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Editorial

Titanium Dioxide Photocatalysis

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Received: 22 November 2018; Accepted: 28 November 2018; Published: 29 November 2018

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1. Definitions, Historical Aspects, and Perspectives

Dating from the seminal work of Fujishima et al. issued in 1971 [1], titanium dioxide (TiO_2) is at the center of intense research devoted to the development of efficient photocatalysts. Among the many candidates for photocatalytic applications, TiO_2 is almost the only material suitable for industrial use. This is because TiO_2 shows a good trade-off between efficient photoactivity, high stability, and low cost [1,2]. The principal applications deal with the use of TiO_2 as a photocatalyst for environmental remediation both in polluted air and waste water treatment [3] and as a material in solar cells [3,4].

The main drawback of TiO_2 photocatalysts still remains their inability for visible light absorption and photoconversion, and most recent research activities have been devoted to the improvement of the optical absorption properties of TiO_2 nanomaterials. Strategies including doping; self-doping; and the realization of composites with plasmonic materials, 2D materials, other semiconductors, and quantum dots are of particular interest [1,2]. Black-TiO_2 visible light active photocatalysts [5], antimicrobial materials [6], photoelectrochemical devices for water splitting, and CO_2 photoreduction [7] are among the hot topics. The rational design elements of interests for efficient TiO_2 catalysts are optical properties, nanocrystal shape, and organization in superstructures. On the other hand, precise crystal shape (and homogeneous size) and organization in superstructure from ultrathin films to hierarchical nanostructures have been demonstrated to be critical for obtaining photocatalyst with high efficiency and selectivity.

The present Special Issue of Catalysts is aimed at presenting the current state of the art in the use of TiO_2 as a photocatalyst, with a special emphasis on new TiO_2 nanomaterials (both powdered catalysts and photoelectrodes) for photocatalytic water splitting, CO_2 reduction, and environmental remediation. In the present Special Issue, we have invited contributions from leading groups in the field with the aim of giving a balanced view of the current state of the art in this discipline.

2. This Special Issue

Dr. Alberto Naldoni and I were honored to accept the kind invitation by Assistant Editor Shelly Liu to act as editors of this Special Issue. We tried to acquire possible authors able to contribute with high-level papers and reviews and we hope we succeeded in this task. This is particularly due to the wonderful and uncomplicated cooperation of Assistant Editor Shelly Liu and her competent team. Moreover, I owe particular thanks to all the authors who contributed their excellent papers to this Special Issue that is comprised of 11 articles, among them 3 reviews, covering key aspects of this topic together with a variety of innovative approaches.

Three comprehensive reviews cover most recent advances in key areas, such as electron transfer dynamics, brookite-based photocatalysts, and copper-modified titania.

The review by Kohtani et al. [8] summarizes the recent progress in the research on electron transfer in photoexcited TiO_2. In particular, the authors point out the key role of the precise control of the structural properties, that is, the maximization of surface shallow traps and minimization of density of deep traps as well as inner (bulk) traps in the development of highly active photocatalysts. The authors also highlight, as a promising strategy, the use of highly uniform TiO_2 nanocrystals with specific exposure of the reactive facets.

Monai et al. [9] provides a comprehensive review of the advancement in the applications of brookite as a photocatalyst. First, the most advanced synthetic methodologies to produce pure brookite and well-defined brookite-containing composites are presented, together with some guidelines for thorough characterization of the materials. Finally, structure/activity relations are summarized and a perspective on the future development of brookite nanostructured materials is given.

The review by Janczarek and Kowalska [10] focuses on the performance enhancement by copper species for oxidative reactions due to their importance in environmental remediation. Two key factors are identified and discussed: plasmonic properties of zero-valent copper and heterojunctions between semiconductors (titania and copper oxides) including novel systems of cascade heterojunctions. The role of particle morphology (faceted particles, core-shell structures) is also described. Finally, future trends of research on copper-modified titania are discussed.

Synthesis of novel nanostructures by different preparation routes is addressed in the papers by Nunes, Liu, and Zelny [11]. Microwave irradiation proved to be an effective synthesis route to produce TiO_2 nanorod sphere powders and arrays at low process temperatures using water as a solvent. The remarkable photocatalytic activity under UV and solar irradiation was ascribed to the presence of brookite but also depends on the nanorod, sphere, and aggregate sizes.

A fast anodizing method [12] was employed to synthesize large-scale (e.g., 300 $\times$ 360 mm) pinecone nanostructured TiO_2 films. The pinecone TiO_2 possesses strong solar absorption and exhibits high photocatalytic activities in photo-oxidizing organic pollutants in wastewater, producing hydrogen from water under natural sunlight. This work shows a promising future for the practical utilization of anodized TiO_2 films in renewable energy and clean environment applications.

A promising approach to fabricate nanostructured TiO_2 films on transparent substrates is self-ordering by the anodizing of thin metal films on fluorine-doped tin oxide (FTO) coupling pulsed direct current (DC) magnetron sputtering for the deposition of titanium thin films on conductive glass substrates and anodization and annealing for the TiO_2 nanotube array [13]. Zelny et al. reported a detailed investigation of mechanical and adhesion properties of Ti films sputtered at different temperatures, showing that a more active TiO_2 nanotube sample towards photoelectrochemical water splitting was obtained from a Ti substrate sputtered at 150 °C, showing the lowest crystallite size, best degree of self-organization, and enhanced charge transfer at the semiconductor/liquid interface.

The use of plasmonic nanomaterials in photocatalysis [14] has gained great attention due to their ability to enhance the reaction yield of semiconductor photocatalysts. In this contribution, Bao et al. coupled plasmonic Ag nanoparticles to high-surface-area TiO_2 nanofibers to achieve a very active photocatalyst toward dye molecule degradation, showing enhanced performance when using the plasmonic Ag/TiO_2 material.

Composites made by semiconductor and graphene [15] are particularly promising to enhance photogenerated charge separation due to the high electrical conductivity of graphene-based nanomaterials. In this article, a new route to couple graphene to TiO_2 was reported, showing the possibility of using ultrasonication to increase the processability and scalability of composite materials for enhanced photocurrent generation and photocatalytic dye degradation as well.

Bernareggi et al. [16] report a strategy based on flame spray pyrolysis to produce Cu- and Cu–Pt-modified TiO_2 for photocatalytic hydrogen production. An optimal loading of 0.05% Cu was found for the most active photocatalyst, which only contained Cu.

Nonmetal doping [17] is a very common approach to increase the light absorption and therefore the photocatalytic efficiency of TiO_2. In this report, S-doped TiO_2 photocatalysts were synthesized and tested for methylene blue photodegradation. An extensive FTIR investigation shined light on the structure–activity relationship of the prepared materials.

The article by Selli et al. [18] provides a new approach for the computational modeling of large titanium dioxide nanoparticles with diameters from 1.5 nm (~300 atoms) to 4.4 nm (~4000 atoms), usually too demanding for theoretical calculation. The authors investigated photoexcitation and photoemission processes involving electron/hole pair formation, separation, trapping, and recombination and provided a description of the titania/water multilayer interface—a relevant case study for photocatalytic systems.

In conclusion, the special issue "Titanium Dioxide Photocatalysis" should be of great interest for all of those involved in the various aspects of this topic, which are discussed in the contributions and review articles. They introduce new synthetic procedures, modeling of structures and reactivity, novel nanostructures, and plasmonic composites, thereby meeting the state of the art of both scientific and technical standards.

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