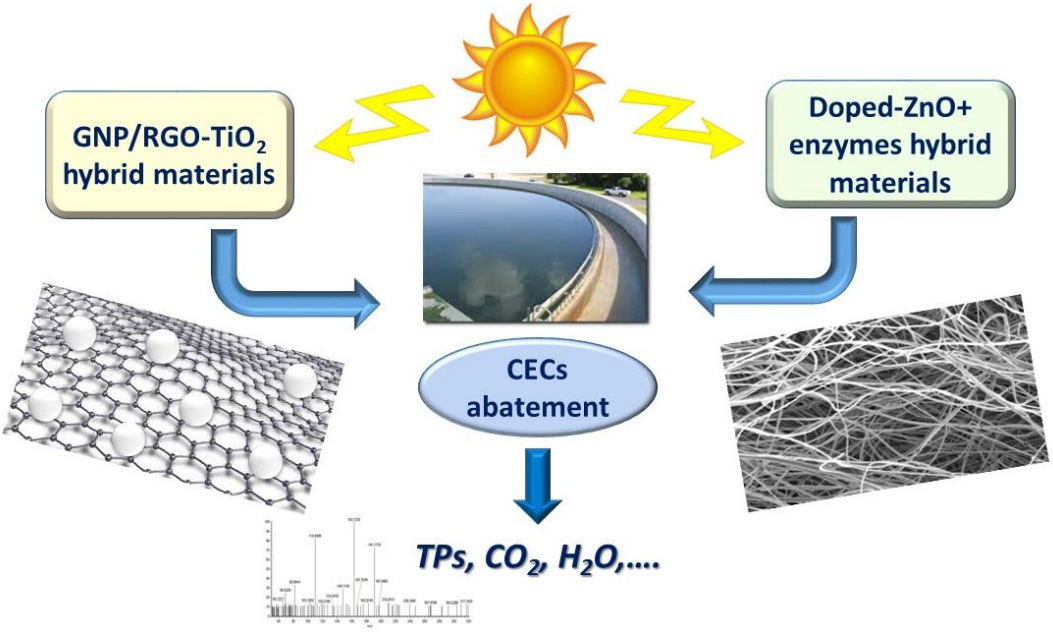

Composite materials for photocatalytic applications: synthesis, characterization and activity evaluation.

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INTRODUCTION

Nowadays environmental pollution is a potential threat for human health and ecosystems. Some pollutants are recalcitrant to traditional wastewater treatments and the study of new strategies for their abatement is currently in progress. Heterogeneous photocatalysis is an Advanced Oxidation Process (AOPs) and it could be employed for environmental remediation. The most used photocatalyst is TiO_2, however its efficiency is lowered down by the high rate of recombination of the pair electron/hole and its activity is limited to the UV region.

The aim of the thesis was to synthetize, characterize and test new composite materials with high photocatalytic efficiency for abating persistent pollutants such as emerging pollutants and for overcoming TiO_2 drawbacks.

Different synthetic strategies were followed to achieve this goal. The first approach led to develop and tailor high quality carbon nanoparticles (CNPs) to produce nanocomposites.

Firstly, we studied the photoactivity of graphene at different stages of oxidation/reduction and, based on the obtained results, we prepared a composite material with commercial P25 and tested it toward the abatement of risperidone, an antipsychotic drug considered as an emerging pollutant. Secondly, graphene sheets were modified on the surface using diazonium chemistry. These modified CNPs were the core of the further developed composite materials graphene-TiO_2 obtained by starting from TiO_2 precursors through hydrothermal method.

The second strategy foresees the preparation of ZnO-based materials as alternative of TiO_2. Cerium was chosen as dopant of the oxide because it can act like a “trap” for the electrons, lowering the recombination rate of the couple e-/h+ and improving its activity.

Another strategy to improve the capability of semiconductors to oxidize substrates is to couple them with enzymes. Enzymes-mediated oxidative treatment has been investigated as an alternative of many traditional processes to remove toxic and recalcitrant pollutants from wastewater. Among them we selected laccase and peroxidase enzymes, already used for the abatement of some contaminants. To permit the exploitation of photocatalysis to the treatment of polluted waters, the catalyst should be in a supported form. Besides, we used the electrospinning to prepare self-supported materials. Nanofibers are characterized by a high surface area suitable for catalytic applications and they could be used as support for catalyst nanoparticles.

RESULTS

Firstly, we investigated some aspects of the photochemistry of GOx: we synthesized and characterized stable GOx suspensions which were then subjected to UV-Vis irradiation for prolonged times. The possible use of GOx as photo-activator was evaluated by using phenol as probe molecule. GOx revealed a double role of photo-activator and reagent in phenol degradation, as competition was assessed between GOx self-transformation/reduction and phenol degradation. Thanks to these results, we could assess which is the more reactive form of graphene based material, i.e. reduced graphene oxide, which has been then used to produce composite materials with TiO_2.

We synthesized, then, composite materials through a hydrothermal method using graphene oxide and commercial P25 as precursors. The materials’ characterization showed an interaction between TiO_2 P25 NPs and rGO sheets (IR, TEM). The photocatalytic performance of TiO_2-rGO catalysts was evaluated under artificial solar light and visible light in distilled water, as well as, different surface waters (at natural pH) with respect to risperidone (antipsychotic drug) degradation. Irrespectively of the irradiated aqueous matrix, the photocatalytic efficiency of the tested composite materials under simulated solar light and

visible light irradiation was higher compared to bare TiO_2-P25. The identification of intermediate compounds, the assessment of mineralization and the evaluation of toxicity were performed as well. LC/HRMS was brought to bear in assessing the temporal course of the photocatalyzed process. Along with risperidone decomposition, the formation of twenty intermediate compounds (TPs) occurred in the presence of TiO_2. Irradiation of risperidone in the presence of the hybrid material resulted in the identification of thirty-four TPs. The transformation of risperidone progressed through the formation of compounds more harmful than the drug itself, as assessed by the measurement of acute toxicity, evaluated using the *Vibrio fischeri* bacteria test. When employing TiO_2-rGO, all the identified transformation products were quicker degraded compared to TiO_2-P25. At the same time both the reduction of toxicity and mineralization were faster achieved than with bare TiO_2-P25.

Another synthetic strategy was to synthetize hybrid materials with multifunctional properties by coupling graphene nanoplatelets (GNP) modified with carboxylic groups to TiO_2 nanoparticles and tested them both as photocatalyst to promote pollution abatement and as tracers of the presence of a model antigen (bovine serum albumin, BSA) in immunochemical assays. The presence of carboxylic groups proved to be crucial in both applications: they improved TiO_2 photocatalytic activity by the interaction between the carboxylic groups on the GNP surface and the hydroxyl groups on TiO_2 surface; and they have been employed to covalently bind the material to BSA. The photoactivity of those materials was exploited for the oxidation of 3,3',5,5'-tetramethylbenzidine for potential immunochemical applications.

In the second strategy Ce-ZnO was synthetized through precipitation and hydrothermal synthesis. Ce-doped ZnO obtained by hydrothermal method showed a higher activity on phenol degradation compared to the one obtained by precipitation method. Consequently, we selected this material for the further studies on hybrid materials obtained by mixing semiconductor oxides and enzymes supporting them on polymeric nanofibers. The combination of photocatalysts and enzymes showed an improvement of the capability of the system on the abatement a mixture of contaminants both in MilliQ and wastewater matrices. Moreover, materials prepared by employing Ce-ZnO showed a higher activity than those obtained with the benchmark TiO_2 P25 (used as comparison material) irrespective of the enzyme/electrospinning treatment.

CONCLUSION

We develop hybrid materials prepared using different strategies. Concerning carbon based materials, the most important result was the evidence of GO and rGO photoactivity on the degradation of organic compounds. The coupling of rGO with TiO_2 permits to achieve a faster mineralization and abatement of the toxicity of the drug and its transformation products of risperidone both under UVA light and solar light, in different matrices.

Besides, hybrid materials obtained coupling graphene sheets functionalized with -COOH groups with TiO_2 permits to obtain a photocatalyst more efficient than pristine TiO_2 for the abatement of dyes, that found also interesting application in the preparation of an immunoassay. The develop material showed peroxidase-like activity before and after formation of the immunocomplex with immobilized anti-BSA and it was stable in harsh conditions where natural enzymes such as peroxidase would be denatured.

The second strategy was to employ Ce-doped ZnO as alternative material to TiO_2. The results showed a higher photoactivity of Ce-ZnO obtained by hydrothermal synthesis compared to P25 and the one obtained by precipitation method. A further increase in the photocatalytic efficiency was obtained by coupling Ce-doped ZnO with enzymes. These hybrid materials showed a synergic effect on the abatement of a mixture of contaminants both in MilliQ and wastewater, so revealing the potential employing of these materials in a tertiary water treatment process.