Femtosecond laser processing of titanium

Kasey Phillips
Beth Landis, Cynthia Friend & Eric Mazur
Harvard University

Hyperdoping Research Meetup 2011
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The periodic table shows elements arranged in groups and periods. The elements are categorized by their atomic number, electron configuration, and chemical properties. The table includes elements from Group I (alkali metals) to Group VIII (transition metals) and periods from Period 1 (He) to Period 7.
You can dope anything with anything.
You can dope anything with anything almost almost with anything.

Chemical selectivity matters
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Why TiO$_2$?
Why TiO$_2$?

UV

CB $\rightarrow$ e$^-$

VB $\rightarrow$ h$^+$

TiO$_2$ electrode

counter electrode

H$_2$O $\rightarrow$ H$_2$

H$_2$O $\rightarrow$ O$_2$

Graetzel, M. Nature (2001)
Why TiO$_2$?

Graetzel, M. Nature (2001)
Why TiO$_2$?

Graetzel, M. Nature (2001)
Why TiO$_2$?

![Graph showing the absorptance of TiO$_2$ across different wavelengths. The graph indicates that TiO$_2$ has high absorptance in the UV region and low absorptance in the visible and infrared regions.](http://bouman.chem.georgetown.edu/S02/lect23/lect23green.html)
Why TiO₂?

TiO₂ absorbance graph showing spectral irradiance (W/m²/nm) and wavelength (nm) with UV, visible, and infrared regions highlighted.

- UV: 5% absorbance
- Visible: 45% absorbance
- Infrared: 50% absorbance

Absorbance values at different wavelengths:
- 0.5 at 250 nm
- 0.4 at 500 nm
- 0.3 at 750 nm
- 0.2 at 1000 nm
- 0.1 at 1500 nm
- 0.05 at 2000 nm

Spectral irradiance peaks at different wavelengths:
- 2.5 at 250 nm
- 2.0 at 500 nm
- 1.5 at 750 nm
- 1.0 at 1000 nm
- 0.5 at 1500 nm
- 0.05 at 2000 nm

Additional information:
- http://bouman.chem.georgetown.edu/S02/lect23/lect23green.html
Produce structured TiO$_2$ surfaces using femtosecond laser processing

Dope TiO$_2$ with nitrogen and chromium

Improve photocatalysis of water at doped TiO$_2$ electrodes
Production of TiO$_2$
Production of TiO$_2$

- fs laser
- O$_2$
- Ti

800 nm
2.5 kJ/m$^2$
50 shots/area
Production of TiO$_2$ microstructures

untreated titanium

laser treated titanium
Production of TiO$_2$

structural data: XPS

Untreated titanium

Laser treated titanium

Binding energy (eV)

Relative counts (a.u.)

8 min sputter

Surface
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Chemical Selectivity

fs laser

N₂

O₂

Ti
Chemical Selectivity

Microstructures

Untreated

O2

Air

N2
chemical selectivity

structural data: XPS

relative counts (a.u.)

binding energy (eV)

O (1s)

Ti (2p)

O₂

air

N (1s)

N₂

untreated
Chemical Selectivity

structural data: XPS

![Graph showing binding energy vs. relative counts for different treatments of TiO₂ and Ti.](image)

- Ti 4⁺
- Ti 0

- Untreated TiO₂
- Untreated Ti
- O₂
- Air
- N₂
Laser fabricated doped TiO$_2$

Laser fabricated doped TiO$_2$

800 nm
2.5 kJ/m$^2$
50 shots/area
Laser fabricated doped TiO$_2$

structural data: XPS

![Graph showing XPS data for Cr (2p), Ti (2p), O (1s), and C (1s) binding energies with relative counts (a.u.) on the y-axis and binding energy (eV) on the x-axis. The graph compares data from 10 min, 20 min, and surface sputtering.]
Laser fabricated doped TiO$_2$

photocatalysis

UV-vis

spectrophotometer
Laser fabricated doped TiO$_2$

photocatalysis

- untreated Ti
- TiO$_2$
- TiO$_2$:Cr 6-10%

normalized absorbance

0 20 40 60

0 0.2 0.4 0.6 0.8 1.0

time (min)
Form nanostructured TiO$_2$ with laser processing

Cannot introduce N$_2$ into TiO$_2$ because of chemical selectivity

Control chromium doping but catalysis is not enhanced

Annealling could increase photocatalysis for laser doped TiO$_2$
Thank you!

Support provided by NSF Graduate Research Fellowship and Harvard Center for the Environment
Goal:

To transform semiconductor band structure to harvest solar energy
Laser fabricated doped TiO$_2$
Production of TiO$_2$

structural data: XPS

We have produced TiO$_2$ with laser processing
Laser fabricated doped TiO$_2$ microstructures

- 0 nm Cr, no doping
- 10 nm Cr, 7% Cr-doped
- 70 nm Cr, 30% Cr-alloy
Chemical Selectivity
Laser fabricated doped TiO$_2$ photocatalysis

![Graph showing normalized absorbance over time for different samples.](image)

- untreated Ti
- TiO$_2$
- TiO$_2$:Cr 6-10%