Femtosecond laser doping of TiO_2 for photocatalysis

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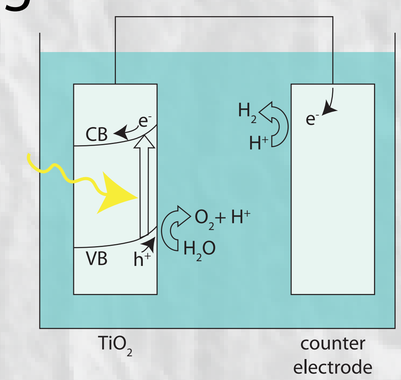
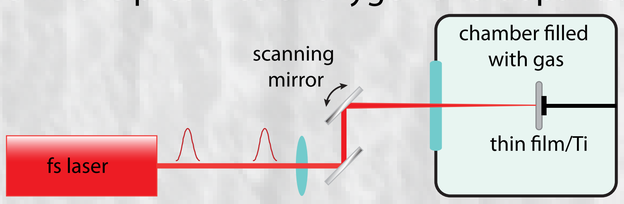
Water splitting

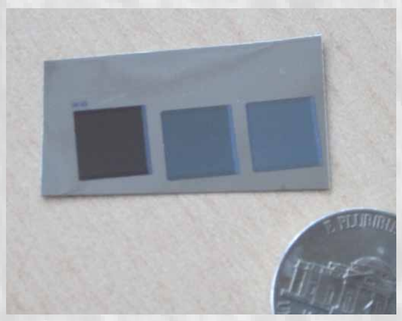
Water splitting is an energetically unfavorable reaction, but it is possible through converting light into charge carriers that facilitate the reaction. We use TiO_2 for the photoanode, but with a bandgap of 3-3.2 eV (λ<400 nm), the rate of photooxidation from the solar spectrum is low. By laser doping, we hope to achieve more efficient water splitting.



Laser processing of titanium

We present a novel method for introducing dopants into TiO_2 by irradiating titanium with a femtosecond laser in the presence of oxygen and dopants. The samples are irradiated with 800 nm light with a fluence of 1.5-2.5 kJ/m². By laser doping TiO_2, we aim to introduce defects that will extend the absorption into the visible regime while texturing the surface to aid in light trapping. Hence, the rate of photocatalysis can be increased by both doping and creating surface structures.

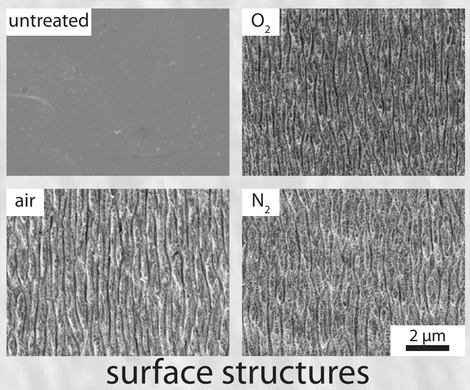



laser treated titanium

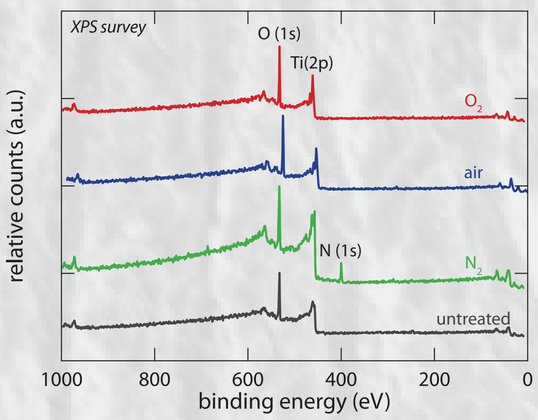

laser interaction

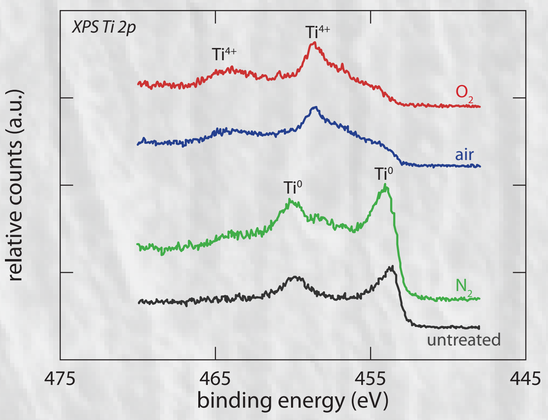
Gas-phase doping

Samples irradiated in oxygen and air produce TiO_2, shown with the Ti^{4+} peaks in XPS (below right). Samples irradiated in N_2 incorporate nitrogen but are non-stoichiometric TiN. We demonstrate that titanium selectively incorporates oxygen over nitrogen, meaning that TiO_2:N has not yet been achieved with our method.



surface structures

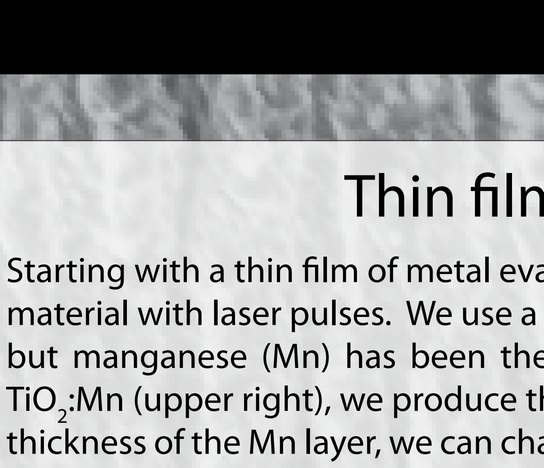


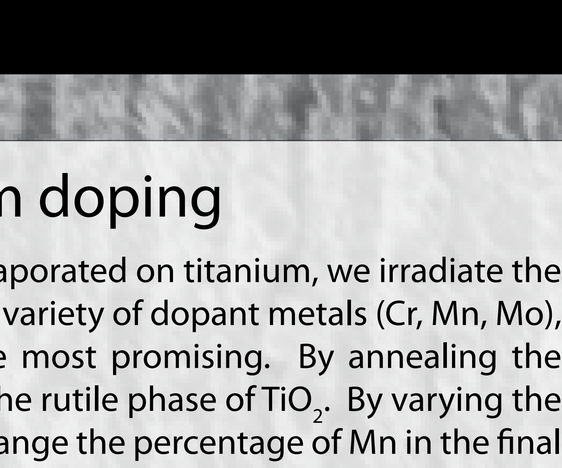


Thin film doping

Starting with a thin film of metal evaporated on titanium, we irradiate the material with laser pulses. We use a variety of dopant metals (Cr, Mn, Mo), but manganese (Mn) has been the most promising. By annealing the TiO_2:Mn (upper right), we produce the rutile phase of TiO_2. By varying the thickness of the Mn layer, we can change the percentage of Mn in the final structure with an oxidation state of predominantly Mn^{2+} (lower right).

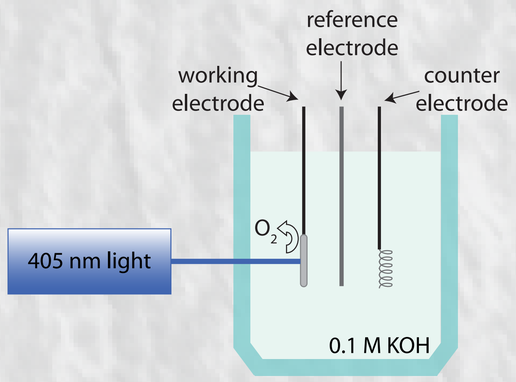
surface structures

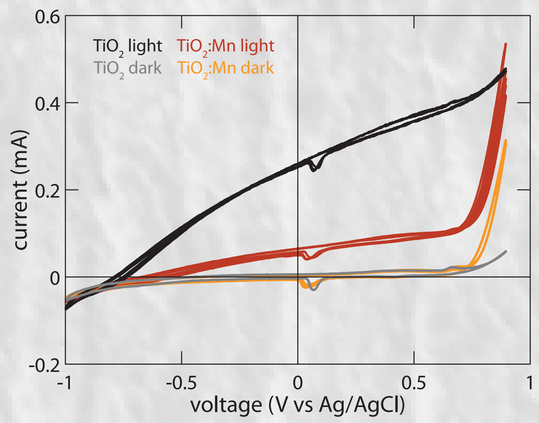




Photocatalysis

To test the ability to split water, we use a 3-electrode setup (left) and illuminate the samples with above-bandgap light. The IV plot for TiO_2 and TiO_2:Mn (30 nm Mn), both annealed to 700° C, is shown below. TiO_2 exhibits more overall photocurrent (0.26 mA at V_{bias} = 0) while TiO_2:Mn shows a higher current for V_{bias} = 0.9 V, corresponding to a higher catalytic activity for oxygen evolution. The samples also exhibit an overpotential of 0.4 V.





We hope to raise the photocurrent in the TiO_2:Mn samples by optimizing the manganese dopant concentration in TiO_2. We also plan to extend the laser doping method to other oxides, including iron oxide and niobium oxide, to test if using oxides with smaller bandgaps will result in more efficient devices that exhibit larger photocurrents.

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