

# Systematic approaches to understand photocatalytic reactions for energy and environment

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Reducing carbon dioxide just with the energy of (sun)light to platform chemicals for the chemical industry (e.g. carbon monoxide, methane) is still a highly desirable process to enable a recycling of this greenhouse gas. Yet, despite more than 40 years of research, the achievable yields in photocatalytic carbon dioxide reduction have not increased significantly, thereby clearly failing to meet demands for industrial implementation. One significant hurdle is our limited understanding of the chemical processes on the molecular scale, in particular under reaction conditions relevant to a future application. This is to a large extent due to the vastly different, and in part badly described, reaction conditions applied in published works, making it practically impossible to compare the different studies.

Our approach is the design of a reactor and a research methodology to enable highly reproducible studies in photocatalytic carbon dioxide reduction. Using solely construction parts suitable for high vacuum applications, we have developed the so-called “high-purity gas-phase photoreactor” with gas chromatographic trace gas analysis, allowing to obtain reproducible results on the ppm level. It can also function as bridge between true single-crystal studies and possible reaction conditions in practical applications.

Using this device, fair comparisons of different photocatalysts suggested in literature has been possible. This revealed the well-known titanium dioxide as one of the best materials, despite its large bandgap. Reliable apparent quantum yields have been determined. Focusing our studies on titania, it has been possible to obtain a rather complete picture of the reaction progress on the molecular scale. The reaction from carbon dioxide to methane is likely not a linear sequence of reduction steps but involves also oxidative steps by a reaction with holes. Even if methane as one-carbon product is formed, intermediates involving a C-C bond are involved. The limiting step is the water oxidation reaction, which does not run to completion. Instead, oxygen-related species are stored on or in titania until the material is saturated and the reaction ceases. These findings indicate that completely other materials, possibly Z scheme systems with suitable cocatalysts, need to be developed that allow a less complex surface reaction pathway.

As an additional example, our systematic work in the transfer of active sites from classical catalysis to photocatalysis will be highlighted. Two examples are presented, in which structurally well-defined thermal catalysts are used in the corresponding photoreaction. We found that isolated vanadate sites on silica are capable to oxidize methanol to formaldehyde selectively, both induced by thermal energy or by light. In a similar manner, the same basic reaction mechanism of gold nanoparticles in both photo- and thermal catalysis is presented for the example of isopropanol oxidation.