Nature Reviews Materials | Published online 4 Jan 2017; doi:10.1038/natrevmats.2016.102

Image courtesy of C. Hohmann, Nanosystems Initiative Munich, Germany.

ARTIFICIAL PHOTOSYNTHESIS

Lights off, gas on!

Beating nature at its own game is never easy. This is particularly true in energy harvesting, where we are still a long way from matching the mastery of nature through photosynthesis. Now, three research teams led by Bettina V. Lotsch, Gunnar Jeschke and Erwin Reisner report the ability to emulate two key components of natural photosynthesis — efficient charge separation through the formation of long-lived trapped radicals, and the decoupling of light-dependent and light-independent processes — to produce hydrogen photocatalytically long after the lights are switched off.

In natural photosynthesis, photoexcitation and effective charge separation facilitate spatially compartmentalized redox reactions in the electron-transport chain, generating NADPH and ATP. These molecules then drive a light-independent cycle to convert carbon dioxide to carbohydrates, oxygen and, in some species, hydrogen. Attempts to mimic these processes typically rely on complex electron relays to prevent electron–hole recombination and involve challenging synthesis methods. Consequently, the 'artificial leaf' is yet to find its way to market.

As the researchers report in *Angewandte Chemie International Edition*, these problems are overcome using cyanamide-functionalized heptazine-based carbon nitride. In previous work, they found that adding a cyanamide functionality to the heptazine units greatly improved the quantum efficiency for photocatalytic hydrogen evolution. Their latest study was conceived to further understand these observations. "Initially, our goal was to study the formation and role of 'functional defects', which may act as catalytically active sites in carbon nitride photocatalysts," explains Lotsch. However, when they irradiated their polymer, they observed entirely unexpected behaviour: in the presence of a suitable electron donor, it underwent a colour change from yellow to a long-lived blue state, indicating the formation of a trapped radical species. "We had not foreseen that our synthetic approach would lead to carbon nitrides that can store a large number of reducing equivalents for long periods of time," says Lotsch.

The blue radical was strongly reducing and could be generated reversibly. The combination of these attributes makes this system well suited for 'dark' photocatalysis. Specifically, the long-lived and highly reducing radical species can be made to give up its electrons to produce hydrogen on demand upon addition of a hydrogen evolution reaction catalyst (here, platinum). The researchers demonstrated that dark photocatalysis could be triggered up to 12 hours after the cessation of light irradiation. "The unusual properties of this carbon nitride material allows us to sidestep the intermittency of solar irradiation, as we can 'store' the energy of the sunlight and release it on demand in the dark phase to produce solar fuels," notes Lotsch.

Despite the promise of this system for the production of solar fuels (such as hydrogen and methane), several challenges exist, as Lotsch explains: "To take our findings from a lab curiosity to the industrial scale, we need to find conditions that couple our system to scalable and practically useful photo-oxidation processes, including, of course, water oxidation." This will involve gaining a deeper understanding and thereby control of structure–property–activity relationships of the polymer in its native and photoreduced forms. It is probably fair to say that solar fuel production can now enjoy a 'dark' future.

Adam Brotchie

> "We had not foreseen that our synthetic approach would lead to carbon nitrides that can store a large number of reducing equivalents for long periods of time"

ORIGINAL ARTICLE Lau, V. W.-h. *et al.* Dark photocatalysis: storage of solar energy in carbon nitride for time-delayed hydrogen generation. *Angew. Chem. Int. Ed.* http://dx.doi.org/10.1002/anie.201608553 (2016)