

An artificial leaf for splitting water

Chemical model systems can be used to study the processes of plant photosynthesis with the goal of tapping sunlight as a source for covering the energy needs of the future. Researchers from Ulm have now developed an artificial leaf based on a manganese-vanadium oxide catalyst which can effectively carry out the critical photocatalytic reaction of splitting water molecules into hydrogen ions and molecular oxygen.



Leaves are natural solar panels. © EDJ

All higher life on earth is based on the ability of green plants, algae and some bacteria to produce energy-rich molecules through photosynthesis. Photosynthesis is the process by which these organisms use the energy from sunlight to synthesise organic molecules from carbon dioxide and water. The process consists of two steps. Only the first step, the splitting of water into molecular oxygen and hydrogen, requires light. Oxygen is released into the atmosphere, effectively as a waste product, while in a second step, hydrogen (more specifically its equivalent of protons and bound electrons) is transferred to CO_2 and the absorbed solar energy is stored as chemical energy in carbohydrates.

The photosynthesis apparatus can be considered a natural solar panel, which, however, is

rather inefficient with the energy provided by the sunlight. Plants utilise only a tiny fraction – about 0.3 percent of the incident sunlight – for the production of chemical energy. The photosynthetic efficiency (i.e. energy conversion efficiency) is about five percent. Modern solar panels that convert light directly into electricity have an energy conversion efficiency of up to twenty percent. However, plants are able to store energy, something that solar panels are unable to do.

More than a hundred years ago, the Italian chemist Giacomo Ciamician predicted that humans would, when the supply of coal runs out, be able to copy the photochemical processes of plants and use the inexhaustible energy of the sun “without smoke and chimneys”. Since Ciamician made his prediction there has been an ever more urgent call for clean and sustainable energy sources. As the demand for energy continues to grow, research into artificial photosynthesis is being carried out in an increasing number of laboratories around the world.

Improving nature

In plant cells, photosynthesis takes place in special organelles, the chloroplasts, which are abundant in the cells of green leaves. In the chloroplasts, which are sometimes referred to as the solar power generators of plants, water molecules are oxidised into molecular oxygen by sunlight in a highly complex enzyme system with a large number of individual components (photosystem II). In several laboratories in the USA, Great Britain and Germany, researchers have recently succeeded in reproducing this reaction in model systems. Initially, the catalysts used consisted of expensive materials such as platinum and iridium, only had a limited lifespan and were damaged during the oxidation of water.

Now, Carsten Streb and Timo Jacob, two professors at Ulm University, and their teams of researchers have made huge progress in the development of an artificial leaf. The catalyst they use consists of a molecular scaffold made of relatively cheap manganese-vanadium oxide and they also use the natural photosystem II reaction centre as model in which four manganese atoms are linked to four oxygen atoms and one calcium atom.

The researchers used specific polymeric metal-oxygen complexes, known as polyoxometalates, to stabilise the reaction centre of their artificial leaf. These complexes are less sensitive to oxygen than the components of the natural reaction centre. The model was therefore better than the natural reaction centre, which tends to be destroyed during oxidation in living leaves



G. Ciamician

[P. Sestini, 1916]

Giacomo Luigi Ciamician, a pioneer of modern photochemistry and in particular of artificial photosynthesis (born: 1857 (Triest), died: 1922 (Bologna)) © Scienza in rete, Italia



Professor Dr. Carsten Streb, Institute of Inorganic Chemistry I at the University of Ulm © KIZ Ulm / Eberhardt

and has to undergo constant repair.

Furthermore, the oxygen production measurements made by Timo Jacob and his team at the Institute of Electrochemistry and the electrochemical characterisations demonstrated that their artificial leaf is as efficient as its natural counterpart.

Turning a vision into reality

Initially, the manganese-vanadium oxide complex was powered with electricity rather than with sunlight. The use of a light-absorbing antenna molecule, which, like the chlorophyll molecules in green leaves, captures photons and passes them on to the reaction centre, makes the model system more like the oxygen-forming complex of the photosystem II of green plants. The researchers are thus able to investigate experimentally the decisive step in the photosynthetic process, i.e. the capture of sunlight energy and its transfer to a catalyst that splits water into oxygen and hydrogen, gain new insights and optimise the system in order to obtain a higher energy conversion efficiency than plants.

It will still take some time before the model systems have reached a technically mature state so that they can be placed on the market. The vision of using artificial leaves for the clean and sustainable production and storage of energy based on photosynthesis is now more pertinent than ever before. In his 1912 article entitled "The Photochemistry of the Future" (Science 36, 385 – 394, 1912), Giacomo Ciamician was already sure that this would, at some stage, become reality: "If our black and nervous civilisation, based on coal, shall be followed by a quieter civilisation based on the utilisation of solar energy, that will not be harmful to progress and to human happiness."



Professor Dr. Timo Jacob, Institute of Electrochemistry at the University of Ulm. © KIZ Ulm / Eberhardt

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