Chemical waves guide to catalysts of the future

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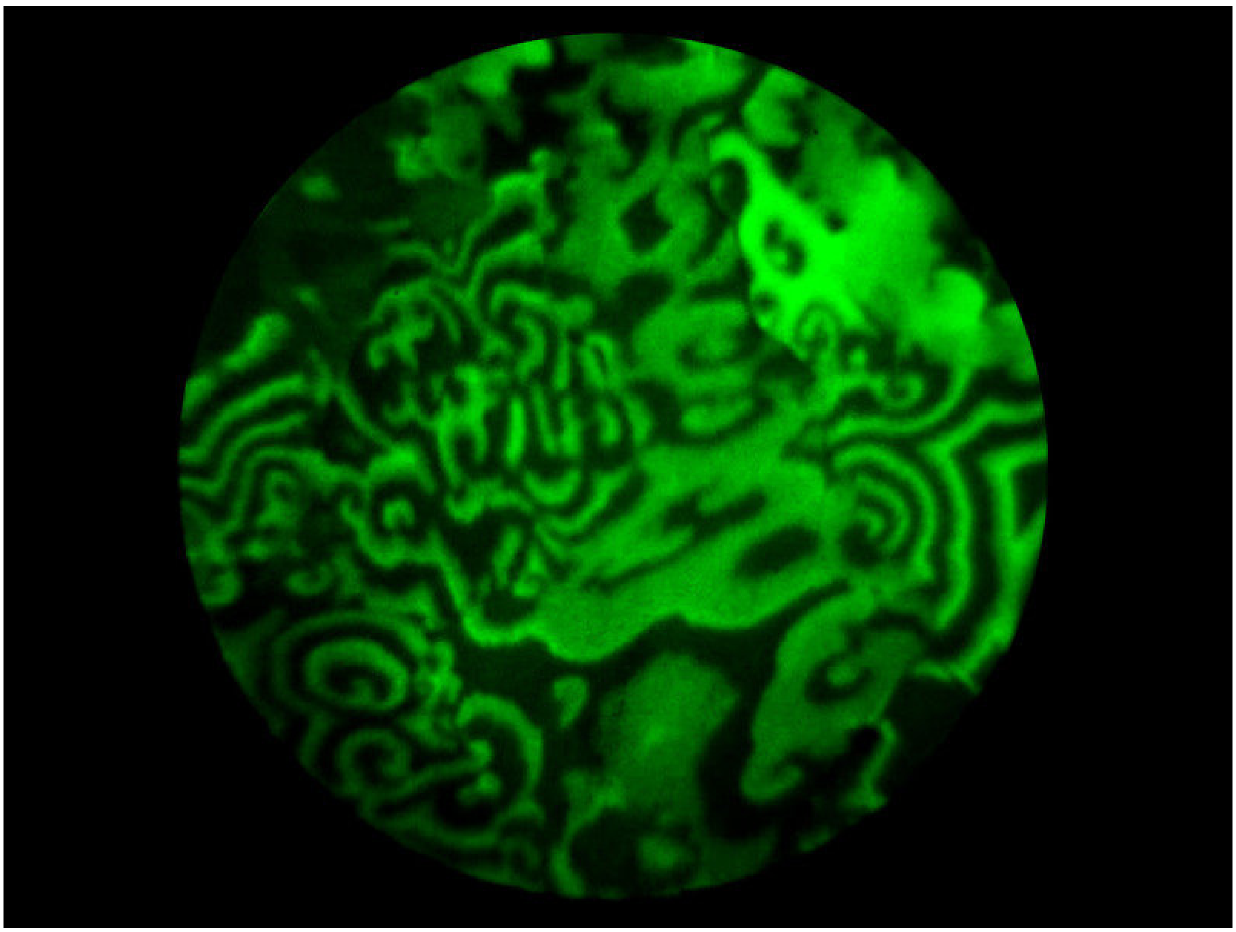


Spiral structures on the crystal. Credit: TU Wien

Spectacular electron microscope images at TU Wien lead to important findings: Chemical reactions can produce spiral-like multi-frequency waves and thus provide local information about catalysts.

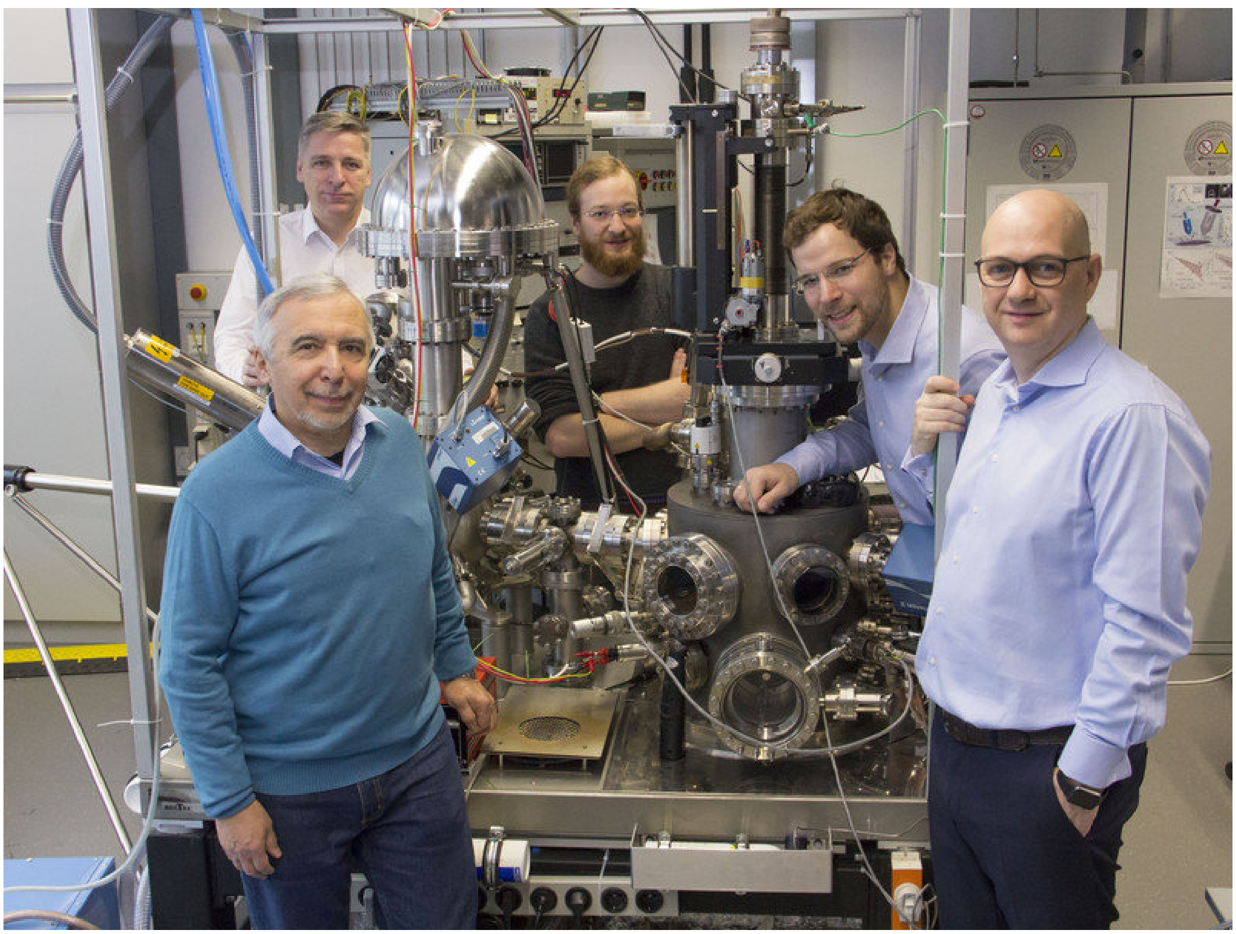
They appear almost hypnotic, like a lava lamp. The waves made visible at TU Wien using a photoemission electron microscope cover the surface of rhodium foil with bizarre patterns which dance around on the surface.

Waves are known in many very different forms; as water waves, light waves or sound waves. But here we are dealing with something quite different – chemical waves. A chemical reaction takes place on the surface of a crystal, but this does not progress in one direction only: instead, it returns periodically to its original state. Depending on the phase of this cyclically progressing reaction, the surface of the rhodium crystal appears as bright or dark under the photoemission electron microscope. This creates a moving wave pattern. The breakthrough achievement was to observe this effect simultaneously on different microscopically small grains of a polycrystalline catalyst. Fascinating spiral structures form there, the movement of which allows us to collect information about the characteristics of the individual grains of crystal.

Rabbits, foxes and crystals

Typically, one imagines a chemical reaction like this: from specific initial reactants one obtains specific final products. But it does not need to be as simple as that. Self-sustaining oscillations may occur, i.e. periodic changes between two different states," explains Professor Günther Rupprechter of the Institute of Materials Chemistry at TU Wien. This is known from very different scientific disciplines, such as hunter-prey models. When foxes eat rabbits to the extent that there are hardly any rabbits left, the foxes starve and their numbers fall, and as a result the rabbit population recovers. Similar patterns occur in property prices; or even in chemical reactions.

The team at TU Wien is studying the oxidation of hydrogen, the basis of any fuel cell. These studies involve exposing rhodium surfaces to an atmosphere of oxygen and hydrogen. Initially molecules of oxygen (O2) are adsorbed on the surface where they dissociate into oxygen atoms. The single oxygen atoms can then diffuse into the crystal and form a thin layer of oxygen beneath the outer rhodium layer. However, this reduces the ability of the surface to bind oxygen. Increasingly, hydrogen is bound instead, which then reacts to form water with the oxygen previously adsorbed. The water leaves the surface again, at some point the number of oxygen atoms has returned to the initial low level, and the whole process starts again from the beginning.



Yuri Suchorski, Johannes Bernardi, Johannes Zeininger, Martin Datler, Günther Rupprechter (left to right). Credit: TU Wien

Different angles, different frequency

"Such oscillating reactions had already been studied by Nobel Prize-winner Gerhard Ertl," explains Professor Yuri Suchorski, the first author of the paper, who, like Professor Rupprechter, worked at Professor Ertl's Berlin Institute before moving to TU Wien. "But now we have taken an important further step: we have managed to achieve a state of numerous oscillations of different frequencies happening concurrently on different grains of the polycrystalline surface." These different grains exhibit crystal lattices which are oriented at different angles to the surface.

These angles play a crucial role: the geometric arrangement of atoms on the surface of a crystal is dependent on the direction in which it is cut. This also determines the frequency with which the chemical reaction undergoes cyclic oscillations.

On a polycrystalline surface, there are then different regions in which the cyclical process occurs at different frequencies. It is precisely this effect that creates those fascinating wave patterns. When a chemical wave moves across the surface and passes from the edge of one grain of crystal to another, it speeds up or slows down, similar to light passing from the air to water.. This changes the complex spiral wave structures according to the particular orientation of the grain surface. "We can then learn a lot about the material from these structures," says Günther Rupprechter. "At a glance we can detect which regions of our surface have superior catalytic characteristics."

On the road to future hydrogen energy

It is necessary to learn more about the catalytic oxidation of hydrogen. "For fuel cells, the mobile energy sources of the future whose sole exhaust gas consists of pure water, we need new materials which help to catalytically combust hydrogen. But as before, these processes are not yet fully understood" says Professor Yuri Suchorski. "There are still many open questions here, and now we have a new, very elegant way to investigate them further."

More information: Yuri Suchorski et al. Visualizing catalyst heterogeneity by a multifrequential oscillating reaction, *Nature Communications* (2018). DOI: 10.1038/s41467-018-03007-3

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