

Jennifer Strunk

Saving the world with CO₂?!

A Bachelor student from my research group was once asked to describe what his research was focused on. Without much thinking about the question, he burst out: “I am conducting research on saving the world, of course!”. As a witness of this communication, I smiled because I very much liked the idea.

The plan sounds so simple: Use carbon dioxide and water and convert it to some industrially useful chemical. It does not even matter which product exactly is obtained, because anything will be of more value than CO₂. But please use only light to conduct the reaction – by using photocatalysts. If such a process can be conducted on the industrial scale, ideally with sunlight or energy-efficient LED light sources, it may indeed contribute to mitigating greenhouse gas emissions and to providing platform chemicals for sustainable production.

Still, it is often hard to believe that our research will ever save the world. Over and over again, different photocatalysts tested in our reactors displayed an activity that amounted to just a bit more than nothing. Even using the famous titanium dioxide P25 (Evonik Industries), usually an extremely active photocatalyst, the concentration of the main product methane reaches 80 ppm after 6 hours, accompanied by roughly 20 ppm of carbon monoxide and a few ppm of hydrogen. Not quite the amounts needed to evoke industrial interest. It became clear that a simple trial-and-error method would not be successful. So, we switched viewpoints by turning the question around: Why does the reaction work, but only so badly? And finally, we made progress.

First and foremost, thermodynamics are against us. Carbon dioxide and water are among the most stable molecules on earth, so pretty much every reaction of the two molecules will feature a positive Gibbs free energy (Figure 1, left). Classical catalysis is then not possible at all, because the catalyst cannot shift the equilibrium. This is also the reason why “photosynthesis” is a more precise term than photocatalysis, but it is almost always neglected in the scientific literature (as is done here). Photocatalysts can drive endergonic reactions, because oxidation and reduction reaction happen spatially separated, and the excited state of the photocatalyst must be taken into account. This is schematically depicted in Figure 1 (center). Considering each of the half reactions alone, they are

thermodynamically favorable, that is, they feature a negative ΔG , because an electron falls down to a lower energy level [1]. Despite carbon dioxide reduction to hydrocarbons becoming thermodynamically possible on photocatalysts, the reverse reaction, namely hydrocarbon oxidation, will always be the thermodynamically favored process, because it features an overall negative ΔG . Suppressing the reverse reaction is, thus, a key challenge, similar to research on photocatalytic water splitting.

Another similarity to water splitting is the highly challenging counter reaction. Although the product of the reduction reaction is the desired one in both cases, the real challenge is the stoichiometrically required oxygen evolution counter reaction [2]. In CO₂ reduction, surprisingly many papers (including early ones by my own group) are published that do not mention the oxidation reaction at all, although it is beyond doubt that some reaction must proceed which consumes the photogenerated holes. Our research with TiO₂ has shown that considerable amounts of the byproduct oxygen, or intermediates on the way to it, can be stored in TiO₂, for example by filling up oxygen vacancies (Figure 1, right). The capacity is large enough so that the CO₂ reduction reaction can run for more than 12 hours straight without producing any oxidation product, before the productivity of methane declines to zero [3]. This means that the catalytic cycle is not closed, but that the titania also acts as “sacrificial reagent” which scavenges oxidation equivalents. At the same time, the inherent trapping of oxygen means that it is not released into the gas phase, so it cannot reoxidize the formed hydrocarbons, a reaction which would already have significant effects on the product concentration as soon as the oxygen concentration exceeds 5 ppm [4]. A modification of titania with the well-known iridium oxide cocatalyst for oxygen evolution indeed produced a photocatalyst that evolved oxygen, and even performed overall splitting of gaseous water with stoichiometric H₂ and O₂ formation, but the resulting system did no longer reduce CO₂ [3]. This may either be due to the rapid reoxidation of the formed hydrocarbons by O₂, or by holes participating in the CO₂ reduction mechanism, as has been suggested by Shkrob et al. [5]. This is subject to current investigations.

Can we address the reaction as chemical engineers, then, and improve yields by an optimization of the reaction conditions? This question we had to answer with a clear “No”. The yield of methane was found to maximize at low CO₂ concentrations [4], and it even proceeded best with no water in the gas phase at all [6]. This may be rationalized by the preferential adsorption of water on the hydrophilic titania, and the formation of hole-trapping carbonates on the surface in presence of excessive amounts of CO₂. Increasing the light intensity had a moderate effect, because the increase in methane yield followed the expected square-root dependence. An interesting observa-

Prof. Dr. Jennifer Strunk
Research Department Heterogeneous Photocatalysis
Leibniz Institute for Catalysis
Albert-Einstein-Str. 29a, D-18059 Rostock
jennifer.strunk@catalysis.de
www.catalysis.de/en/research/heterogeneous-photocatalysis
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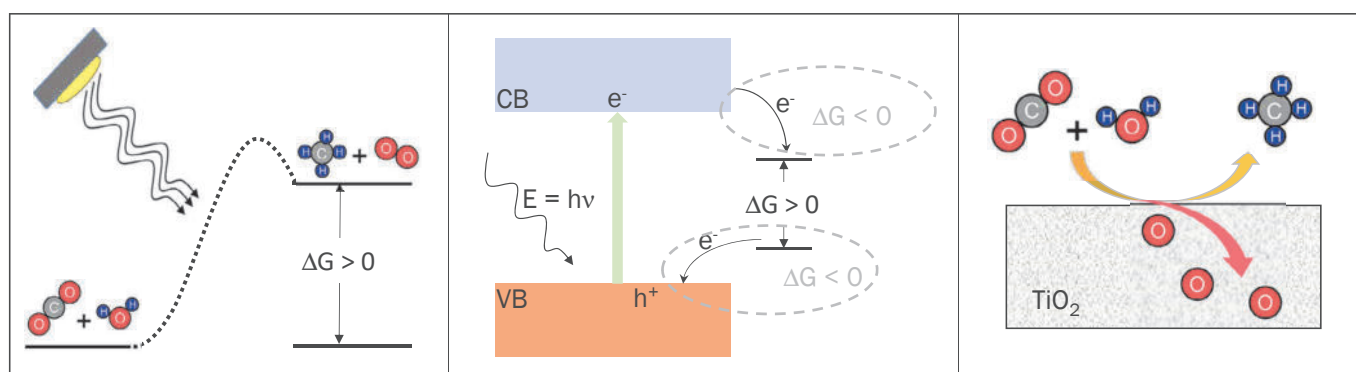


Fig. 1: Visualization of the key challenges in photocatalytic CO_2 reduction. Left: Overall endergonic nature of the process, which favors the reverse reaction. Center: Schematic endergonic reaction carried out with a photocatalyst, in which the reduction and oxidation reaction alone are thermodynamically favored; modified from Ref. [1]; Copyright Wiley VCH, 2021. Right: Schematic representation of the storage of oxygen species in TiO_2 .

tion was a positive effect of an increased reaction temperature. Raising the temperature from room temperature to 60°C , i.e. by roughly 30 degrees, led to an approximate doubling of the methane yield, indicating that the reaction mechanism included some classical catalytic steps that are expectedly accelerated by a temperature increase [6].

Lastly, we also wanted to know whether it is truly the mediocre catalytic properties of titania that limit the methane yields, or if the photophysical properties – light absorption and charge carrier lifetime – were maybe even worse. Determination of the apparent quantum yields revealed that those of overall water splitting with $\text{IrO}_x/\text{TiO}_2$ were already four times as high as those of CO_2 reduction with bare TiO_2 , and true photocatalytic (exergonic) reactions such as organic pollutants degradation featured even higher apparent quantum yields. Consequently, light absorption and charge carrier properties would allow higher yields, and indeed the catalytic properties are our main problem [7].

So, what is the way forward? Can we ever make a photocatalytic conversion of carbon dioxide industrially viable? Some say that electrocatalysis is instead the way to go. While I am not doubting that the achievable efficiencies and selectivities in electrocatalytic CO_2 reduction are higher nowadays, I am not willing to give up on a photocatalytic process. We operate the reaction entirely without a liquid phase, which is currently much closer to industrial bulk chemical production in gas-solid heterogeneously catalyzed reactions. Mass transport is much faster in such two-phase compared to three-phase systems. Omitting the liquid phase may also facilitate product separation, because we do not face dissolution phenomena in the electrolyte. In any case, I am convinced that we should not limit ourselves to either of the two options but put research effort into both of them.

This means, we have to deliver. Indeed, our research helped to discover potential avenues to advance photocatalytic CO_2 reduction, many of which we pursue in our current BMBF project *PRO-DIGY* (FKZ: 033RC024) with partners from Berlin, Oldenburg, and Karlsruhe. Firstly, we should choose a co-reactant that does not require to evolve oxygen as counter reaction. One example is the photocatalytic dry reforming of methane to generate synthesis gas ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$), whereby the methane may be accessed sustainably from biogas. Another interesting option is a combined light-driven and photothermal process, in which the

light also heats up the reactor, so that light energy (the electronically excited state) and thermal energy (to overcome activation barriers) are combined to increase the efficiencies. Lastly, photocatalysts other than TiO_2 need to be used, ideally in the form of Z scheme systems, that separate reduction and oxidation reaction on two different semiconductors which both absorb visible light.

Still, an industrial-scale photocatalytic CO_2 reduction process will likely not emerge in the near future, but we will need patience and perseverance. To cite another former member of my group, it may take “about twenty years and two months”. Considering that this quote originates from the year 2012, we may be almost halfway there. So, don’t give up but hang in there!

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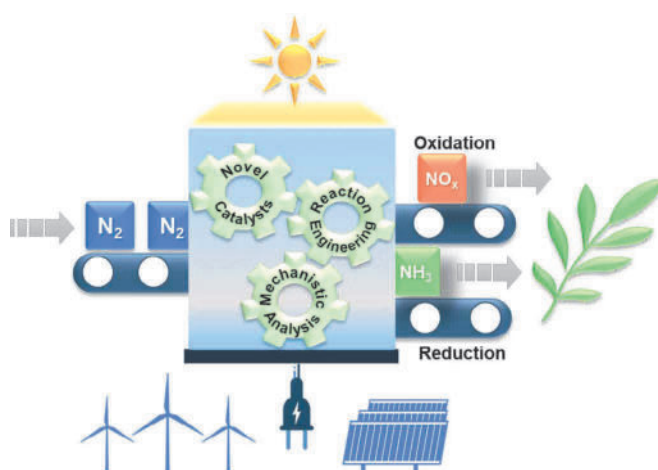
After school I decided to study Chemistry because I, too, wanted to save the world, namely by recycling plastic waste. However, during my advanced studies in Industrial Chemistry at Ruhr-University Bochum, synthesis gas chemistry, in particular methanol synthesis on zinc oxide-based catalyst, caught my attention. So, I performed research on this topic in both my diploma thesis in 2003 and 2004, and in my PhD thesis thereafter until 2008 under the supervision of Martin Muhler.

Getting the chance to work with famous Alexis T. Bell at UC Berkeley afterwards, I frankly would have accepted pretty much every research topic. So, it was a little bit pure luck that I started to work with single-site catalysts based on supported titanium and vanadium oxide species in selective methanol oxidation. Such materials, as I found out then, were also known as efficient photocatalysts. Still in Berkeley, I drafted a research proposal for the BMBF call “Technologies for sustainability and climate protection”, to set up the junior research group *PhotoKat* on photocatalytic CO₂ reduction back “home” at the Ruhr-University. It was successful, so in October 2010 I returned to Martin Muhler’s lab, with 1.1 Mio. Euros in tow. And now I did recycle waste – the ultimate waste molecule carbon dioxide. In 2014, I was hired as research group leader at the MPI for Chemical Energy Conversion in Mülheim, in cooperation with the Center for Nanointegration Duisburg-Essen, to set up a new collaborative research group on “Nanobased Heterogeneous Catalysts” (*NanoCat*). Photocatalytic carbon dioxide reduction accompanied me there.

Since January 2017 I am Head of the research department Heterogeneous Photocatalysis at LIKAT, and associate professor at the University of Rostock. Ever since 2010, the expertise in the group continuously expanded, first to semiconductor physics, then to photoelectrochemistry, and in Rostock to organometallic synthesis, molecular catalysis, and transient optical spectroscopy. In addition, I brought the very practical, optimistic approach to problems common in the Ruhr region (“Was nicht passt, wird passend gemacht!” ~ what does not fit is made to fit) with me – so here we are to save the world after all!

News

New DFG Priority Programme (SPP 2370) „Interlinking catalysts, mechanisms and reactor concepts for the conversion of dinitrogen by electrocatalytic, photocatalytic and photoelectrocatalytic methods (“Nitroconversion”)



In view of the increasing CO₂ concentration in the atmosphere, ongoing energy transition, and the development of alternative concepts for the activation of small molecules, new approaches for artificial N₂ conversion are in demand. This includes (photo)electrocatalysis or photocatalysis, which can be operated decentralized under less harsh conditions powered by renewable electricity or light.

The Priority Programme 2370 “Nitroconversion” focuses on the development of heterogeneous **electrocatalytic, photocatalytic & photoelectrochemical N₂ conversion reactions** for delocalized and **sustainable N₂ conversion pathways** with, as a long term objective, an overall energy consumption and space-time yield comparable to the Haber-Bosch process. This will be achieved by getting insights into structure/activity relationships for catalysts including experimental and theoretical design strategies, developing novel reactor and electrode concepts to overcome N₂ mass transfer limitations, and by using novel analytical techniques to get insights into underlying mechanisms to be able to design catalysts rationally, and to develop new reaction pathways. It is explicitly not limited to N₂ conversion to ammonia but will also include research on oxidative conversions.

Call for proposals ends on October 29th, 2021.

More information available at <https://www.spp2370.uni-bayreuth.de/en/index.html>

Contact: **Prof. Dr. Roland Marschall**
(roland.marschall@uni-bayreuth.de)