Femtosecond laser doping of TiO_2 for solar harvesting

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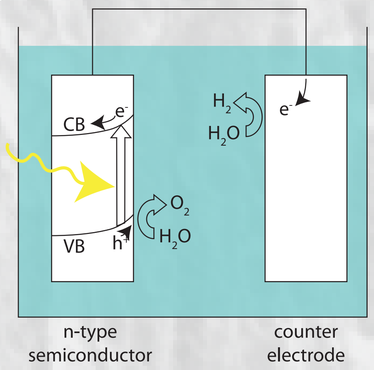
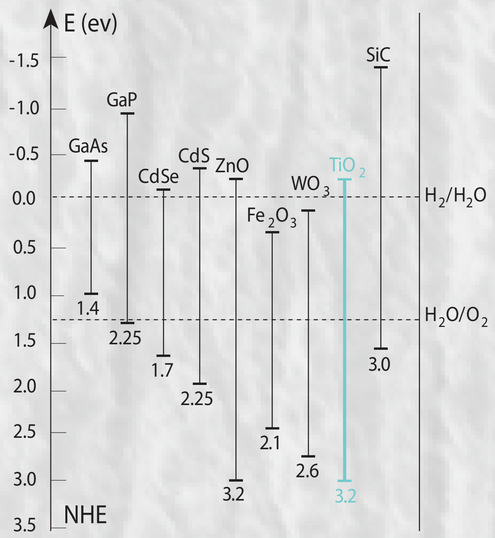
Water Splitting

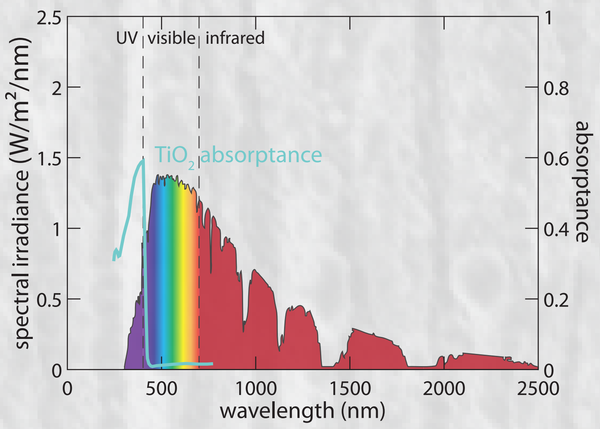
Although water splitting is an energetically unfavorable reaction, it is possible through the use of a photoelectrochemical cell (right), which absorbs light and excites an electron-hole pair. The hole is used for oxidation and the electron is shuttled to the counter electrode for hydrogen reduction.



Why TiO_2

Water splitting requires a material with a bandgap that spans the reaction potentials for hydrogen reduction (H_2/H_2O) and water oxidation (H_2O/O_2). TiO_2 is one of the few materials that meets this criteria, as shown to the right. However, TiO_2 only absorbs in the UV (λ<400 nm), thus using 5% of the solar spectrum (below).



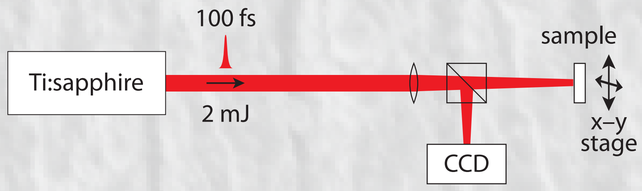


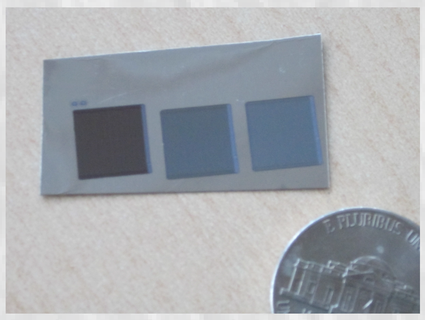
By doping TiO_2, we aim to increase its absorption by introducing an intermediate band into the bandgap. Visible light photocatalysis should achieve higher efficiency water splitting.

Surface Structures on 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 nitrogen. The rate of photocatalysis can be increased by introducing surface structures and through hyperdoping. Enhanced absorptance has been demonstrated for laser-doped silicon.

Our research hopes to present an innovative approach to dope TiO_2 for visible light water splitting.

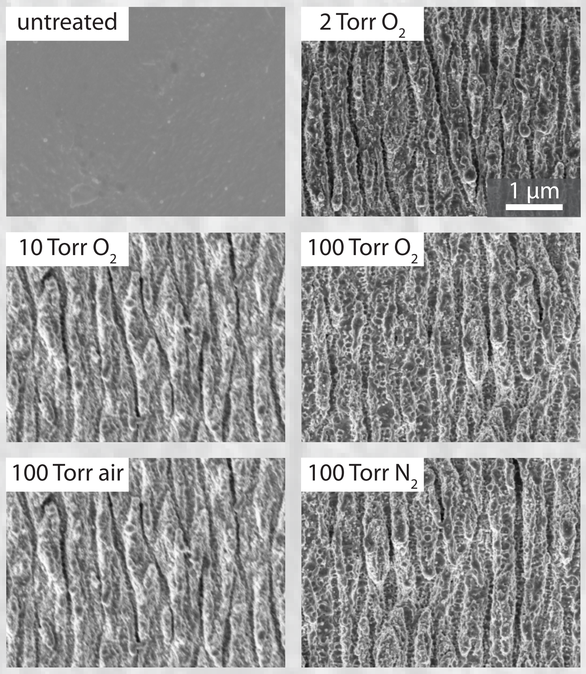




laser treated titanium

laser interaction

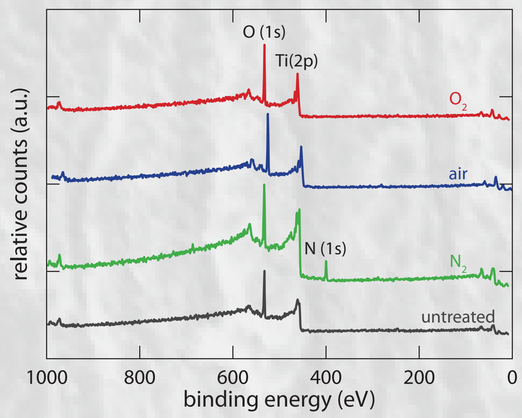
Surface Structures on Titanium

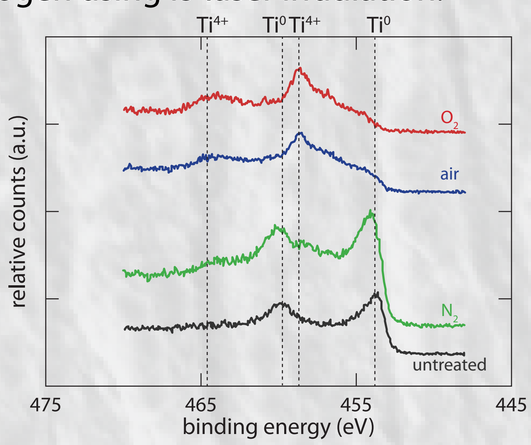


Irradiation of titanium metal under various ambient conditions yields laser-induced periodic surface structures (LIPSS). The periodicity of the structures is equal to 268 nm, which is the wavelength of laser light divided by the refractive index of titanium. The LIPSS are attributed to the interference of the incident laser light with excited surface plasmon polaritons. This grooved pattern of the surface structures is expected for near-damage-threshold laser fluences and multiple laser pulses.

Chemical Selectivity

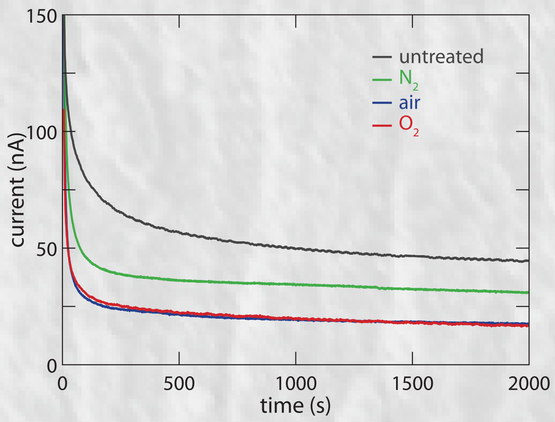
Samples irradiated in oxygen and air produce TiO_2, shown through the Ti^{4+} peaks in XPS (below right). Samples irradiated in N_2 incorporate nitrogen but are shown to be non-stoichiometric TiN. We demonstrate that oxygen and nitrogen incorporation exhibits chemical selectivity, meaning that we will not be able to dope TiO_2 with nitrogen using fs-laser irradiation.





Moving Forward

We hope to overcome the chemical selectivity with nitrogen by using other dopants, such as chromium and manganese, to make mixed metal oxides that will absorb visible light and split water more efficiently.



Using electrochemistry (right), we have also found that laser formed TiO_2 is more stable than untreated titanium in biologically relevant solutions, making femtosecond laser-structured titanium a good candidate for biomedical devices.

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