

## PHOTOCATALYSTS

## Closing the gap

Photocatalysts such as titanium dioxide that use sunlight to split water and produce hydrogen would be a clean and sustainable solution to many problems, but their efficiency is currently too low to be widely used. Two approaches to engineer the surface properties of titanium dioxide offer hope that its efficiency can be increased.

Ulrike Diebold

Imagine you throw a little bit of some miraculous stuff into a bucket of water, hold it in bright sunlight, and out bubbles hydrogen. Suppose further that you use this hydrogen to fill up your (fuel-cell-powered) car, which spits out only water from the exhaust pipe when you drive it. This would certainly solve our looming environmental and energy problems, wouldn't it?

Well, in principle, this 'miraculous stuff' exists — it is a photocatalyst<sup>1</sup>, a material that is able to catalytically split water when activated by light. The prime photocatalyst, titanium dioxide, remarkably is even safe, abundant and inexpensive<sup>2</sup>. The problem is that it is rather inefficient in producing hydrogen, thus researchers have tried to improve its efficiency for several decades, ever since the phenomenon was discovered in the early 1970s<sup>3</sup>. Two recent studies<sup>4,5</sup> describe novel approaches that rest entirely on modifying the surface of TiO<sub>2</sub>.

Photocatalysts are semiconductors: materials where the highest energy states occupied by electrons (the valence band) and the lowest unfilled states (the conduction band) are separated by a bandgap (Fig. 1a). Absorption of a sufficiently energetic photon promotes an electron from the valence band into the conduction band, leaving behind a hole. These photoexcited electrons and holes can initiate chemical reactions at the photocatalyst's surface — reducing H<sup>+</sup> to H<sub>2</sub> and oxidizing water to O<sub>2</sub>, for example. TiO<sub>2</sub> has a wide bandgap of 3 eV, however, so it can only absorb the UV portion of the solar spectrum. This part amounts to just 4% of the solar radiation, and not all of it is converted into chemical energy by the photocatalyst.

If one modified the TiO<sub>2</sub> somehow to make the bandgap smaller, then a larger fraction of the solar spectrum would be absorbed and could be put to use. A popular approach is doping: substituting a foreign element for a few of the materials' cations or anions, or both<sup>6</sup>. Dopants introduce additional energy states within the bandgap. The initially transparent or white TiO<sub>2</sub> changes its colour, a clear sign that light is now absorbed over a wider range of wavelengths. This increase in light absorption does not necessarily translate into higher photocatalytic activity, however.

Often, trap sites are introduced that act as recombination centres for the photoexcited charge carriers. When the electrons and holes meet they annihilate and create heat; sometimes increased recombination can render the doped material less efficient than the undoped one.

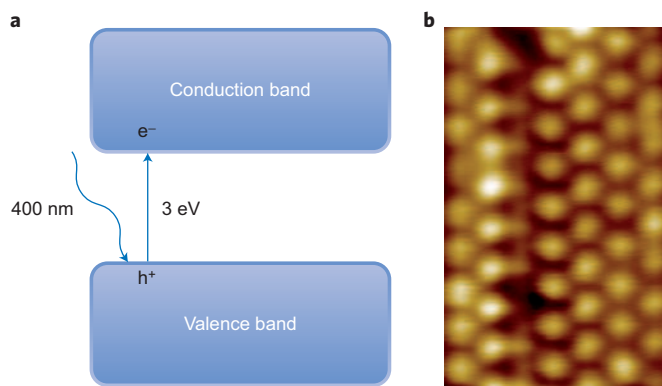
To design a better photocatalyst, it is critical to identify the nature of such bandgap states, as well as their position relative to the band edges. This is best achieved through working with 'model systems' — large single crystals that can be inspected with a whole arsenal of techniques<sup>7</sup>. The group of Matthias Batzill now report such a study in *Nature Chemistry* that uses a TiO<sub>2</sub> rutile (011) sample<sup>4</sup>. An earlier report<sup>8</sup> had suggested that this surface is particularly active for the oxidative half-reaction, that is, for reactions initiated by the photo-excited hole. Furthermore, the TiO<sub>2</sub> rutile (011) surface breaks up adsorbed water molecules into a hydroxyl and a proton even without light<sup>9</sup>.

After cleaning the TiO<sub>2</sub> rutile (011) surface by argon ion irradiation and annealing the sample in a low pressure of oxygen, Batzill and colleagues found that the surface atoms had re-arranged themselves, forming a beautiful hexagonal pattern (Fig. 1b). Photoemission spectra showed a peak at the upper edge of the valence band, which, it was argued, was caused by a reduced bandgap within the newly formed two-dimensional TiO<sub>2</sub> phase.

This would close the gap to effectively ~2.1 eV, pushing the optical absorption edge into the visible (590 nm), and achieving the goal of harvesting a larger fraction of the solar spectrum. In addition, upwards band-bending was observed, which should drive photo-excited holes to the surface, where they could be available for oxidation reactions.

The combination of experimental techniques in this work gives direct insights into the atomic-scale details of the TiO<sub>2</sub> single-crystal surface. At this point there is not enough experimental evidence, however, to decide what exactly the structure of the hexagonal surface phase is. Batzill and colleagues propose<sup>4</sup> that it constitutes a novel cubic phase of TiO<sub>2</sub>; it would be exciting if this hypothesis could be verified in future experiments. To be effective, a catalyst needs to have a high surface area, so the material must be present in the form of tiny particles. It remains to be seen if this new surface phase can also be created on much smaller crystals and if its promise holds up under realistic photocatalytic conditions.

A group led by Samuel Mao took a different approach to making TiO<sub>2</sub> a more efficient photocatalyst, which they report in *Science*<sup>5</sup>. They synthesized nanosized TiO<sub>2</sub> and reduced it in a hydrogen atmosphere. The material turned black; certainly a good sign when you want to absorb as much light as possible. Indeed, the onset of optical absorption was



**Figure 1** | TiO<sub>2</sub>-based photocatalysis. **a**, Absorption of a 3-eV-photon excites an electron from the valence band into the conduction band. The photo-excited electron and the remaining hole can induce redox reactions at the surface and produce H<sub>2</sub> from water. **b**, A novel hexagonal surface phase at the TiO<sub>2</sub> (011) surface<sup>4</sup> has a smaller bandgap and holds promise for photocatalysis with visible light.

measured to be around 1 eV (~1,200 nm). In the first photocatalytic test reaction — the decomposition of methylene blue under artificial sunlight — the black TiO<sub>2</sub> showed a higher efficiency than the white material, as well as good long-term stability. Moreover, in a second experiment, the black TiO<sub>2</sub> produced H<sub>2</sub> at a high rate, effectively turning 24% of the incident sunlight into chemical energy. It should be mentioned that it was not the full water photolysis that was followed in this experiment, however. Mao and colleagues used methanol as a sacrificial agent for the oxidative half-reaction, and platinum as a co-catalyst for the hydrogen-reduction part. It is nevertheless remarkable that, with the production of 10 mmol H<sub>2</sub> per gram of photocatalyst for each hour of solar radiation, the yield was two orders of magnitude above that of other photocatalysts under comparable conditions<sup>1</sup>.

So what happened during the high-temperature treatment in hydrogen that produced a much more efficient black catalyst? According to materials characterization studies described in ref. 5 it was again an altered surface layer that did the trick. The initial, white, TiO<sub>2</sub> consisted of nanocrystals of anatase around 8 nm in size. After treatment,

the core of the particles stayed crystalline but the outer shell consisted of a ~1-nm-thick amorphous layer that probably contained substantial amounts of hydrogen. The group made sure the H<sub>2</sub> they observed did not come from the material itself but was indeed produced photocatalytically. According to computations, the highly defective amorphous layer causes an up-shift of the TiO<sub>2</sub> valence band edge, which narrows the bandgap.

Interestingly, the contention that an amorphous surface layer yields a better photocatalyst goes against conventional wisdom. Normally, materials should be highly crystalline to avoid detrimental recombination sites. Why, then, is this not the case in this 'disorder-engineered' material? The work will certainly provide food for thought for other researchers. Well-resolved valence-band spectra and a more thorough experimental characterization of bond angles, distances, and orientations are needed to fully understand what is special about this material. Modelling a disordered structure is a non-trivial task; by definition, disorder is geometrically ill-defined, so it is not clear what model one should set up in first-principles calculations. Also, it would be much better if one could use

another sacrificial agent rather than methanol (for example, something that is already in the water, such as an organic pollutant), and find ways to eliminate the expensive platinum co-catalyst.

Nevertheless, engineering an inexpensive, black photocatalyst is certainly a major step in the right direction. As both recent works<sup>4,5</sup> point out, surface engineering might be a valuable new approach. Maybe future generations can one day indeed use photocatalysis to produce hydrogen as the ultimate clean fuel. □

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