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Editorial

Editorial Catalysts: Special Issue on Recent Advances in TiO_2 Photocatalysts

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The development of civilization and the massive use of traditional energy sources has led to progressive environmental degradation that requires immediate action. Particularly, the elaboration of environmentally friendly methods of removing pollutants from various types of water, and a search for ecological energy sources, have been the focus of researchers in recent decades. Advanced oxidation processes (AOPs) seem to be addressing both of these issues. AOPs are highly effective due to the formation of reactive oxygen species, especially hydroxyl radicals, which act as oxidizing agents. Among AOPs, semiconductor photocatalysis, especially with titanium dioxide (TiO_2), has a great potential for the decontamination of water and wastewater, exhaust gases, and disinfection [1–8]. This inexpensive, stable, and non-toxic catalyst provides very good removal efficiency. The heterogeneous photocatalytic process, as well as new TiO_2-based materials applied in biomedical fields, energy storage, and energy conversion devices, can contribute to improving the quality of the natural environment [9–11]. High-efficiency TiO_2-based photocatalysts are also successfully used in photocatalytic water splitting and photoconversion, providing a low-cost and environmentally friendly production method of clean fuels [12,13]. Separation of the photocatalyst particles after treatment is the main disadvantage of the suspended process. Therefore, for implementation, incorporated photocatalysts are recommended. However, it should be noticed that, in principle, the processes with immobilized catalysts are much slower than those in which suspended particles are applied. The higher efficiency of the latter can be explained by a larger surface area of suspended catalysts compared to the immobilized system. To reduce the costs, special attention has also been paid to the usage of visible light (in particular solar light/sunlight) as a "clean reagent" to initiate or accelerate chemical reactions [14].

High stability and photocatalytic activity make TiO_2 the most popular photocatalyst. However, due to the large energy band gap, its activity in the range of natural solar light is quite limited. For this reason, the development of new TiO_2-based photocatalysts active in the visible range has become a new research trend [1,3,6,13,15–19]. The effectivity can also be improved by modifying TiO_2 with noble metals [2,13,15] or by Ti^{3+}-self-doped TiO_2 modification [11].

This Special Issue reports recent progress and developments in the synthesis or modifications of TiO_2 catalysts, including metal and non-metal doping, surface deposition of noble metals, semiconductor coupling, and dye sensitizing. Research focusing on promoting visible light TiO_2 photocatalytic applications for environmental protection was appreciated. Furthermore, research into understanding the mechanism of photocatalysis, photocatalytic ozonation, as well as photoconversion and water splitting have been important subjects for this Special Issue.

Three review papers were accepted for this Special Issue which focused on the improvement of visible light photoactivity of TiO_2. Bokare and co-workers presented an excellent overview of TiO_2 nanoparticle modifications with graphene quantum dots (GQDs) and its potential for energy and biomedical applications [9]. The authors discussed in depth the synthesis of TiO_2–GQD nanocomposites with regard to structural characteristics and their photocatalytic mechanisms. The high potential of TiO_2–GQD nanocomposites has been shown in the context of the photocatalytic degradation of micropollutants, H_2 production from water splitting, and dye-sensitized solar cells, as well as biomedical applications including drug delivery, biosensing, tissue engineering, and applications as contrasting agents in bioimaging [9]. Assessing improvements in photoelectrochemical performance in environmental, energy, and catalytic applications of carbon-doped TiO_2 was the main goal of Hua and co-workers' review paper [17]. Herein, the synthesis methods, as well as surface characteristics of C-doped TiO_2-based materials, were presented. The center of attention of the third manuscript was the development of advanced Ti^{3+}–TiO_2 used for the efficient solar energy harvesting of TiO_2 photocatalysts [11]. A detailed discussion of Ti^{3+}–TiO_2 preparation was presented, along with a very interesting analysis of modifications by metal and nonmetal doping, semiconducting coupling, and stoichiometry modification, and the impacts on photogenerated charge separation and photocatalytic activity were demonstrated [11].

Due to the great potential in a variety of applications in solar energy conversion and environmental purification, semiconductor photocatalysis has gained considerable popularity in this field. Therefore, TiO_2 photocatalysis is one of the most popular AOPs applied for the oxidation of a wide range of organic compounds in an aqueous environment, but also in the air.

Among various water and wastewater treatment methods, the TiO_2-based technology has garnered considerable attention for the removal of contaminants of emerging concern. However, the problem of dye removal from textile wastewater and the possibility of reusing treated effluent has also been addressed in some studies.

Borowska et al. showed that noble metal modifications of TiO_2 enable the successful removal of sulfamethoxazole under natural light irradiation [2]. Ran and co-workers demonstrated that TiO_2 can degrade carbamazepine under UVA–LED [8]. In both articles, the operational process parameters were evaluated concerning the highest photocatalytic efficiency. Do et al. mostly focused on developing the analytical detection of antibiotics and their validation for photocatalytic degradation [20]. The application of TiO_2 nanotube arrays (TNAs) and nanowires on nanotube arrays (TNWs/TNAs) for an antibiotic mixture (lincomycin, doxycycline, oxytetracycline, sulfamethazine, and sulfamethoxazole) degradation under UV–VIS irradiation was investigated [20].

Butman's group demonstrated the photocatalytic degradation of Rhodamine B using two forms of TiO_2, namely, biomorphic fibrous TiO_2 ([21]) and TiO_2-pillared montmorillonite ([22]) under UVA irradiation. TiO_2 fibers (calcined 600 °C with a ratio of anatase:rutile of 40:60) led to the complete degradation of Rhodamine B after 20 min of treatment. Moreover, SiO_2–TiO_2-coated catalysts could be reused [21]. In the experiments with a TiO_2-pillared catalyst that was hydrothermally treated and activated, complete removal was obtained after almost 2 h, whereas dielectric barrier discharge plasma in the presence of photocatalysts was used and complete degradation was achieved after only 8 s [22]. Methylene blue degradation was investigated in the presence of polyaniline-wrapped, manganese-doped titanium oxide (PANi/Mn-TiO_2) [16] as well as Au–Ag co-decorated TiO_2 ($Au_xAg_{(1-x)}/TiO_2$) [15] under visible light. Surprisingly, the presence of inexpensive and environmentally friendly natural dyes (anthocyanin pigments) improved the visible light photocatalytic activity of TiO_2 [1]. Stainless-steel foam coated with TiO_2 grafted with anthocyanins originating from a Maqui-Blackberry system was successfully applied for Aniline blue removal [1]. However, despite the efficient degradation of dye solutions in the presence of TiO_2-catalysts, the application of TiO_2 catalysts for industrial textile wastewater treatment was not satisfactory, even when it was enhanced by the presence of ozone [23]. Solvolysis enhanced the Eosin B removal during sonophotocatalysis (TiO_2 and UVA) [5].

TiO_2-based photocatalytic air purification is also an essential problem worth investigating. Therefore, the elimination of various volatile organic compounds (VOCs) by photocatalytic processes with TiO_2 catalysts was also presented in this Special Issue.

Bettoni and co-workers demonstrated the experimental and theoretical investigation on the TiO_2 catalytic elimination of methane, hexane, isooctane, acetone, and methanol, following the microscopic mechanism based on the Langmuir–Hinshelwood approach [24]. Bellardita et al. investigated the degradation of 2-propanol, ethanol, and toluene under visible light in the presence of brookite TiO_2–CeO_2 composites in their study [19]. It was found that the addition of cerium oxide to brookite TiO_2 favored the total oxidation to CO_2. Moreover, the combination of thermocatalysis and photocatalysis mechanisms was considered [19]. The effect of QDs-sensitized TiO_2 composite types ($AgInS_2$, SnS, CuS_2, Bi_2S_3) on the decomposition of toluene was investigated by Malankowska and co-workers [25]. LED light irradiation (λmax = 415 nm and λmax = 375 nm) was applied. A synergistic effect between QDs and the TiO_2 matrix was found to occur. Moreover, TiO_2/$AgInS_2$ and TiO_2/SnS exhibited higher photoactivity than the pristine TiO_2 and QDs under 375 nm [25]. Natural daylight was used to remove toluene and α-pinene during photocatalysis with Cu_2O–Au–TiO_2 [6]. Lee's group demonstrated the excellent photocatalytic activity of Cu_2O–Au–TiO_2 towards toluene and α-pinene degradation, compared to pure TiO_2, Cu_2O–TiO_2, and Au–TiO_2 [6].

NO_x removal and CO_2 reduction were investigated as well [4,7]. The results demonstrated that graphene oxide (GO)- and carbon nanotube (CNT)-modified TiO_2 materials resulted in a higher conversion efficiency of nitrogen oxides (NO_x) under simulated solar light compared with the commercial Degussa P25 [7]. Moreover, metalloporphyrin TCPP-M (M = Co, Ni, Cu) loaded onto TiO_2 exhibited a much better photocatalytic CO_2 reduction into CO in comparison to TiO_2 [4].

As illustrated in this Special Issue, excellent research has been conducted in the field of TiO_2 photocatalysts. Eater pollutant degradation, air purification, photocatalytic conversion, H_2 production, NO_x conversion, and CO_2 conversion are presented, as well as the development of new TiO_2-based materials. In total, 24 manuscripts from the research groups coming from twelve different countries (China, Italy, Thailand, Korea, Canada, Norway, Poland, Germany, Portugal, Spain, Russia, and Vietnam) have been published. The variety of scientific approaches make this Special Issue very successful and indicate new directions for further research.

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