Photocatalysis and Sonocatalysis for Environmental Applications: Synergy or Competition?

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Editorial

Photocatalysis and Sonocatalysis for Environmental Applications: Synergy or Competition?

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This Editorial refers to the Special Issue entitled "Photocatalysis and Sonocatalysis for Environmental Applications: Synergy or Competition?", which aimed to highlight the common aspects and challenges of photocatalysis and sonocatalysis for the degradation of organic pollutants in aqueous solutions. Both techniques have been extensively studied in previous decades with regard to potential environmental remediation, and they are sometimes seen as competitors. However, the fundamental mechanisms of these processes leading to the degradation of pollutants are very different. Heterogeneous photocatalysis is based on the photoexcitation of semiconducting particles, typically TiO_2, ZnO, CdS and ZnS [1,2]. The semiconductor absorbs photons equal to or higher than that of the band gap to promote an electron from the valence band to the conduction band, leading to electron/hole pair formation. The electron hole enables the oxidization of water molecules, producing strongly oxidizing $^{\bullet}OH$ radicals, or the oxidization of the adsorbed organic molecule itself. In addition, the electrons promoted to the CB are able to reduce the oxygen to superoxide radical $O_2^{-\bullet}$. Therefore, the presence of oxygen is essential in photocatalytic oxidation processes. In this view, charge separation is vital for the efficiency of semiconducting photocatalysts. For this reason, a huge number of papers have reported on the synthesis of semiconducting photocatalysts doped with metallic and non-metallic nanoparticles with enhanced electron/hole charge separation [3]. On the other hand, sonocatalysis involves the simultaneous action of heterogeneous catalysts and sonochemistry [4]. Sonochemistry originates from the acoustic cavitation phenomenon: the nucleation, growth, and transient collapse of gas/vapor microbubbles in liquids submitted to power ultrasound. In general, three sites of sonochemical activity can be distinguished: the gas phase inside the collapsing bubble, the overheated liquid reaction zone extending several hundred nm from the bubble surface, and the bulk solution, where secondary chemical processes may occur [5]. In aqueous solutions, drastic conditions inside the cavitation bubble generate nonequilibrium plasma, leading to sonochemical water molecule splitting [6]. Hydrogen atoms mostly recombine inside the bubble, forming hydrogen gas. In contrast, $^{\bullet}OH$ radicals can reach a liquid reaction zone where they oxidize organic molecules or recombine, yielding H_2O_2, which could react in the bulk solution. According to this mechanism, there are multiple impacts of ultrasound on heterogeneous catalysts: (i) the mechanical effects of cavitation may disperse catalyst aggregates, remove the passivating layer from the catalyst surface, and accelerate the mass transfer in the vicinity of the catalyst; (ii) local heating produced by a collapsing bubble could accelerate the catalytic process; and (iii) chemically active species that emerge from a cavitation bubble may promote the catalytic cycle. The effects of ultrasound are strongly influenced by ultrasonic frequency: a low frequency (ca. 20–100 kHz) promotes mechanical effects; however, chemical effects prevail at high frequencies (ca. 100 kHz–1 MHz) [7]. Therefore, choosing an appropriate ultrasonic frequency is a critical point for efficient sonocatalytic processing.

The papers presented in this Special Issue are listed in the List of Contributions.

It is worth mentioning that these contributions highlight the major trends in heterogeneous photocatalysis and sonocatalysis for environmental applications. Contribution

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1 focused on the development of photocatalyst morphology to improve the photodegradation of pollutants in aqueous solutions and to enhance the reusability of photocatalysts. The authors reported the synthesis of CuO/ZnO/CQD/PAN nanocomposites with ternary heterostructures (CZC@PAN), where CQD and PAN are the carbon quantum dots and the polyacrylonitrile nanofibers, respectively. It was shown that the photocatalytic degradation rate of methylene blue over CZC@PAN was 99.04% under a mercury lamp for 3 h and 99.56% in natural sunlight for 4 h, respectively. The high photocatalytic activity of CZC@PAN was attributed to the creation of p-n CuO/ZnO heterojunctions and to the loading of carbon dots, which promoted the photo response ability of CZC@PAN and efficient charge separation. It is also important for catalyst morphologies to allow easy recovery and reuse. Contributions 2 and 3 explored the thermal effects in photocatalytic processes with heterogeneous catalysts. Introducing heat into photocatalytic processes has attracted a great deal of attention in the last decade, because it may significantly improve the photoconversion efficiency [8,9]. In addition, self-heating photocatalytic systems can consume lower amounts of energy in the conversion of substrates into desired products [10]. A study of photothermal H_2 production from butanol isomers (1-BuOH, 2-BuOH, and t-BuOH) over Ti@TiO_2 core–shell nanoparticles (Contribution 2) showed that the photothermal effect shown with 1-BuOH/2-BuOH isomers can be attributed to the thermally induced transfer of photogenerated, shallowly trapped electron holes to highly reactive free holes at the surface of TiO_2 and further hole-mediated cleavage of the O-H bond. This conclusion correlates with the photothermal mechanisms of TiO_2-based photocatalysts found using photoelectrochemical [11] and isotopic H/D studies [12]. Contribution 3 considered the utilization of a solar light concentrator with a constant radiation intensity of 1000 W/m^2 for the photodegradation of Magenta effluent originating from the graphic industry over a TiO_2/Fe_3O_4 nanocomposite. It was shown that at the elevated temperature of about 50–80 °C and pH = 6.5, discoloration efficiency of about 95.6% could be reached. These results indicate that parabolic solar light concentrators represent a promising option for thermally assisted photocatalytic dye degradation at the large scale.

Regarding sonocatalytic processes of organic pollutants' degradation, the major trend considered in this Special Issue is focused on the combination of sonochemistry with other methods, such as high-voltage plasma discharge coupled with ultrasonic treatment and Fenton reagent (Contribution 4), and the coupling of power ultrasound with photocatalysis, called sonophotocatalysis (Contribution 5). In Contribution 4, it was shown that the addition of $FeCl_2$ greatly enhanced the efficiency of the acoustic cavitation-assisted (20 kHz) plasma decomposition of Rhodamine B. Under the studied experimental conditions, the decomposition efficiency reached almost 80%, which was 20% greater than that in the case without Fenton reactions. In addition, argon injection into the reactor greatly improved Rhodamine B degradation. While argon is not involved in the chemical reaction, it assists plasma generation by lowering the underwater dielectric breakdown voltage. As a result, more chemically active hydrogen and oxygen-containing ions and radicals are generated when argon is introduced into the reactor, providing further promotion of Rhodamine B decomposition. Finally, Contribution 5 discussed the opportunities represented by sonophotocatalysis, as well as its limitations, for environmental remediation. In fact, several studies have reported that low-frequency ultrasound (20–40 kHz) can enhance the photocatalytic degradation of pollutants [13,14]. The thorough study in Contribution 5 revealed a 200–300% synergetic effect between the 20 kHz ultrasound and TiO_2 photocatalytic degradation of Bisphenol A in aqueous solutions under UV LED light irradiation (λ = 300 nm). However, it was found that the sonophotocatalytic degradation could not be steadily maximized by ultrasonic energy input. Instead, there is a limiting value providing optimal conditions depending on the TiO_2 concentration. Sonophotocatalysis may contribute to the effectiveness of photocatalytic degradation reactions by resolving problems related to the opacity and aggregation of the catalyst. The composition and morphology of TiO_2-based photocatalysts are not adversely affected during sonophotocatalytic treatment. In fact, particle disaggregation induced by power ultrasound may actually enhance the

surface area of a photocatalyst, making photochemically generated oxidizing species more assessable for organic substrates. In principle, sonophotocatalysis could be considered as a candidate for futuristic environmental applications, but serious technical problems related to the scaling up of such a hybrid process and catalyst-related recycling issues will hinder the development of large-scale applications of sonocatalysis in general and sonophotocatalysis in particular.

Conflicts of Interest: The author declare no conflict of interest.

List of Contributions:

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