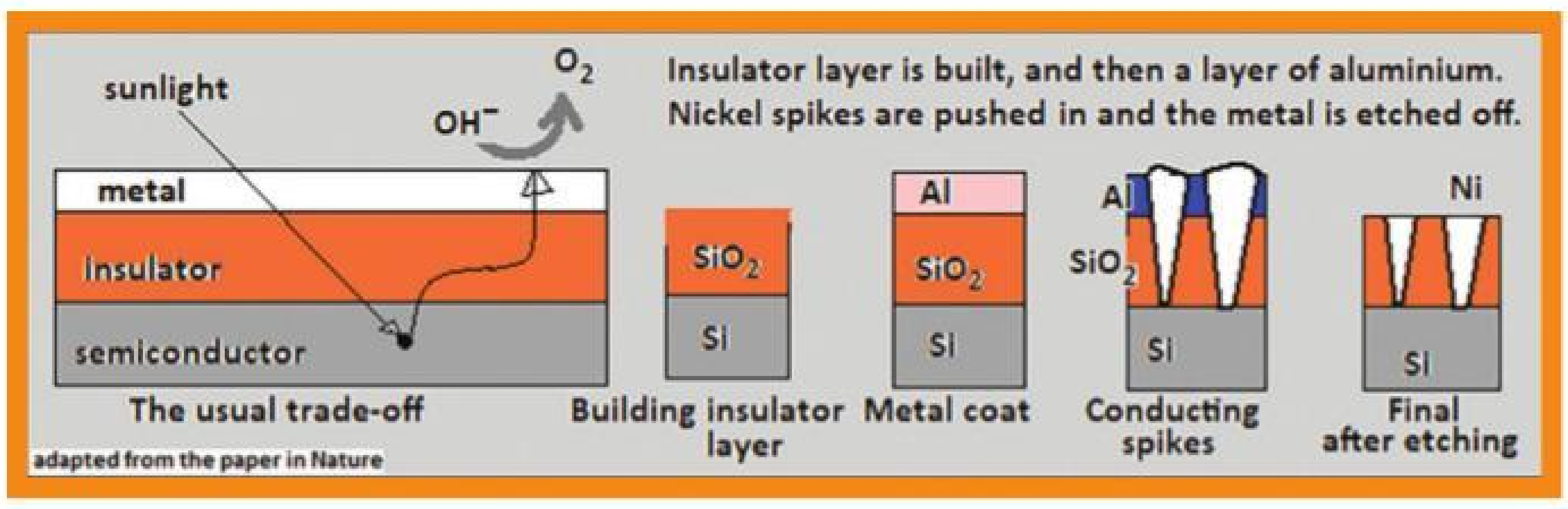
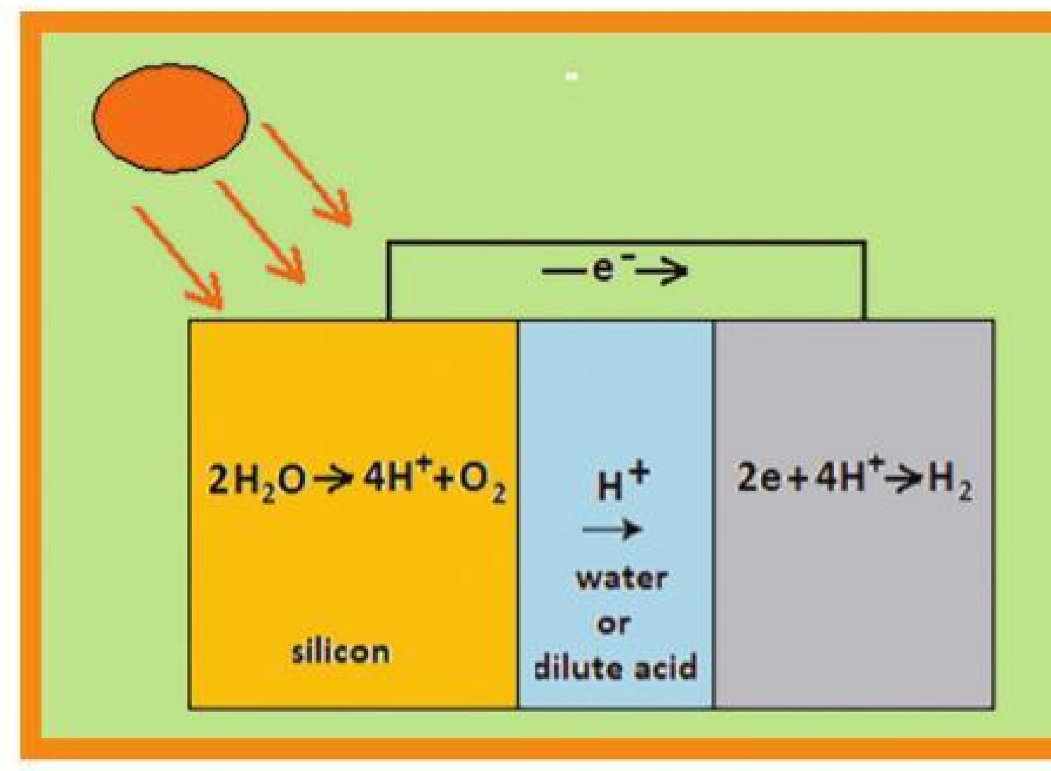
Doing better than Nature?

A large scale, low-cost method to generate hydrogen has been developed





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Sunlight is finally the only source of all the energy that the Earth can use. There is heat stored deep below the surface of the Earth, which did not come from the Sun, but we have no way to tap this resource. What we need, in these times of energy and environmental crises, is a way to put sunlight directly to use.

Solar cells and wind energy are the answers, of course. But they are intermittent, and it is not easy to store electricity. Nature's method is to store solar energy as carbon. Could technology do it better? Soonil Lee, Li Ji, Alex C De Palma, and Edward T Yu, from the University of Texas at Austin and Fudan University, Shanghai, write in the journal, *Nature Communications*, of improvements in devices to use sunlight to extract hydrogen fuel from water. Hydrogen can be used directly as fuel, and it does not produce carbon dioxide on combustion.

Nature's method of storing sunlight in carbon is by photosynthesis. Green plants, by a miracle of evolution, use sunlight to separate the components of carbon dioxide, as carbon compounds and pure oxygen. The carbon remains in wood and plant material, or buried underground as coal and mineral oil. Humans and animals need plants and vegetation as food, as we are carbon-based, but we cannot afford to continue using fossil fuels.

Biofuels are considered "carbon neutral", because they are made from "recent" plant matter. The carbon released when these fuels are burnt is hence the same as was "recently" absorbed — unlike the case of fossil fuels, which were formed centuries ago. In the same way, methods have been sought to replicate photosynthesis in human-made fuel cells, creating fuel materials from carbon dioxide, so that the fuels could also be considered carbon neutral. While these are attractive options, cultivation for biofuels would need large tracts of land, and artificial photosynthesis is still at the stage of a concept.

The serious new contender is hydrogen gas. Although mineral oil fuels, like petrol, contain both carbon and hydrogen, the heat produced by burning a kilogram of hydrogen is three times the heat from a kg of petrol. Once compressed for use in the fuel tank of a hydrogen-powered vehicle, hydrogen would hence be more efficient, apart from giving off only water vapour as the product of combustion. The only question is, where is the hydrogen to come from? Coal and petroleum are there underground, but hydrogen has to be produced!

The usual methods of producing hydrogen are through electrolysis or when steam is passed over burning coal. The first method needs electricity to work and the second method is itself a source of carbon dioxide emission. It is true that there is electricity from solar cells, but there are other uses for electricity. Should we use it for electrolysis, which is somewhat wasteful, for producing hydrogen? A method of generating hydrogen directly with the help of sunlight is hence what looks like a good solution.

The means that we have to put photons of light to work, for the solar cell, or to create hydrogen, is with the help of the silicon crystal. Metals, like copper, gold and silver, are good conductors of electricity because of their atomic structure as the atoms have fewer electrons in their outermost shell. With most electrons in the inner layers almost blocking the attraction of the nucleus, the outer electrons are loosely bound. In the form of crystals, some of the outer electrons float free, and help conduct electricity.

Silicon is an element with a halfway atomic structure, the outer shell has four electrons, which is half-way to the "full" state of eight electrons. The outer shell electrons are somewhat loosely bound, and silicon is called a semiconductor. What this implies is that there are no free electrons, like in metals, but a photon of light can nudge an electron into the free state. This is the property that makes silicon the material used in solar cells, where the electrons released from silicon atoms are harnessed — to generate electricity from light.

In the hydrogen producing device, called a photoelectrochemical cell, or a PEC cell, a pair of silicon plates is immersed in water, and water acts as a conductor. In the same way as in the solar cell, the silicon when exposed to light, gives off an electron, and becomes positively charged. While the electron travels to the other plate, the positive charge attracts negative oxygen ions and repels positive hydrogen ions. The hydrogen ions drift to the other plate, where they meet electrons and are released as hydrogen gas. The device is hence a neat way of generating hydrogen, except for the trouble that brews at the first end, where the oxygen must be dealt with.

Corrosion

At this end, the release of oxygen causes severe corrosion and degradation of the silicon crystal. We have mentioned earlier that metals are elements whose atoms have fewer outer shell electrons. As the "complete shell" is the stable configuration, metals form compounds where the few outer shell electrons are given up. And they are given up to non-metals, like oxygen or sulphur, the atoms of whose outer shells have more electrons and can gain a few more, to become "complete". The silicon plate where oxygen is released hence reacts with oxygen and is rapidly corroded.

The strategy has to save the silicon plate to protect the surface, and the method used is with the metal-insulator-semiconductor, or MIS structure. A thick insulating layer would give good protection but would also impede the splitting of the water molecules and release of hydrogen. "Typically, there is a trade-off between efficiency and stability when optimising insulator thickness," says the paper in *Nature Communications*, as the context of the workaround that the authors propose.

One material that is used as the insulator is a layer of silicon dioxide, which oxygen cannot corrode, and would protect the silicon surface. A layer that would allow the PEC cell to work, however, needs to be just nanometres thin, which is not enough, as a protection. What the authors of the paper have devised is to provide conduction pathways through a thick layer of silicon dioxide, to allow electrical conduction, but still protect the surface.

The paper says one solution followed was to use a thick insulator layer, but create areas where the insulation broke down, to allow conduction. The process did work, but was complex, the paper says. What the team has done instead, is to build a thick insulating layer over the silicon slab and then overlay it with a thin film of aluminium. Annealing the structure, at 550°C for 24 hours, leads to spikes of aluminium going through the insulator, to create conducting channels. The aluminium is now etched away, and the spikes filled with nickel, which is conducting, as well as a catalyst that promotes the splitting of water.

The procedure is low-cost and can be employed on a large scale. And the results are generation of hydrogen at low intensity light exposure, high capacity and excellent stability, the paper says. With hydrogen-driven cars, buses and trucks, even trains being developed, an efficient and sustainable source of hydrogen would hasten their wider acceptance.

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MARKED BY PERSISTENCE

Here's how pesticides behave when they are added to soil and plants

TAPAN KUMAR MAITRA

Pesticides are introduced into the soil for destroying soil-dwelling pests, nematodes, and the pathogens of bacterial and fungal diseases. Pesticides also get into the soil after treatment of the green organs of plants — they are washed off by atmospheric precipitation and carried off by the wind. They may get into the soil in the form of their residues contained in leaves, roots, etc.

Depending on the conditions, poisonous chemicals may remain in the soil unchanged and retain their toxicity for a more or less prolonged period. The property of pesticides to withstand the decomposing action of physical, chemical, and biological (biochemical and microbiological) processes characterises their persistence.

The persistence of various compounds when studied in the same conditions (or of the same compound, but in different soils), is characterised by the parameter T0.5 (the half-life). The latter denotes the time during which the content of the relevant pesticide in the soil is halved in comparison with the original amount. To evaluate this parameter, soil samples are taken and analysed from a dynamic viewpoint in logarithmically multiple intervals.

By determining in the same intervals, the dynamics of the content of pesticide residues in cultivated plants, one can evaluate the parameter T0.5 and the harvest time. It must be noted that a pesticide getting into the soil may decompose into a whole series of metabolites whose persistence, phytotoxicity, features of behaviour and transformation must be studied just as thoroughly as those of the original substances.

The persistence of pesticides in the soil depends on their chemical and physical properties, the dose, formulation (powder, liquid, etc), the type of soil, its moisture content, temperature, and physical properties, composition of the soil microflora, specific composition of the growing plants, and features of soil tilling.

With respect to the rate of their decomposition in the soil, pesticides can be divided into the following groups,

- Organochlorine insecticides — a decomposition period over 18 months.
- Derivatives of triazine, urea, and picloram — about 18 months.
- Derivatives of benzoic acid and amides of various acids — about 12 months.
- Phenoxyalkylcarboxylic acids, nitriles, derivatives of toluidine — six months.
- Derivatives of carbamic acid — up to three months.
- Organophosphorus substances — less than three months.

It must be noted that in many cases the type of soil and especially its microflora are the main factors determining the duration of decomposition of most pesticides. Even very persistent substances under the influence of certain microorganisms may rapidly decompose with complete destruction of the molecules.

Pesticides incorporated into the soil in the form of granules persist in it for a longer time than powders or liquid substances. As a rule, they are more persistent in soils with a high content of organic matter and a silt fraction.

Movement of pesticides in the soil

Pesticides and their metabolites are found in the soil in a labile state with all three of its phases and can therefore migrate along the soil profile in horizontal and vertical directions. Poisonous chemicals move in the soil owing to molecular diffusion with the capillary moisture, the descending flow of gravitational water, root system of plants, and as a result of displacements when the soil is being tilled.

Pesticides travel over larger distances with the stream of water appearing after rainfall or irrigation. The rate and depth of vertical movement depend on the solubility and dose of the pesticide, the features of its adsorption and desorption, its volatility (vapour pressure), and also on the intensity of evaporation of the soil moisture. During prolonged rainfall or irrigation, poorly adsorbed hydrophilic pesticides move downward along the soil profile together with the water.

With the advent of dry weather, with increased evaporation, the pesticide solution rises along the capillaries to the surface of the soil. When evaporation and washing out are in equilibrium, pesticides well soluble in water travel downward, while poorly soluble ones are retained in the upper layer of the soil. If the concentration of a poisonous chemical in the soil solution diminishes owing to decomposition, washing out, or evaporation, part of the pesticide adsorbed by the colloids in the soil may again enter the soil solution owing to desorption.

Investigations have shown that hexachlorocyclohexane migrates insignificantly in the soil. The pesticide is mainly distributed in the soil as a result of its mechanical cultivation. Carbaryl in chernozem, grey forest, and soddy-podzolic soil penetrated to a depth of 50-70 centimetres, which is associated with its very slight adsorption by the soil colloids. In sandy loam soil, HCH migrates better than heptachlor.

Among herbicides, derivatives of the aromatic carboxylic acids have the highest mobility in soil, and toluidine derivatives, the lowest. Dipyridyl herbicides, which are greatly adsorbed by the soil, do not virtually migrate along its profile. Even in sand, diquat moves not deeper than eight cm. The derivatives of phenylacetic and benzoic acids, weakly adsorbed by the soil and well soluble in water, can migrate to a depth of up to three metres. The derivatives of urea also migrate poorly in the soil. Triazine herbicides (simazine, atrazine, prometryne, propazine) owing to their slight solubility in water and great adsorption by the soil migrate in the latter to a limited extent.

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PLUS POINTS

Brain waves to speech

In a worldwide first, United States researchers have developed a neuroprosthetic device that successfully translated the brain waves of a paralysed man into complete sentences, according to a scientific paper published recently.

"This is an important technological milestone for a person who cannot communicate naturally," said David Moses, a postdoctoral engineer at the University of California San Francisco, and one of the lead authors of the study in the *New England Journal of Medicine*. "It demonstrates the potential for this approach to give a voice to people with severe paralysis and speech loss."

The breakthrough involved a 36-year-old man who had a stroke when he was 20 that left him with anarthria — the inability to speak intelligibly, though his cognitive function had remained intact.

Every year, thousands of people lose the ability to talk due to strokes, accidents or disease. Past research in this area has focused on reading brain waves via electrodes to develop mobility prosthetics that allow users to spell out letters. The new approach was intended to enable more rapid and organic communication.

UCSF researchers had previously placed electrode arrays on patients with normal speech who were undergoing brain surgery, to decode the signals that control the vocal tract in order to express vowels and consonants, and were able to analyse the signals into words. But the concept had not been tried out on a paralysed patient to prove it could offer clinical benefit.

The team decided to launch a new study called Brain-Computer Interface Restoration of Arm and Voice, and the first participant asked to be referred to as Bravo1. Since suffering a devastating brainstem stroke, Bravo1 has had extremely limited head, neck, and limb movements, and communicates by using a pointer attached to a baseball cap to poke letters on a screen.

The researchers worked with Bravo1 to develop a 50-word vocabulary with words essential to his daily life like "water," "family," and "good," then surgically implanted a high-density electrode over his speech motor cortex. Over the next several months, the team recorded his neural activity as he attempted to say the 50 words and used Artificial Intelligence to distinguish subtle patterns in the data and tie them to words.

To test it had worked, they presented him with sentences constructed from the vocabulary set, and recorded the results on a screen. They then prompted him with questions like "How are you today?" and "Would you like some water?" which he was able to answer with responses like, "I am very good," and "No, I am not thirsty."

The system decoded up to 18 words per minute with a median accuracy of 75 per cent. An "auto-correct" function, similar to that used in phones, contributed to its success.

"To our knowledge, this is the first successful demonstration of direct decoding of full words from the brain activity of someone who is paralysed and cannot speak," said Bravo1's neurosurgeon Edward Chang, a co-author. An accompanying editorial in the journal hailed the development as "a feat of neuro-engineering," and suggested advancements in technology such as smaller surface electrodes might help improve accuracy even further.

— The straits times/agencies