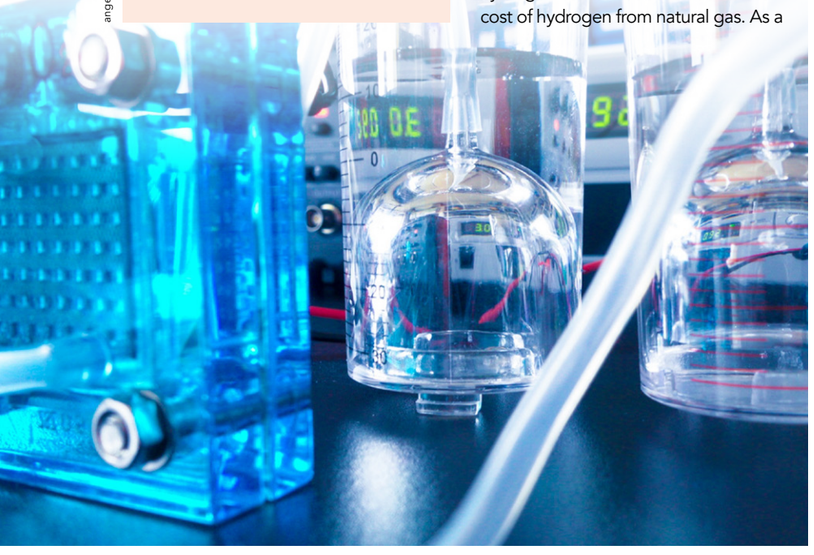
Hydrogen? Just add water and sunlight

Hydrogen has been sold to the public as having the potential to be the ultra-clean fuel for the future's economy. What's less likely to be mentioned is that 96% of hydrogen is produced from natural gas, coal or other fossil fuels – producing it using renewable electricity is simply too expensive. To realise hydrogen's full potential, the world needs better means of splitting water into hydrogen and oxygen. Professor Kazunari Domen at the University of Tokyo/Shinshu University is performing research into how we can improve a method which generates hydrogen from only water and sunlight: photocatalysis.



angellodeco/Shutterstock.com

Hydrogen has developed a name for itself as the ultra-clean fuel of the future. If you ran a car on hydrogen, only water would come out of its exhaust pipe.

But there's a problem. About 96% of the world's hydrogen is formed from fossil fuels, the majority of which is produced by the steam reforming of natural gas. Methane has its hydrogen atoms removed, forming hydrogen gas, and the atoms are replaced with oxygen – forming carbon dioxide which is a greenhouse gas. One tonne of hydrogen comes at the expense of creating 9 to 12 tonnes of carbon dioxide.

It's true that there are methods for producing hydrogen which don't rely on fossil fuels – electrolysis of water is perhaps the more famous hydrogen-production method. However, its energy consumption means that the resulting hydrogen comes at about double the cost of hydrogen from natural gas. As a result, only 4% of the world's hydrogen is produced by electrolysis.

PHOTOCATALYSTS

If hydrogen is really going to be the low-carbon future fuel, or even a minor part of a green economy, we will need another method to produce hydrogen.

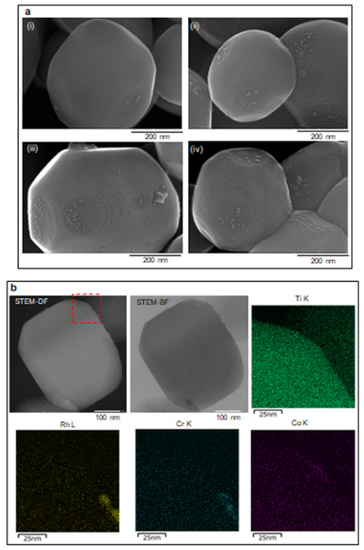
Photocatalysts are semiconductor materials that absorb light and catalyse reactions using the collected energy. Photocatalysts are beginning to receive research attention for their ability to convert water into hydrogen and oxygen using just sunlight.

Photocatalysts used for water splitting are generally a fine powder. At a laboratory scale, the particulate photocatalyst is conventionally suspended in water so that the powder is distributed around the whole volume of water.

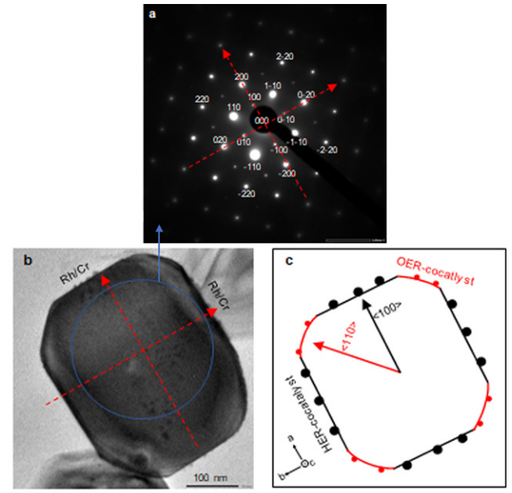
SCALING UP

But will this system work at a larger scale? A suspended particulate reactor would require shallow water, but even with water 1 cm deep, the weight of water in the reactor would be 10 kg per square meter. This very thin layer of water would need continuous stirring to maintain the suspension, which is difficult over a large area. As a result, the more this technology is scaled, the less likely it would be to work.

Professor Kazunari Domen, at the University of Tokyo is researching solutions to scalability issues for these photocatalysts. His research focuses on a more scalable approach: 'fixed particulate photocatalysts'. His group constructed a reactor composed of two acrylic panels, with room between them for a thin layer of water to sit on top of a sheet of the photocatalyst deposited onto a sheet of glass. Rather than swilling around in the water, the photocatalysts are fixed in place on "photocatalyst sheets".



Scanning electron microscope images showing morphology of $SrTiO_3$:Al photocatalysts with almost 100 % IQY.



Detailed structure of a $SrTiO_3$:Al photocatalyst particle with HER and OER co-catalysts.

If hydrogen is really going to be the low-carbon future fuel… we will need scalable and low-cost methods to produce hydrogen without CO_2 production.

In 2019, Prof Domen published details of his group's laboratory scale tests, initially of smaller 5-by-5 cm photocatalyst sheets under bright UV light illumination with a depth of 1 mm. The photocatalyst was 'aluminium-doped strontium-titanium oxide' ($SrTiO_3$:Al), and is one of the most active photocatalysts for water splitting at ambient pressure using sunlight – good properties for real-world applications.

With bench-scale testing confirming that the fixed panel photocatalyst method was viable – able to evolve hydrogen and oxygen at a reasonable rate, Domen and his team built several larger panel reactors with a total area of 1 m^2, to demonstrate the scalability of fixed particulate sheets.

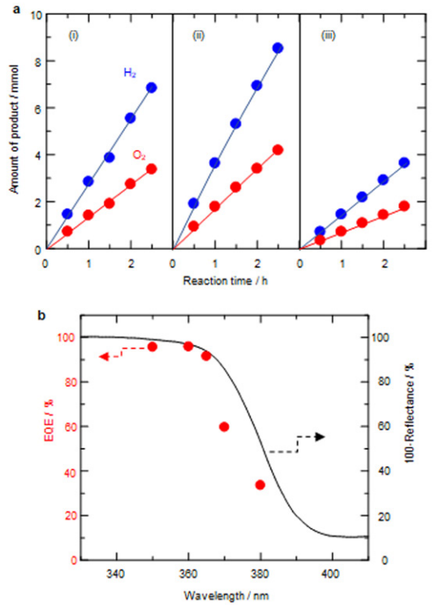
A panel with only 1mm of water was capable of rapid hydrogen and oxygen production without the need to stir or force convection through the reactor. But how efficiently? The key figure Domen is looking at is the solar-to-hydrogen energy conversion efficiency (STH).

The STH of the panels is around 0.4% under natural sunlight, which was comparable to the STH from laboratory-scale experiments under simulated sunlight. However, it is estimated that commercial photocatalytic solar hydrogen production would require an STH around 5-10% to be financially viable.

TUNING THE PHOTOCATALYST

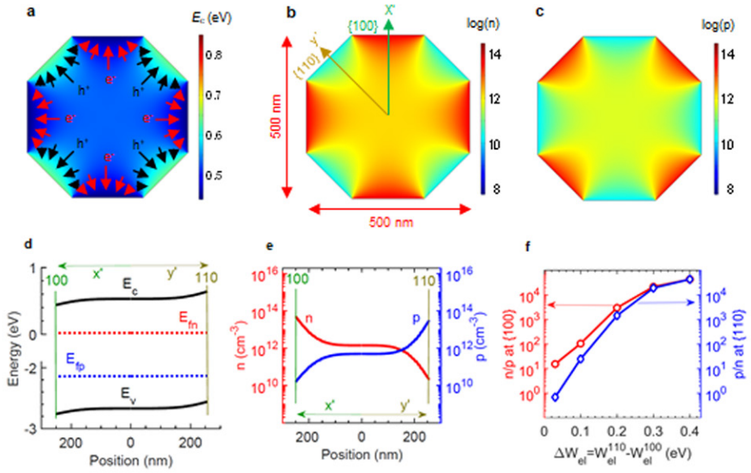
Domen's latest research, published in *Nature*, demonstrated methods to construct highly efficient photocatalyst particles using $SrTiO_3$:Al as a typical example. The photocatalyst must have a high apparent quantum yield (AQY), a measure of the efficiency that photons which introduced into a reactor are used in the water splitting reaction. The AQY value is important because it is essential to improve the STH value – the solar energy to hydrogen conversion.

Over the last few years, various refinements had improved the AQY of this photocatalyst to 69%. And finally AQY reached more than 95% at 350-360 nm, which is almost upper limit of AQY because it means nearly 100% of internal quantum yield (IQY). IQY is the efficiency of photon utilisation absorbed by photocatalyst itself.



a: Time courses of H_2 and O_2 evolutions on three different photocatalysts;
b: AQY(EQY) at several wavelengths.

www.researchoutreach.org



Simulated electric field, and e- and h+ distribution inside two-dimensional model structure.

The approach involves locating efficient co-catalysts like rhodium, chromium and cobalt at suitable position of a particulate photocatalyst using a manufacturing method called photodeposition.

These co-catalysts were chosen because they are highly active for specific parts of the water-splitting reaction: rhodium-chromium oxide for the hydrogen evolution step, and cobalt oxide for the oxygen evolution step.

When co-catalysts are added into a photocatalyst they usually become randomly distributed in the photocatalyst material. Photodeposition makes it possible to instead direct the distribution of the co-catalysts at the proper facets on the surface of the photocatalyst particle. By this method, Domen's team was able to create a photocatalyst with ideal distribution of co-catalysts on different facets; some of rhodium and chromium, and some of cobalt.

The theory is that there exists electric field inside of well-crystalised photocatalyst particles, and photoexcited electrons and holes are carried to different facets through a few-hundreds nanometre length. The electrons arrive at hydrogen evolution co-catalysts consisting of rhodium and chromium immediately produce hydrogen molecules by using proton, and holes arrive at oxygen evolution co-catalysts consisting of cobalt produce oxygen molecules by using hydroxyl anions.

After manufacturing this photocatalyst and repeatedly testing the reaction to check reproducibility, Domen's team had found what they were looking for. It has the highest AQY values recorded for any water-splitting photocatalyst – as high as 95.9% under near-UV light with a wavelength of 360 nm.

A panel with only 1mm of water was capable of rapid hydrogen and oxygen production without the need to stir.

ACCESSING THE VISIBLE SPECTRUM

These super-high AQYs are a confirmation of something important: a particulate photocatalyst can drive the overall water splitting reaction at a very high QY. In fact, Domen's photocatalyst can split water almost as efficiently as Nature's very best equivalent: photosynthesis.

Or at least, this is true under certain circumstances. The difference is that in photosynthesis, photons are utilised across a very wide range of frequencies, throughout the spectrum of visible and near-UV light, in the water splitting reaction. In comparison, Domen's version of the $SrTiO_3$:Al photocatalyst works well under near-UV, but its AQY decreases for photons in the visible region: the AQY of the catalyst at 380 nm – the border of UV and visible – is only 33.6%, that is due to the absorption of only UV light.

The photocatalyst under simulated sunlight gives an STH of only 0.65%. This isn't a touch on the 5-10% target, but it was never going to be. The problem is that the STH obtainable from $SrTiO_3$:Al photocatalysts is limited to less than 1.4% even if the AQY reaches 100% at all wavelength regions below 380 nm.

This is because the photocatalyst being used only absorbs UV light. Domen's catalyst was getting close to an AQY value of 100%, which demonstrates that other photocatalysts with visible light absorption may be able – through tweaking the composition and distribution of co-catalysts – to see similar increases in their AQYs.

NON-OXIDE PHOTOCATALYSTS

The next steps in this research are to perform the same process for visible-light-active water-splitting photocatalysts. Some non-oxide photocatalysts such as Ta_3N_5 and $Y_2Ti_2O_5S_2$ have been reported as effective candidates.

Currently, these photocatalysts exhibit AQYs around 0.1%. However, Domen is optimistic that if improvements can be made to these catalysts on a similar scale to $SrTiO_3$:Al then they could easily reach and exceed the 5-10% STH target. His laboratory is, in his own words, "committed to developing such innovative and essential photocatalysts".

Domen's most recent research is not just promising – it is exciting. It stands as a proof concept for water-splitting using photocatalysts using just sunlight, and a signpost towards truly clean hydrogen production.

Behind the Research

Dr Kazunari Domen

E: domen@chemsys.t.u-tokyo.ac.jp
E: domen@shinshu-u.ac.jp **T:** +81-26-269-5225
W: http://www.domen.t.u-tokyo.ac.jp/english/index_framepage_E.html

References

- Takata, T; Jiang, J; Sakata, Y; Nakabayashi, M; Shibata, N; Nandal, V; Seki, K; Hisatomi, T; Domen, K. (2020). Photocatalytic Water Splitting with Quantum Efficiency of Almost Unity. *Nature*, 581:411–414. doi:10.1038/s41586-020-2278-9.
- Goto, Y., Hisatomi, T., Wang, Q., Higashi, T., Ishikiriyama, K., & Maeda, T. *et al.* (2018). A Particulate Photocatalyst Water-Splitting Panel for Large-Scale Solar Hydrogen Generation. *Joule*, 2(3), 509-520.
- Hisatomi, T., & Domen, K. (2019). Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts. *Nature Catalysis*, 2(5), 387-399.
- Lyu, H., Hisatomi, T., Goto, Y., Yoshida, M., Higashi, T., & Katayama, M. *et al.* (2019). An Al-doped SrTiO3 photocatalyst maintaining sunlight-driven overall water splitting activity for over 1000 h of constant illumination. *Chemical Science*, 10(11), 3196-3201.
- Wang, Q., Hisatomi, T., Jia, Q., Tokudome, H., Zhong, M., & Wang, C. *et al.* (2016). Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%. *Nature Materials*, 15(6), 611-615. doi:10.1038/nmat4589.
- Wang, Q., Hisatomi, T., Suzuki, Y., Pan, Z., Seo, J., & Katayama, M. *et al.* (2017). Particulate Photocatalyst Sheets Based on Carbon Conductor Layer for Efficient Z-Scheme Pure-Water Splitting at Ambient Pressure. *J Am Chem Soc*, 139(4), 1675-1683. doi:10.1021/jacs.6b12164.
- Wang, Q., Nakabayashi, M., Hisatomi, T., Sun, S., Akiyama, S., & Wang, Z. *et al.* (2019). Oxysulfide photocatalyst for visible-light-driven overall water splitting. *Nature Materials*, 18(8), 827-832.
- Wang, Q., Okunaka, S., Tokudome, H., Hisatomi, T., Nakabayashi, M., & Shibata, N. *et al.* (2018). Printable Photocatalyst Sheets Incorporating a Transparent Conductive Mediator for Z-Scheme Water Splitting. *Joule*, 2(12), 2667-2680.
- Wang, Z., Inoue, Y., Hisatomi, T., Ishikawa, R., Wang, Q., & Takata, T. *et al.* (2018). Overall water splitting by Ta_3N_5 nanorod single crystals grown on the edges of $KTaO_3$ particles. *Nature Catalysis*, 1(10), 756-763.

THE UNIVERSITY OF TOKYO

SHINSHU UNIVERSITY

Research Objectives

Prof Domen's group explores photocatalytic water splitting and develops water splitting panels for renewable hydrogen production on a large scale.

Detail

Kazunari Domen
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan

Bio

Kazunari Domen received a Ph.D. (1982) Honours in Chemistry from the University of Tokyo. He has been Professor since 2004 and University Professor of The University of Tokyo since 2019. He was appointed Special Contract Professor at Shinshu University in 2017.

Funding

ARPChem Project of New Energy and Industrial Technology Development Organization (NEDO; METI)

Collaborators

- Associate Prof T. Hisatomi, Shinshu University
- Prof Y. Sakata, Yamaguchi University
- Prof. A. Kudo, Tokyo University of Science

Personal Response

Can you explain in more detail how it will be possible to apply what you have learned from $SrTiO_3$ to the photocatalysts which are more active under visible light?

"To develop photocatalysts with 5-10% STH based on what we have learnt from $SrTiO_3$:Al, it is necessary to use a wide range of visible light responsive photocatalysts such as $Y_2Ti_2O_5S_2$ and Ta_3N_5 and to devise suitable preparation methods of highly crystalised, low defects density and suitable size of the particles. Then, suitable co-catalysts for water splitting on those particulate photocatalysts must be developed. It is also necessary to develop a water splitting panel and total system of solar hydrogen production, including an efficient hydrogen separation membrane, all which must be scalable, low cost and adhere to safety standards."