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Doctoral Dissertation
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Effects of polymorphs and of Fe-doping on the properties of engineered nano TiO₂ for photocatalytic degradation of emerging pollutant

By

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Summary of the thesis

In this research work, I focused my attention on TiO₂ nanoparticles synthesis and their physico-chemical characterization for their application in the photocatalytic degradation of emerging contaminants. Below, a brief resume of my results is proposed.

TiO₂ is a worldwide known material suitable for photocatalysis, which suffers from two main drawbacks: quick recombination of energy carriers and wide band gap. To overcome the problems described before, two main strategies were adopted: i) the promotion of heterojunctions among polymorphic structures typical of TiO₂ (anatase, brookite, and rutile), which can help to reduce the electron and holes recombination with particular attention to the role of the brookite phase and ii) the introduction of Fe (which is abundant, low toxic and economic) to enlarge the range of light absorption through the visible region.

Three different sol-gel synthesis methods to tune the physico-chemical properties of TiO₂ NPs were developed for the photocatalytic degradation of a drug (paracetamol), an herbicide (simazine), a pesticide (N-Phenylurea) and two azo-dyes (Acid Orange 7 and Crystal Violet). These compounds are called emerging contaminants since they have been measured nowadays thanks to new detection methods. The presence in the groundwater and surface water at very low concentrations ($\mu\text{g L}^{-1}$ or ng L^{-1}) makes their abatement difficult through the traditional methods enforcing global attention on these substances.

An accurate physico-chemical characterization of the samples offered the opportunity to understand the influence of the synthesis method parameters on the three TiO₂-based materials' properties. Furthermore, introducing a proper amount of iron precursor in the three synthesis procedures allowed the synthesis of Fe-

doped TiO₂ NPs. A detailed physico-chemical characterization of the doped samples offered a better comparison among doped samples and their photocatalytic efficiency.

The adopted synthesis methods included two soft-template-assisted sol-gel synthesis methods and one template-free method. The first synthesis method described was based on a direct micelles system aiding the formation of mesoporous TiO₂ NPs with inter- and intra-particle mesoporosity (labeled as M-TiO₂ sample). In the second case, the sol-gel synthesis process was confined inside reverse micelles (labeled as RM-TiO₂ sample). The third described synthesis method was based on a template-free sol-gel method under pH control. This synthesis method allowed tuning the polymorphic structure of TiO₂ NPs with the aim of improving the presence of heterojunction among polymorphs (labeled as AB and ABR samples, where A is for anatase, B for brookite and R for rutile). AB and ABR samples showed a mixed polymorphic structure composition with extended heterojunction presence.

The three synthesis methods were adapted for the iron-doped samples. Different weight percentages of iron were introduced to investigate Fe amount and the photocatalytic properties.

The effect of iron doping was evidenced by a red shift of the samples' absorption edge, an influence on their crystallite dimension and on the surface charge, affecting, therefore, their interaction with the water pollutants.

The photocatalytic properties of the undoped materials were tested toward the degradation of paracetamol and N-Phenylurea. The AB sample, probably taking advantage of the anatase/brookite heterojunctions, was the best photocatalyst among the synthesized samples for paracetamol and N-phenylurea degradation (under 1 SUN).

Another promising sample for paracetamol photocatalytic degradation was the M-TiO₂. This material showed a kinetic constant of paracetamol degradation under visible light irradiation, comparable with the kinetic constants obtained by AB and P25 (commercial benchmark) samples.

The photocatalytic properties of the Fe-doped samples, obtained with the two soft-template-assisted sol-gel methods, were tested under visible light for the degradation of two azo-dyes target molecules: Acid Orange 7 (AO7, an anionic dye) and Crystal Violet (CV, a cationic dye). The results were compared among the

same materials with different doping amounts (1, 2.5, and 3.5 wt. % Fe). In both cases, the sample with an iron content of 2.5 wt. % showed the best photocatalytic performance.

The Fe-doped AB samples (with 0.05, 1, 2.5 wt. % Fe) were tested for the photocatalytic degradation of simazine either under solar-simulated or UV light. The samples showed a moderate photocatalytic efficiency under solar-simulated light but confirmed the positive effect of anatase/brookite heterojunction presence. Under UV light source, promising results were obtained with the sample containing 0.05 wt % of iron.

In conclusion, in this Ph.D. thesis, three different synthesis methods were proposed to engineer the amount of TiO₂ nanoscale polymorphs and to dope them with iron. It was demonstrated that these photocatalysts can be efficiently used to degrade different types of emerging pollutants in water under simulated solar light.