Structured photocatalysts for the removal of emerging contaminants in aqueous solution under solar light

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OBJECTIVES AND NOVELTY

The aim of this investigation is the synthesis of structured photocatalysts and their evaluation in the removal of emerging contaminants under solar radiation.

The materials synthesized were TiO_2-based heterostructures and metal-organic frameworks (MOFs). The first group includes two approaches, consisting on carbon-modified TiO_2, and the immobilization of TiO_2 on carbonaceous supports, such as activated carbons (ACs) and carbon-microspheres. These approaches have in common the use of lignin as carbon source, thus providing a promising way for the valorization of this large-scale industrial residue from cellulose pulp manufacture and the future biorefinery based on lignocellulosic wastes. Regarding the MOFs, the attention is focused on the synthesis of materials with remarkable optical and structural properties. The synthesized materials were tested as photocatalysts for removing emerging contaminants, particularly some pharmaceuticals and personal care products, using solar light. The performance was followed by the removal efficiency and stability upon successive cycles. The oxidation mechanisms and degradation pathways of the target contaminants were also investigated.

RESULTS

This work aimed to outline the results presented through a compendium of six papers published in peer-reviewed scientific journals.

The first paper, "C-modified TiO_2 using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen" (Chemical Engineering Journal 358 (2019) 1574-1582), deals with the synthesis of carbon-modified TiO_2 photocatalysts for the degradation of acetaminophen (ACE). The doping of TiO_2 with C as interstitial carbon provoked distortions in the TiO_2 lattice in those materials heated under N_2. In the air-treated samples, C atoms were removed by means of partial combustion, leading to Ti^{3+} defects and oxygen vacancies. All synthesized materials were tested in the photocatalytic removal of ACE under solar light. The improved efficiency compared to bare TiO_2 can be attributed to the presence of those oxygen vacancies and defects in the TiO_2 lattice, acting as trap centers and reducing the recombination rate of the photogenerated charge carriers.

Besides the C doping of TiO_2, another approach investigated in this research is the preparation of carbon supports to build heterostructures with photocatalytic applications. This is the aim of the second paper, "Effect of activating agent on the properties of TiO_2/Activated Carbon heterostructures for solar photocatalytic degradation of acetaminophen" (Materials 12 (2019) 378-395). Following the chemical activation of lignin with $FeCl_3$, $ZnCl_2$, H_3PO_4 and KOH as activating agents, several activated carbons (ACs) were obtained. Subsequently, TiO_2 was solvothermally anchored on the surface of those activated carbons (Figure 1a). The nature of the activating agent affected both the values of surface area and the superficial charge. Regarding the optical properties, the heterostructures showed band gap (E_g) values almost equal or slightly higher than the TiO_2 counterpart, suggesting that the construction of the heterostructures did not modify the band gap nor the light absorption edge due to the limited interaction between the AC and the TiO_2. Based on the promising results obtained with TiO_2/Fe-C heterostructure, a more detailed study was conducted exploring the influence of the synthesis conditions on the photocatalytic activity towards different pharmaceuticals. This was the aim of the third paper, "Degradation pathways of emerging contaminants using TiO_2-activated carbon heterostructures in aqueous solution under simulated solar light" (Chemical Engineering Journal 392 (2020) 124867). Different TiO_2/AC heterostructures were prepared by three different methods, namely solvothermal (ST), microwave-assisted (MW) and sol-gel (SG) synthesis. XRD patterns demonstrated that the MW procedure achieved the anatase crystallization without needing subsequent thermal treatment, being the fastest synthesis route, requiring only 30 min to obtain the heterostructure. TiO_2/AC-MW achieved the highest conversion and mineralization in the breakdown of ACE, ibuprofen (IBU) and antipyrine (ANT). The proposed degradation pathway of the pharmaceuticals mainly involved ring cleavage, hydroxylation, decarboxylation and dealkylation reactions, leading to different short-chain compounds (but also to the formation of coupled species).

Hydrothermal carbonization (HTC) of lignin with $FeCl_3$ and the subsequent use of the resulting hydrochar as support to prepare TiO_2-carbon photocatalysts for the removal of pharmaceuticals from water under solar light irradiation was also investigated. This was the aim of the fourth paper, "TiO_2-carbon microspheres as photocatalysts for effective remediation of pharmaceuticals under simulated solar light" (Separation and Purification Technology 275 (2021) 119169). This study was carried out in collaboration

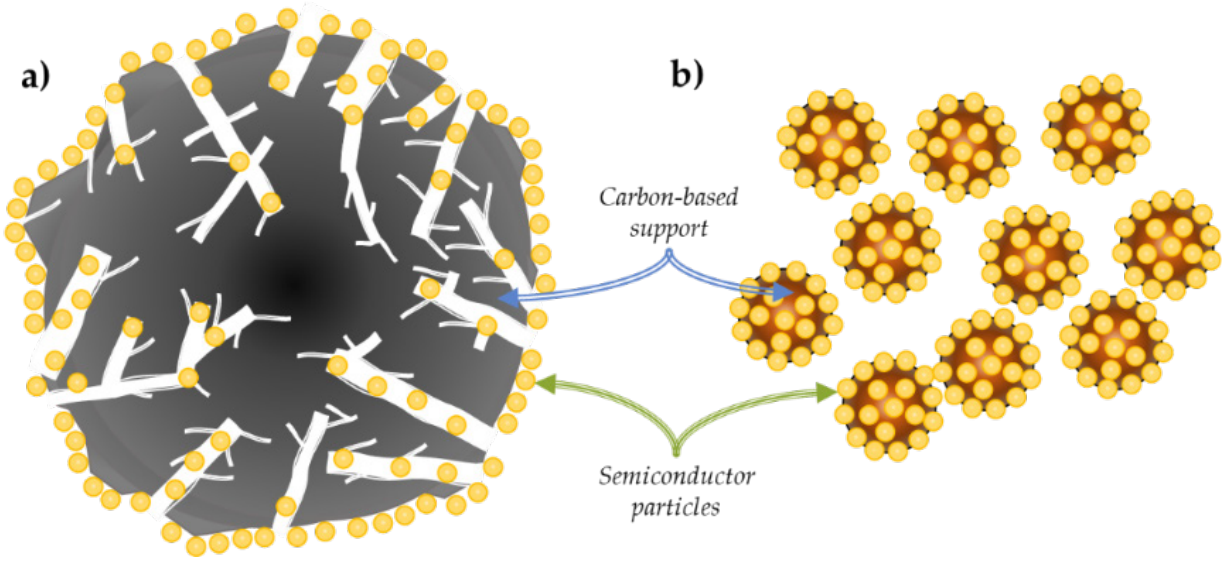

Figure 1. Illustration of TiO_2 anchoring on (a) AC and (b) C-spheres.

with the University of Cincinnati (Ohio, USA), under the supervision of Professor Dionysios D. Dionysiou. In this study, spherical carbon microparticles (Figure 1b) were prepared by means of an innovative two-step approach ($FeCl_3$-mediated HTC of lignin followed by pyrolysis of the resulting hydrochar). Increasing the HTC holding time led to a larger average particle size and lower surface area and microporosity.

With the aim of exploring other types of structured photocatalysts, the following two papers were focused on the investigation of metal-organic frameworks (MOFs). The fifth paper of this research, "Mixed Ti-Zr metal-organic-frameworks for the photodegradation of acetaminophen under solar irradiation" (Applied Catalysis B: Environmental 253 (2019) 253-262), assesses the synthesis of NH_2-MIL-125(Ti) modified through the incorporation of a Zr precursor, leading to different MOFs by varying the molar ratio of Zr. The results of photoluminescence tests suggested the decrease of the recombination rate and promotion of the photocatalytic activity probably because the Zr-doping added energy levels that can act as electron-hole traps. The sixth work, "Solar photocatalytic degradation of parabens using UiO-66-NH_2" (Separation and Purification Technology 286 (2022) 120467), is the result of a collaboration with the Universidade do Porto (Portugal) under the supervision of Dr. Maria José Sampaio. In this study, UiO-66-NH_2 (a Zr-based MOF) was tested for the removal of methylparaben (MP) in different water matrices. The almost complete conversion was achieved after 1 h of solar radiation in both distilled and river water samples, whereas the efficiency decreased in the effluent of a wastewater treatment plant secondary treatment, most probably due to the turbidity and the higher content of organic matter. A continuous flow study demonstrated the high stability and steady performance of the MOF upon 30 h on stream. The photocatalytic performance of the MOF was also tested in the removal of ethylparaben and propylparaben, being observed that the efficiency was influenced by the length of the alkyl side chain.

CONCLUSIONS

Regarding the preparation of different heterostructured photocatalysts, it can be concluded that: i) the heat treatment in air of carbon-modified TiO_2 produces partial combustion of carbon atoms, allowing the formation of oxygen vacancies and defects in the TiO_2 lattice, thus reducing the recombination rate; ii) different agents for the lignin activation affected the porous texture and the acidic character of the carbonaceous surface. The anchoring of TiO_2 on carbon supports did not modify the E_g but increases the settling rate; iii) $FeCl_3$-assisted hydrothermal carbonization of lignin yielded carbon microspheres.

On the other hand, and regarding the evaluation of the photocatalytic performance under solar light: i) structured photocatalysts demonstrated good performance under solar light in the elimination of emerging contaminants; ii) the oxidation mechanism mainly ascribed to $O_2^{\bullet-}$ radical, with significant contribution of h^+ and $HO^\bullet$. Different reaction pathways proposed, involving hydroxylation, dealkylation, decarboxylation and ring-opening reactions; iii) the reusability of the photocatalysts depicted no significant variations in the performance and in the main properties of the heterostructures.

RELATED PUBLICATIONS

Gómez-Avilés, A., Peñas-Garzón, M., Bedia, J., Rodriguez, J.J., Belver, C. C-modified TiO_2 using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen. *Chemical Engineering Journal* 358, 2019, 1574-1582. (doi: 10.1016/j.cej.2018.10.154)

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