

the fewer the number of steps required and the more efficient the synthesis. Thus interest in using catalysts created by nature is rising significantly — indeed, the use of hydrolytic enzymes has already been industrialized. Now, much work is being carried out to harness the chemistry of oxidoreductases — a class of enzymes that catalyse the transfer of electrons from one molecule to another. These properties mean that they could be used for catalysing useful reactions such as enantioselective reductions and oxidations.

So far the practical use of oxidoreductases has been hampered by the complicated mechanism by which they operate. They are dependent on chains of helper molecules that supply electrons to the oxidoreductase enzyme and facilitate the desired redox reaction. These helper molecules generally consist of several other enzymes and co-factors and would be costly and difficult to reproduce in an industrial setting. Now, scientists from Spain and The Netherlands have created a simplified system in which water is used to deliver electrons to the oxidoreductases in place of the natural co-factors.

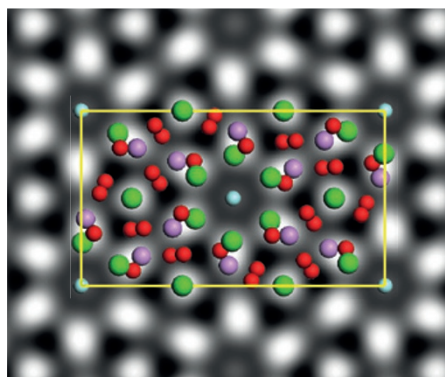
Until now water has featured in biocatalysis only as a solvent. However, Avelino Corma, Frank Hollmann and co-workers have used light-driven water oxidation to allow the water itself to act as an electron donor, supplying an oxidoreductase biocatalytic reaction in which conjugated double bonds were reduced selectively with 66% conversion and 86% e.e. after just six hours with UV light. The water oxidation used to drive the reaction was carried out using metal-doped TiO₂ photocatalysts. The system also worked under visible light, displaying comparable enantioselectivities but slightly smaller yields (over 50%) and longer reaction times (9 hours). The next steps for Corma and his team will be to carry out further mechanistic studies, optimize the reaction conditions and expand the discovery to other biocatalytic redox transformations. RD

ELECTRON MICROSCOPY

Jaws up close

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Sharks have extremely healthy teeth, not only because they shed them often, but also because they are protected by a very hard layer of enameloid that guards against caries. This biomineral consists of bunches of single-crystal fluorapatite nanorods with a matrix of organic material and



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knowing its exact structure could explain its impressive properties — which might ultimately provide useful information for human dentistry. Direct imaging of biominerals with single-atom sensitivity, however, has proved difficult. This is because acquiring transmission electron microscopy images with high resolution requires a strong electron beam, which damages the biomineral and consequently it has so far only been possible to obtain nanoscale structural information.

Using a new aberration-corrected scanning transmission electron microscopy technique with a ‘low-dose’ electron beam, Zhongchang Wang from Tohoku University has led a team of researchers that now present an atomically resolved image of the complex fluorapatite structure of shark teeth. High-angle annular-dark-field images can resolve the heavier calcium atoms, but it is the structure of the light fluorine atoms that are most interesting. After all, it is the caries-reducing effects of fluorine that have saved many a human tooth. The team accomplishes this task with annular-bright-field images revealing the exact positions of the fluorine atoms in the fluorapatite.

The fluorine atoms are shown to be surrounded by a hexagon of calcium atoms. Adjacent to these hexagons reside equilateral triangles that feature pairs of closely spaced oxygen atoms at their tips and another calcium atom in the centre. Contour plots of this structure’s charge density — obtained from density functional theory calculations — suggest that the calcium–fluorine bond has a highly covalent character. This bonding might be the secret to healthy teeth because it seems to be the strength-limiting factor. With this new low-dose electron microscopy method in the imaging toolkit, we can expect a wealth of atomic-scale information on various biominerals soon. LM

Written by Enda Bergin, Ruth Doherty, James Hennessy and Leonie Mueck.

blogroll

Drops in a bucket

How cold is cold, and how big is a drop of liquid?

As I write this column on a cold mid-January morning, North Americans are finding out that the phrase ‘cold snap’ is terribly outdated and that we should be using ‘polar vortex’ instead to describe the cold air that dropped temperatures as much as 30 °C below normal. Nevertheless, using the speed of gas molecules — and even cars — to prove his point, Matt Strassler who blogs at Of Particular Significance suggests (<http://go.nature.com/1yt2P9>) that maybe it really wasn’t that cold after all. Although you can’t disagree with the arguments he makes, the desire to put on an extra sweater before venturing outside remains very real. The discussion in the comments is also worth reading. Matt’s point, however, is that the cool-down was just a drop in the bucket.

Speaking of drops, Mike, who writes at the Amboceptor blog, recently took a look (<http://go.nature.com/Ww3USD>) at what makes up ‘a drop’ and fractions-of-a-drop when they are described in experimental procedures. Focusing on a diagnostic test for typhoid that was first reported in 1910, Mike finds that descriptions such as ‘full-sized drop’, ‘half drop’ and ‘quarter drop’ led, unsurprisingly, to irreproducible results that prompted some testy debate in the medical literature of the day. The post concludes by noting that, “those of us with access to space-age technology like micropipettes should count our blessings.”

Lastly, pitch-drop experiments have been discussed extensively this past year, but Michael de Podesta of the Protons for Breakfast blog offers some unique thoughts about them (<http://go.nature.com/fax9JE>). These include how timescales vary with the observer and how “although all the forces are all constant, the response is not. This is like many processes in nature, but it seems an especially apt analogy for climate change”. And polar vortices too.

Written by John Spevacek, who blogs at <http://www.rheothing.com/>