

Editorial

Editorial Catalysts: Special Issue on Recent Advances in TiO₂ 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 (TiO₂), 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 TiO₂-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 TiO₂-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 TiO₂ 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 TiO₂-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 TiO₂ with noble metals [2,13,15] or by Ti³⁺-self-doped TiO₂ modification [11].

This Special Issue reports recent progress and developments in the synthesis or modifications of TiO₂ catalysts, including metal and non-metal doping, surface deposition of noble metals, semiconductor coupling, and dye sensitizing. Research focusing on promoting visible light TiO₂ 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 TiO₂. Bokare and co-workers presented an excellent overview of TiO₂ nanoparticle modifications with graphene quantum dots (GQDs) and its potential for energy and biomedical applications [9]. The authors discussed in depth the synthesis of TiO₂-GQD nanocomposites with regard to structural characteristics and their photocatalytic mechanisms. The high potential of TiO₂-GQD nanocomposites has been shown in the context of the photocatalytic degradation of micropollutants, H₂ 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 TiO₂ was the main goal of Hua and co-workers' review paper [17]. Herein, the synthesis methods, as well as surface characteristics of C-doped TiO₂-based materials, were presented. The center of attention of the third manuscript was the development of advanced Ti³⁺-TiO₂ used for the efficient solar energy harvesting of TiO₂ photocatalysts [11]. A detailed discussion of Ti³⁺-TiO₂ 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, TiO₂ 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 TiO₂-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 TiO₂ enable the successful removal of sulfamethoxazole under natural light irradiation [2]. Ran and co-workers demonstrated that TiO₂ 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 TiO₂ 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 TiO₂, namely, biomorphic fibrous TiO₂ ([21]) and TiO₂-pillared montmorillonite ([22]) under UVA irradiation. TiO₂ 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, SiO₂-TiO₂-coated catalysts could be reused [21]. In the experiments with a TiO₂-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-TiO₂) [16] as well as Au-Ag co-decorated TiO₂ (Au_xAg_(1-x)/TiO₂) [15] under visible light. Surprisingly, the presence of inexpensive and environmentally friendly natural dyes (anthocyanin pigments) improved the visible light photocatalytic activity of TiO₂ [1]. Stainless-steel foam coated with TiO₂ 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 TiO₂-catalysts, the

application of TiO₂ 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 (TiO₂ and UVA) [5].

TiO₂-based photocatalytic air purification is also an essential problem worth investigating. Therefore, the elimination of various volatile organic compounds (VOCs) by photocatalytic processes with TiO₂ catalysts was also presented in this Special Issue.

Bettoni and co-workers demonstrated the experimental and theoretical investigation on the TiO₂ 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 TiO₂–CeO₂ composites in their study [19]. It was found that the addition of cerium oxide to brookite TiO₂ favored the total oxidation to CO₂. Moreover, the combination of thermocatalysis and photocatalysis mechanisms was considered [19]. The effect of QDs-sensitized TiO₂ composite types (AgInS₂, SnS, CuS₂, Bi₂S₃) on the decomposition of toluene was investigated by Malankowska and co-workers [25]. LED light irradiation ($\lambda_{\max} = 415$ nm and $\lambda_{\max} = 375$ nm) was applied. A synergistic effect between QDs and the TiO₂ matrix was found to occur. Moreover, TiO₂/AgInS₂ and TiO₂/SnS exhibited higher photoactivity than the pristine TiO₂ and QDs under 375 nm [25]. Natural daylight was used to remove toluene and α -pinene during photocatalysis with Cu₂O–Au–TiO₂ [6]. Lee's group demonstrated the excellent photocatalytic activity of Cu₂O–Au–TiO₂ towards toluene and α -pinene degradation, compared to pure TiO₂, Cu₂O–TiO₂, and Au–TiO₂ [6].

NO_x removal and CO₂ reduction were investigated as well [4,7]. The results demonstrated that graphene oxide (GO)- and carbon nanotube (CNT)-modified TiO₂ 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 TCPPM (M = Co, Ni, Cu) loaded onto TiO₂ exhibited a much better photocatalytic CO₂ reduction into CO in comparison to TiO₂ [4].

As illustrated in this Special Issue, excellent research has been conducted in the field of TiO₂ photocatalysts. Eater pollutant degradation, air purification, photocatalytic conversion, H₂ production, NO_x conversion, and CO₂ conversion are presented, as well as the development of new TiO₂-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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