

Structured Semiconductors in Photocatalysis

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1. Introduction

Photocatalysis appears as an interesting approach for different applications, with the possibility of using sunlight as a sustainable and renewable source of energy. This technology is based on the use of a semiconductor that can be excited by light with an energy higher than its band gap inducing the formation of energy-rich electron-hole pairs, which can be involved in redox reactions. Recent progress explored the chemical nature of structured semiconductors with the object to improve their electronic and optical properties, enhancing their photoresponse under different conditions. This Special Issue collects original research papers, reviews, and commentaries focused on the challenges for the design of structured semiconductors with photocatalytic applications, thus including synthesis, characterization of new photocatalysts, studies of activity and stability, and the mechanisms of photocatalytic reactions.

2. Structured Semiconductors in Photocatalysis

This Special Issue includes outstanding studies focused on structured semiconductors in photocatalysis for different applications. In this sense, Bobape et al. [1] synthesized CuO-TiO₂ nanocomposites using *C. Benghalensis* plant extracts. They analyzed the effect of the CuO to TiO₂ ratio on the morphological, optical, electrochemical, and photodegradation efficiency. The XRD data confirmed the tenorite structure of the CuO and the anatase phase of the TiO₂. The voltammogram of the CuO-TiO₂ 30/70 electrode showed the highest response current density, suggesting a higher specific capacitance in this structured semiconductor. This sample also showed the highest photocatalytic degradation efficiencies against methylene blue, ciprofloxacin, and sulfisoxazole, with hydroxyl radicals being the primary species responsible for the photodegradation. In another study, Matussin et al. [2] synthesized CeO₂ and palladium-doped CeO₂ photocatalysts via the microwave-assisted synthesis method. The authors observed mixed phases of CeO₂/Ce₂O₃, although the Ce₂O₃ phase gradually disappeared upon doping with a higher percentage of Pd. The presence of Pd resulted in a decrease in the band gap energies, and the photoluminescence intensities were also quenched with Pd doping. Pd-CeO₂ NPs showed enhanced activities under visible light irradiation in the photodegradation of methylene blue and photoantibacterial activities. Chue et al. [3] prepared a hexagonal wurtzite ZnO photocatalyst via precipitation method. CuS nanoparticles and PbS quantum dots were loaded onto ZnO via a hydrothermal method to obtain a CuS/PbS/ZnO heterojunction photocatalyst. The CuS/PbS/ZnO photocatalyst showed significant absorption capabilities in the ultraviolet to near-infrared spectral regions, and effectively reduced the recombination of electron-hole pairs during a photocatalytic reaction. This catalyst demonstrated the best water splitting effect. Furthermore, after adding a 0.25 M mixed solution of Na₂S and Na₂SO₃ as the sacrificial reagent, the hydrogen production efficiency from water splitting reached 6654 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ after 5 h. Tien et al. [4] synthesized a new binary MoS₂/Co₃O₄ nanohybrids. The heterojunction presented an S-scheme structure that acted as electron traps and promoted light absorption capacity for the degradation of methyl orange under visible light. The photocatalyst also showed excellent stability and recyclability over five



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consecutive cycles, without noticeable changes in the nanocomposite structure. The boosted photocatalytic degradation and redox activities of $\text{MoS}_2/\text{Co}_3\text{O}_4$ can be attributed to the created S-scheme heterostructure to facilitate the separation of and delay recombination of photoinduced charge carriers. In another study, Rezgui et al. [5] studied a heterogeneous photo-electro-Fenton process, which is an attractive technology for the removal of recalcitrant pollutants. To better exploit the presence of an irradiation source, a bifunctional catalyst with TiO_2 nanoparticles embedded into an iron–chitosan matrix was developed. The catalytic activity of the catalyst was improved by the optimization of the loaded TiO_2 content. The prepared composite catalysts based on TiO_2 , Fe_3O_4 , and chitosan were called $\text{TiO}_2/\text{Fe}_3\text{O}_4$ -CS beads. The best catalyst with an optimal ratio $\text{TiO}_2/\text{Fe} = 2$ exhibited a high efficiency in the degradation and mineralization of chlordimeform insecticide. Under the optimum conditions, a real effluent loaded with 30 mg L^{-1} of the insecticide was efficiently treated, leading to $80.8 \pm 1.9\%$ TOC reduction after 6 h of treatment, with total removal of the pollutant after only 1 h. Hudandini et al. [6] loaded Ag onto ZnO by an ultrasonic spray pyrolysis system at different Ag contents (1, 5, and 10 wt%). An increase in the ZnO-Ag activity compared with pristine ZnO was observed at a carrier gas ratio of 0:1 with reaction rate constants of 0.0059 and 0.0025 min^{-1} , respectively, in the degradation of textile wastewater under UV light irradiation. Babyszko et al. [7] analyzed the modification of titanium dioxide with fumed silica. The $\text{SiO}_2/\text{TiO}_2$ photocatalysts were obtained by the sol-gel method and were then calcined under an argon atmosphere. Various SiO_2 weights (2–17.2 wt.%) were prepared. The modification of titanium dioxide with SiO_2 inhibited the increase in crystallite size of anatase and brookite during calcination and the decrease in specific surface area values. The photocatalytic activity was determined based on the decomposition of methylene blue under UV irradiation. All the obtained $\text{SiO}_2/\text{TiO}_2$ photocatalysts showed higher activity compared to the starting TiO_2 . Dies et al. [8] prepared fluoride-doped TiO_2 (F- TiO_2) photocatalysts by an efficient and simple one-step synthesis and tested them in the UV-photo-degradation of methylene blue and bisphenol A. F- TiO_2 defeated commercial TiO_2 , and almost complete pollutant removal was achieved within 30 min. The energy consumption was reduced as a result of the suitable reactor set-up, which reduced light scattering, and by the application of a long-pulse radiation procedure, where the lamp was switched off during periods of continued degradation. This enhanced the overall photocatalytic performance. Under these conditions, 80% of dye removal was attained within 15 min of radiation with an energy consumption of only $0.070 \text{ Wh min}^{-1}$, demonstrating a much better efficiency when compared to previously reported data. The catalyst was reusable, and its performance can be improved by the addition of H_2O_2 . The results were validated by BPA degradation and the treatment of real wastewater with both pollutants. Harris et al. [9] investigated ZnO powders prepared by alkali precipitation using different $[\text{Zn}(\text{acetate})_2(\text{amine})_x]$ compounds to alter the particle size and aspect ratio. Slow precipitations from 95°C solutions produced micron-scale particles with morphologies of hexagonal plates, rods, and needles, depending on the precursor used. Powders prepared at 65°C with rapid precipitation yielded particles with minimal morphology differences, but the particle size was dependent on the precursor used. The smallest particles were produced using precursors that yielded crystals with low aspect ratios during high-temperature synthesis. Particles produced during rapid synthesis had sizes ranging from 21 to 45 nm. The materials prepared using precursors with less volatile amines were found to retain more organic material than ZnO produced using precursors with more volatile amines. The amount of organic material associated with the nanoparticles influenced the photocatalytic activity of the ZnO, with powders containing less organic material producing faster rate constants for the decolorizing of malachite green solutions under ultraviolet illumination, independent of particle size. $[\text{Zn}(\text{acetate})_2(\text{hydrazine})_2]$ produced ZnO with the fastest rate constant and was recycled five times for dye degradation studies that revealed minimal to no reduction in catalytic efficiency. Akitunde et al. [10] studied disinfection and photocatalytic degradation of organic contaminants using visible light-activated $\text{GCN}/\text{Ag}_2\text{CrO}_4$ nanocomposites. The organic pollutants studied were 2,4-

dichlorophenoxyacetic acid and methyl chlorophenoxy propionic acid present in Killex[®], a commercially available herbicide, bovine serum albumin (BSA) protein, and SARS-CoV-2 spike protein. The disinfection experiments were conducted on wastewater secondary effluent. Overall, the results indicate that GCN/Ag₂CrO₄ nanocomposite is a promising photocatalyst in degrading organic pollutants and disinfecting microorganisms under visible light irradiation within a reasonable time. Lang et al. [11] evaluated a TiO₂-CNT-Ag ternary composite film synthesized using the plasma-enhanced chemical vapor deposition method by simultaneously feeding a carbon nanotube (CNT)/Ag suspension and titanium tetraisopropoxide gas. The performance of the TiO₂-composite film for the degradation of rhodamine 6G under simulated solar light irradiation was evaluated. The rate constant of the prepared TiO₂-CNT-Ag for rhodamine 6G degradation was approximately 1.8 times greater than that of the prepared TiO₂. This result indicates that the addition of CNT and Ag significantly improved the photocatalytic activity of the prepared films. This same research group prepared TiO₂-Ag nanoparticle composite films by plasma-enhanced chemical vapor deposition (PECVD) using a mixture of aerosolized AgNO₃, which was used as an Ag nanoparticle precursor, and titanium tetraisopropoxide, which acted as the TiO₂ precursor [12]. Notably, the use of PECVD enabled a low process temperature and eliminated the need for pre-preparing the Ag nanoparticles, thereby increasing the process efficiency. The photocatalytic activity of the deposited films was determined by assessing the degradation of methylene blue under UV light irradiation. The Ag ions were successfully reduced to metallic nanoparticles and were embedded in the TiO₂ film. The best photocatalytic activity was achieved for a 1 wt% Ag-loaded TiO₂ composite film, which was 1.75 times that of pristine TiO₂. Finally, Sanni et al. [13] studied the synthesis approach (thermal polyol and deposition-precipitation) regarding the dispersion of Ag/AgBr nanoparticles dispersed on activated carbon prepared from chemically impregnated pinecone to increase their photocatalytic efficiency on the degradation of tetracycline.

This Special Issue also includes two reviews. The first one is a work by Venezia et al. [14] that described the state of the art of the current design strategies and emerging trends to hierarchical catalysts. Nature mimicking implies the design of nanostructured materials, which can be assembled into a hierarchical structure, thus outperforming the features of the neat components because of their multiple length scale organization. This approach can be effectively exploited for the design of advanced photocatalysts with superior catalytic activity for energy and environment applications with considerable development in the recent six years. The review presented different synthesis strategies, including template-free structuring, and organic, inorganic, and hybrid templating. Furthermore, emerging approaches based on hybrid and bio-waste templating were also highlighted. Finally, a critical comparison among available methods was carried out based on the envisaged application. The second review by Sreedhar and Noh [15] described the advancements in solar desalination of seawater by various Ti₃C₂ MXene-based morphologies for freshwater generation. The study explained key features such as light absorption, reflection, multiple internal reflection, hydrophilicity, lower thermal conduction, light-to-heat generation, and salt rejection for achieving efficient desalination output throughout the visible and broadband region. Specifically, it explored the self-floating and salt rejection nature of various state-of-the-art 2D Ti₃C₂ MXene structures. Among the different morphologies, Ti₃C₂ MXene in the form of a membrane is believed to be a promising morphology that effectively desalinates seawater into freshwater.

It can be concluded that structured semiconductors have key characteristics for many kinds of applications and purposes [16]. Probably, due to their high tunability and versatility, we will assist in the future with a fast development of these amazing materials that can be fundamental for many applications.

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