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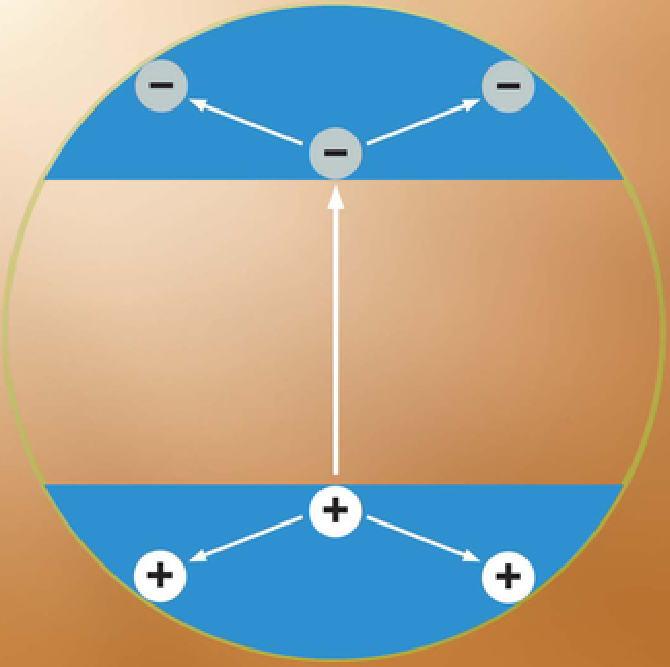
Edited by
Xinchen Wang, Masakazu Anpo, and Xianzhi Fu

UV-Visible Photocatalysis for Clean Energy Production and Pollution Remediation

Materials, Reaction Mechanisms, and Applications

With a Foreword by Professor Detlef Bahnemann



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Materials, Reaction Mechanisms, and Applications

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Contents

Part III Photocatalytic Reduction of CO_2 and Fixation of N_2 *187*

UV-Visible Photocatalysis for Clean Energy Production and Pollution Remediation: Materials, Reaction Mechanisms, and Applications – A Preface

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First of all, I like to take this opportunity to congratulate the editors on this exceptional collection of feature and review articles assembled within their new book titled *UV-Visible Photocatalysis for Clean Energy Production and Pollution Remediation: Materials, Reaction Mechanisms, and Applications*, thus managing to bring together (almost) all major authorities in the field of photocatalysis worldwide at once. And I like to thank them for this opportunity to contribute a small preface for their excellent book.

The research field of photocatalysis has seen well over 40 years of active research now and currently appears to be in its heydays. Many industrial applications of this technology are already available on the market today such as air and water cleaning devices, self-cleaning surfaces, solar cells, and even solar fuel generators. However, unfortunately, several even of the most basic principles of photocatalysis are still far from being understood today. Nowadays, different experimental techniques are most certainly available to study some of the most important and crucial features of TiO_2 photocatalytic systems. Time-resolved analytical tools such as transient optical spectroscopy, for example, seem to be ideally suited to study the generation, trapping, and transfer of electrons and holes, that is, the “initiators” of all photocatalytic processes, in particular, when different detection methods such as transient optical spectroscopy and microwave conductivity measurements are combined. The respective data analysis is found to be very complex, and it has been shown that photoelectrochemical concepts involving band bending and particle–particle contacts need to be considered in depth [1].

While the generally accepted mechanistic picture uses a single photocatalyst particle excited by a single photon to explain the entire photocatalytic world, recent research results have created the need of more elaborate mechanisms involving, for example, three-dimensional self-assembled particle agglomerates acting as antenna and charge transfer systems for their comprehensive interpretation. It is through these ensemble and cooperative properties that even widely used effects such as photoinduced superhydrophilicity are currently being explained, even though considerable scientific controversies still exist today as to the (only) correct model [1].

One of the most important limitations for the application of photocatalytic techniques for water decomposition, carbon dioxide fixation, and ammonia synthesis from molecular nitrogen is that when employing pure water as the only reductant, all of these processes are usually found to be rather inefficient. This is generally related to the fact that the simultaneous reduction of H_2O, $CO_{2,}$ and N_2 with the oxidation of water yielding O_2 (or even H_2O_2) is a complex multistep reaction involving (at least!) four electrons. Using sacrificial molecules as electron donors can remarkably improve the production of the reduction products with the holes being scavenged by these molecules, thus reducing the charge carrier recombination significantly. Furthermore, as O_2 is not produced, the back reaction to produce water is suppressed, increasing the yield of reduction products and avoiding a subsequent gas separation stage. However, it should be noted here that even the yield of the H_2, CO (or, e.g. CH_3OH or CH_4), and NH_3 formation will eventually be reduced by competing reduction reactions with the products formed upon the oxidation of the sacrificial reagents [2].

Organic compounds such as alcohols, organic acids, and hydrocarbons can act as efficient hole scavengers (that is, as electron donors) for the photocatalytic fuel generation process. In particular, methanol is frequently used as sacrificial reagent. For practical applications, the utilization of methanol will only be environmentally sensible provided that it is derived from biomass or from toxic residues that must be disposed of. Adding methanol as electron donor to react irreversibly with the photogenerated holes can enhance the photocatalytic electron/hole separation efficiency, resulting in higher quantum yields. Since electron donors are consumed in the photocatalytic reaction, their continuous addition is required to sustain the photocatalytic fuel production. Two possible mechanisms are proposed for the photocatalytic oxidation of methanol: (i) the direct oxidation by photogenerated holes and (ii) the indirect oxidation *via* interfacially formed $^{\cdot}OH$ radicals that are products of trapping valence band holes by surface –OH groups or adsorbed water molecules. It is still a challenge to distinguish between the two mechanisms in practice due to the lack of suitable probe techniques [2].

While the choice of sacrificial electron donors for studies concerning the photocatalytic formation of, e.g. molecular H_2 appears to be rather large, the sacrificial photocatalytic oxidation of water is only reported for a rather limited variety of electron acceptors. By far the vast majority of the research groups working on this topic employs silver cations, Ag^+, as electron acceptors, resulting in the fact that the photocatalytic formation of molecular oxygen is accompanied by the deposition of metallic silver nanocontacts on the semiconductor's surface. Obviously, this will lead to irreversible optical changes of these systems due to the plasmonic absorption band of the silver nanoparticles in the visible spectral region. Moreover, noble metal nanoparticles are known for their catalytic activity, resulting most likely in changes in the chemical and photochemical properties of these systems. Furthermore, it has been suggested and also experimentally verified that the role of suitable sacrificial electron acceptors such as Ag^+ is highly underestimated [3]. In particular, their possible involvement in the actual water oxidation mechanism has so far not been discussed and accepted. We are convinced that it is most certainly highly indicated to study the role of such metal cations in photocatalytic water oxidation in detail. Their catalytic role has rather recently been proposed for the first time; however, it could be part of a much more general mechanism, thus opening up new design features for photocatalytic and photoelectrochemical energy-to-fuel conversion systems. I am convinced that this is even more true for photocatalytic systems that can be activated by visible or even NIR illumination.

Finally, I like to emphasize that photocatalytic processes are inherently one-electron transfer reactions. In particular, when nanocrystalline photocatalysts are employed under solar illumination, the time interval between the absorption of two photons by one (that is, the same) photocatalyst particle is in the order of milliseconds. Hence, two free radical intermediates, that is, one reduced as well as one oxidized product of the reactions induced by the first photon, need to wait together (!!) for at least this time period on the very small surface of the same nanoparticle before having a chance to somehow form more stable products by being reduced or oxidized, respectively, again. Despite being crucial chemical species, the formation and fate of these initial free radical products are rather rarely studied [4]. The same applies to the formation as well as to further reactions of the stable reaction intermediates: it is fair to state that hardly any current (or even former) study is able to account for a full qualitative or even quantitative analysis of all reaction products formed during the photocatalytic redox processes, as these studies (almost) all just focus on the "desired" products, i.e. H_2, CO, CH_4, or NH_3 (to name but a few). This is one of the main reasons for my initial statement regarding the still rather incomplete understanding of the basic principles of photocatalysis.

In summary, it is fair to say that the impressive collection of review and feature articles combined into this really nice book clearly shows the fascinating development within the research area of visible light-driven photocatalysis during the last decade [5]. I am convinced that we will see a similar progress in the future and already look forward to the next summarizing contribution by "our" editors.

Hannover and Saint-Petersburg, 31.08.2022

Detlef Bahnemann

Detlef Bahnemann

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