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Editorial

Towards Green, Enhanced Photocatalysts for Hydrogen Evolution

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The constant growth of energy demand joined with the adverse effects on the global environment induced by use of fossil fuels is increasingly requiring new routes to obtain clean and renewable energy sources. Hydrogen photocatalytic production by water splitting or aqueous-phase reforming of different organics has been under deep investigation for some years; H_2 gas is the most desirable energy vector because the only product by combustion is water. H_2 could be obtained at the large scale in the near future by exploiting inexhaustible, green sources such as sunlight, wastewater and biomass derivatives, if efficient, recyclable and safe photocatalysts will be designed.

Besides a review article, this Special Issue gathers research on the preparation, characterization and application of new organic/inorganic composites endowed with photo(electro)-catalytic properties. These materials were tested under either UV–visible or, even more conveniently, under visible light for H_2 evolution in "sacrificial water splitting" or "photoreforming" systems.

A new 3D porous carbon nitride catalyst has been proposed by Qiu et al. [1]. The material was synthesized by a simple bottom-up procedure entailing self-assembly of a melamine–cyanuric acid complex followed by ethanol and glycerol intercalation prior to calcination. This route has the merit to yield a 3D hierarchical pancake-like highly porous carbon nitride with enhanced light-harvesting capacity, expanded band gap, prolonged charge carriers' lifetimes, and higher surface area and reduction ability towards hydrogen ions to produce gas-phase H_2, compared to the bulk material. Under visible-light radiation and platinum as a co-catalyst, the hydrogen evolution rate (HER) from triethanolamine aqueous solution was 430 μmol g_{cat}^{-1} h^{-1}, 9-fold larger than that afforded by non-porous carbon nitride. The semiconductor showed photochemical stability. Indeed, it was successfully reused for three additional photoreactions. The behavior of the novel catalyst was studied in water containing a fine chemical, as a proof-of-concept sacrificial agent. Three other research studies focused on H_2 evolution from water in the presence of more sustainable electron donors, such as saccharides and alcohols [2–4], testing new catalysts as well.

Carbon nitride–perovskite composites, which presently denote a cutting-edge research field, were investigated as new photoactive micro-sized materials for H_2 evolution from glucose aqueous solution as a representative sacrificial biomass [2]. In particular, the synergism between the newer lead-free perovskite and carbon nitride, due to improved charge carrier separation derived from the positive band-alignment between the two semiconductors, has been exploited to set up a sacrificial water splitting system working under simulated solar light. The H_2 production was optimized by a design of experiments, achieving an HER higher than 900 μmol g_{cat}^{-1} h^{-1}, 12-fold larger compared to pure carbon nitride. The best-performing composite also provided H_2 with no metal co-catalyst, and in the presence of untreated starch, selected as an abundant and low-cost biopolymer, and therefore exploiting the sacrificial role of a raw polysaccharide. Despite the lower surface area, the perovskite–carbon nitride composite results were attractive compared to nanometric P25 TiO_2, relative to H_2 evolution.

Citation: Profumo, A.; Speltini, A. Towards Green, Enhanced Photocatalysts for Hydrogen Evolution. *Catalysts* **2021**, *11*, 93. https://doi.org/10.3390/catal11010093

Received: 8 January 2021
Accepted: 8 January 2021
Published: 12 January 2021

A representative biomass-derived substrate such as ethanol has been selected in the research of Luo et al. [3] to demonstrate the feasibility of a more sustainable method of obtaining H_2. Indeed, the contemporary production of bioethanol has reached several tens of million tons per year, and the possibility of ethanol photoreforming under mild conditions is of great relevance. This paper by Luo shows that coupling selective decoration with Au nanoparticles of TiO_2 nanorods and the TiO_2/Cu_2O p–n junction produces H_2 along with acetaldehyde. The latter is stoichiometrically formed because the C–C cleavage of ethanol does not occur, resulting in no release of greenhouse gases such as carbon dioxide. Under simulated solar light, the new photocatalytic system $Au@TiO_2/Cu_2O$ affords an HER higher than 8500 μmol $g_{cat}{}^{-1}$ h^{-1} over the composite $Au@Cu_2O/TiO_2$ and $Au@TiO_2$, and it maintains unchanged performance for at least five consecutive catalytic runs.

In the report by Adamopolous and co-workers [4], a nano-sized TiO_2/WO_3 bilayer catalyst was employed as a photoanode in a photoelectrochemical cell to produce H_2 from aqueous ethanol solution. The system proposed, which involved photoelectrocatalytic alcohol reforming, takes advantage of the high oxidative power and visible light absorption of WO_3, used in the photoanode, stabilization of charge carriers by electron-transfer from TiO_2 to WO_3, and passivation of tungstate surface states, which reduces the number of charge recombination sites involved by the titania layer. The latter constituent also scatters back to the bottom WO_3 layer part of the incident light resulting in a higher photocurrent production, proportional to the applied voltage, thus in greater H_2 formation at the cathode of the cell.

This Special Issue also includes a review article focused on the application of 2D materials and composites as potential photocatalysts for water splitting [5]. With more than 200 references covering the last two decades, but with particular attention to the papers published in recent years, after providing the reader with some introductory sections summarizing the fundamentals of water splitting photocatalysis, the application of various materials is presented and discussed through comprehensive tables reporting key information about each photocatalytic system (e.g., catalyst band gap, light source, type and amount of co-catalyst, sacrificial agent used, and HER). The paper covers selected studies on graphitic carbon nitride and graphene-based photocatalysts, metal phosphides, metal organic frameworks and derivatives, together with those on the more recent phosphorene. The review emphasizes the progress in modern nanomaterial applications, for instance by metal nanoparticles doping, surface functionalization, synthesis-controlled morphology, which are essential to achieve the most desired properties, i.e., low charge recombination, high light harvesting capability, good electron conductivity, fast kinetics, and large surface area. From the survey by Saleem and co-authors, it emerged that the use of 2D materials, their combinations and derivatives, are now at the basis of further advancements in photocatalytic water splitting.

We take the chance to thank the authors and their co-authors for the contributed publications to this Special Issue.

Funding: This research received no external funding.

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

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