Splitting water: Developing catalysts to create hydrogen fuel

Francesc Illas

Hydrogen has the potential to be the cleanest fuel we have, but not while it is sourced from fossil fuels. **Professor Francesc Illas** has been trying to find a catalyst that can help create hydrogen fuel via an alternative method: by splitting water using visible light

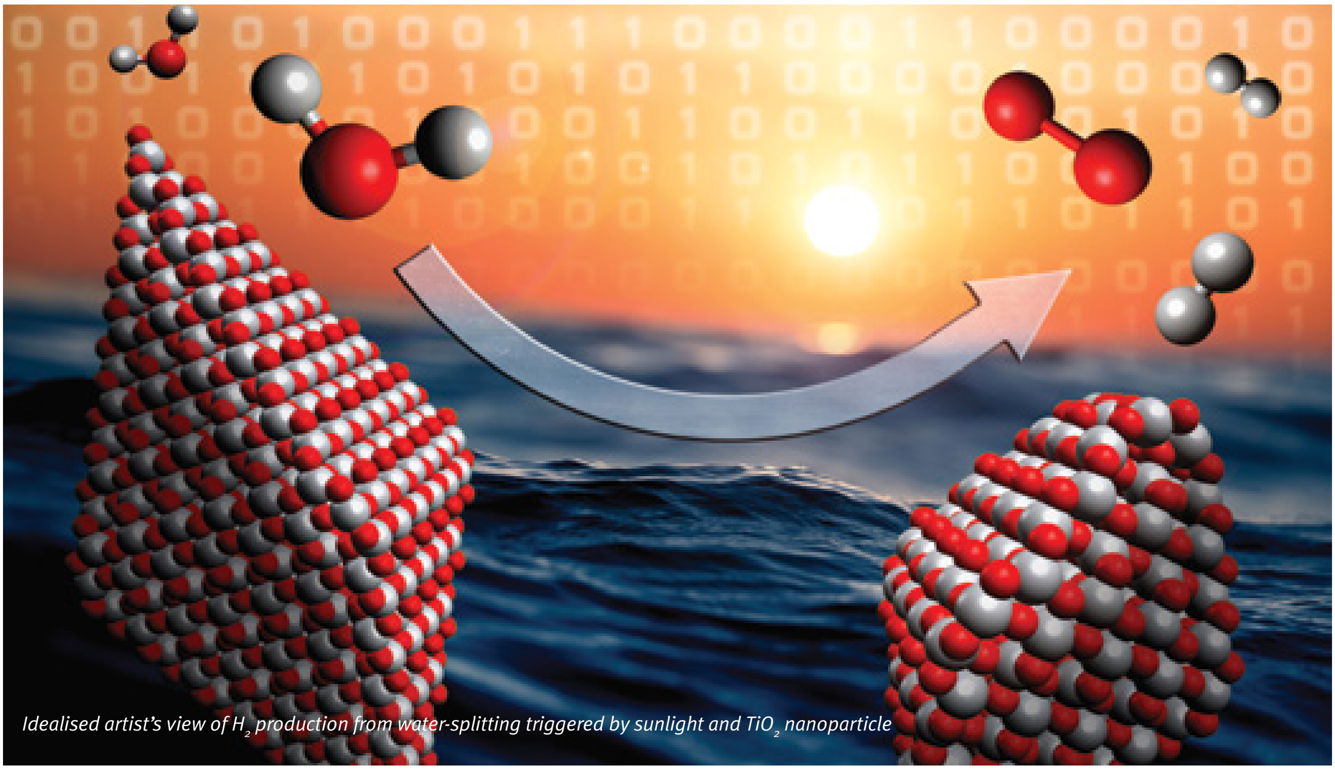
When hydrogen burns in air,it releases an abundance of energy and produces nothing but harmless water vapour. Its potential as a totally clean, non-polluting fuel is unrivalled.

However, the majority of hydrogen produced today comes from fossil fuels, eliminating some of its green credentials. Developing renewable methods for producing hydrogen is therefore a crucial step towards creating a hydrogen economy that can help alleviate the pressure put on our environment by the use of fossil fuels.

A seminal work from Fujishima and Honda in 1972 on the electrochemical photolysis of water opened up the possibility of using light to split water into hydrogen and oxygen. The implications of this work were enormous, as it offered a direct way to use solar energy to obtain hydrogen from just water.

Since this paper was released, it has been shown that water splitting via a catalyst of TiO_2 nanopowder can spontaneously occur under ultraviolet radiation. Unfortunately, over 40 years of research and thousands of papers have not been enough to find photocatalysts with activity in the visible region of sunlight higher than that of TiO_2 under ultraviolet radiation. This severely limits practical applications since sunlight at the Earth's surface contains only a small amount of ultraviolet radiation.

Professor Francesc Illas of the University of Barcelona explains the problem: "For photocatalytic water-splitting to be of practical use, we either need to able to harvest light in the ultraviolet region where TiO_2 performs best, or we need to modify TiO_2 so that it can exhibit the same characteristics under visible light.



Idealised artist's view of H_2 production from water-splitting triggered by sunlight and TiO_2 nanoparticle

"The first possibility has to be discarded since, fortunately for life, the Earth's surface receives only a small amount of ultraviolet radiation from the sun. Therefore, we need to work out how to make TiO_2 work as a catalyst in visible light. A necessary first step towards doing this is to understand how the catalyst's properties are related to its microscopic atomic and electronic structure, taking into account the state of the electrons at a quantum level."

Recent experimental advances have indeed shown that tailored TiO_2 nanoparticles can be synthesised that exhibit distinct photocatalytic activity in various reactions including water-splitting. However, the link between the properties of a given nanoparticle and its photocatalytic activity has not yet been established.

"The electrochemical photolysis of water offers a direct way to use solar energy to obtain hydrogen from water"

In the past, most of the research carried out to understand these properties has focused on studying the bulk and surfaces of the crystalline form of TiO_2, but this does not resemble the structure of TiO_2 particles that are generally used. The COMPHOCAT project, which has been allocated 50 000 000 core hours on the MareNostrum supercomputer, thus aims to study the properties of TiO_2 at the nanoscale, building models which closely resemble the nanoparticles used in practice.

Illas and his team have created models of several versions of TiO_2 where all electrons of all atoms are explicitly included and treated at the quantum mechanical level including relativistic effects. The geometry of each particle is determined from total energy minimisation, a technique used to obtain the most stable arrangement of atoms in space for any particular molecule. The electronic properties are then studied as a function of the size and shape of the nanoparticle.

Following a systematic study of the electronic structure of TiO_2 nanoparticle models with different sizes, shapes, compositions, and environments, a database has been constructed of candidate nanoparticles with appropriate absorption spectra in the visible light window.

But having activity within the visible light spectrum is only one of the required properties for a potential water-splitting catalyst. The process of photocatalysis occurs when light causes an electron in the catalyst to move from an occupied energy band to an unoccupied one. This leaves a hole in the former band, and creates a net positive charge in the hole's location. This hole in the catalyst then makes it able to remove electrons from other reactants, and the electron is able to be transferred to other species thus reducing them. This is how TiO_2 is able to split water into hydrogen and oxygen. "It is very important that the excited state in which the electron-hole pair created by photo-excitation lasts long enough, or water-splitting will not occur," says Illas. "Additionally, the hole and the excited electron must be spatially separated so that the reaction with the hole can take place before electron-hole recombination takes place."

The results gathered so far in the project are not yet sufficient to design a suitable photocatalyst for water-splitting, but constitute a first step. "Many attempts to improve TiO_2 based photocatalysts involve changing their chemical composition in various different ways," says Illas. "Knowing how the electronic structure evolves with size and shape allows us to investigate the changes introduced by doping and this should help us to make progress in the desired direction."

The support of PRACE has been invaluable to the project, both in terms of the time given on the MareNostrum supercomputer and the support of the staff. "Working with PRACE has been a privilege; without the supercomputing facilities provided by this programme our study could not have been carried out," says Illas. "The type of calculations involved in COMPHOCAT required assistance from the technical staff of the Barcelona Supercomputing Centre to speed up the efficiency and parallelisation of the installation of the FHI-aims code, a sophisticated seamless parallel computer program based on numerical atom centered orbitals."

Non-renewable hydrogen production methods can only serve as a short-term supply for the hydrogen economy. If research like this can lead to an efficient and reliable renewable strategy for hydrogen production, it will help bring us that much closer to a world in which we no longer have to rely on fossil fuels.

For more information

www.ub.edu/cmsl/xino.html

Resources awarded by PRACE

This project was awarded 50 million core hours on MareNostrum hosted by BSC, Spain

Publications

"Size Dependent Structural and Polymorphic Transitions in ZnO: from Nanocluster to Bulk", F. Viñes, O. Lamiel-Garcia, F. Illas, and S. T. Bromley, Nanoscale, 9 (2017)

"When anatase nanoparticles become bulk-like: Properties of realistic TiO2 nanoparticles in the 1 – 6 nm size range from all-electron relativistic density functional theory based calculations" by O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley, F. Illas, J. Chem. Theory and Comput., 13 (2017)