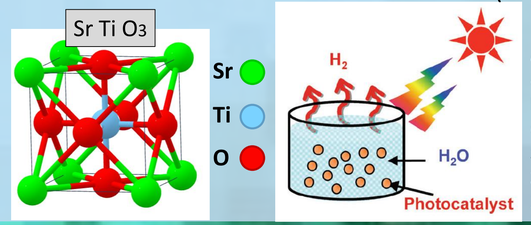
Dopant Distributions for Visible Light Absorption in Photocatalytic Nanoparticles

Blake Dorame, Materials Science Engineering
Mentor: Peter A. Crozier, Piyush Haluai
School for Engineering Matter, Transport & Energy

How are Rhodium Dopants Distributed in Strontium Titanate Nanoparticles?

Application

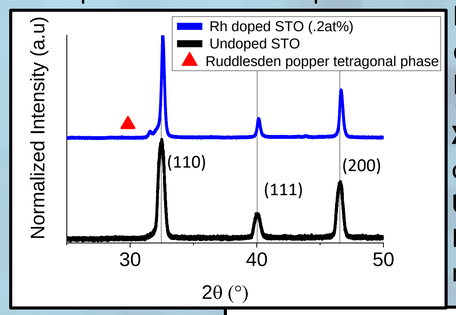
Renewable hydrogen fuel can be produced using a photocatalytic reaction, in which strontium titanate (STO) splits water molecules using sunlight. Higher reaction efficiencies can be achieved by doping the STO with low concentrations of Rhodium (.2at%).



A. Kudo & Y. Miseki. *Chem. Soc. Rev.* **2009**, *38*, 253-278.

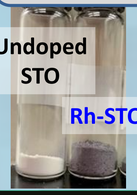
Macroscopic Characterization

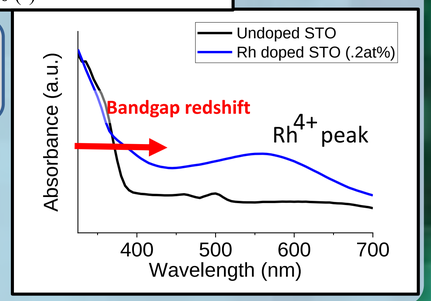
XRD and UV-vis are techniques used to reveal the cubic crystal structure and light absorption properties of both doped and undoped STO samples. On a macroscopic level the Rh appears to be successfully doped into the lattice.



XRD: No Rh oxide is present
UV-vis: Bandgap has redshifted

Bandgap
3.2eV **2.7eV**
Kawasaki et al., 2012

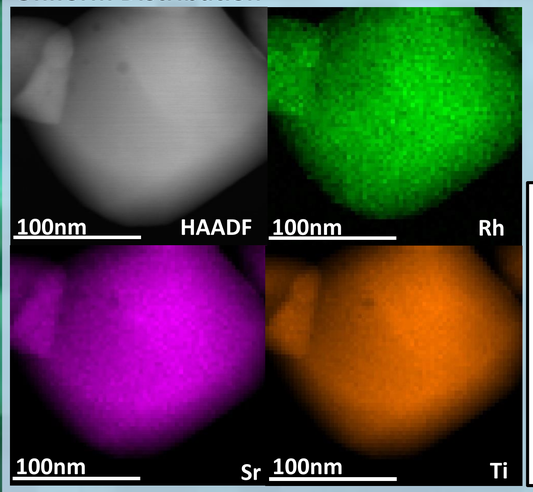




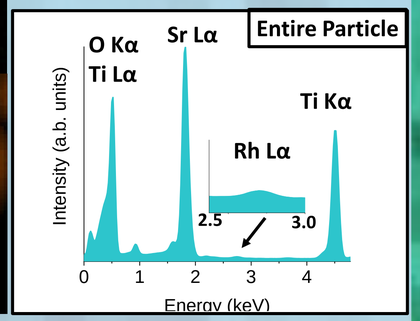
Scanning Transmission Electron Microscopy

STEM-EDS is a spatially resolved spectroscopy technique used for determining the composition of individual Rh doped STO nanoparticles. This allows us to look at doping profiles and search for compositional heterogeneities.

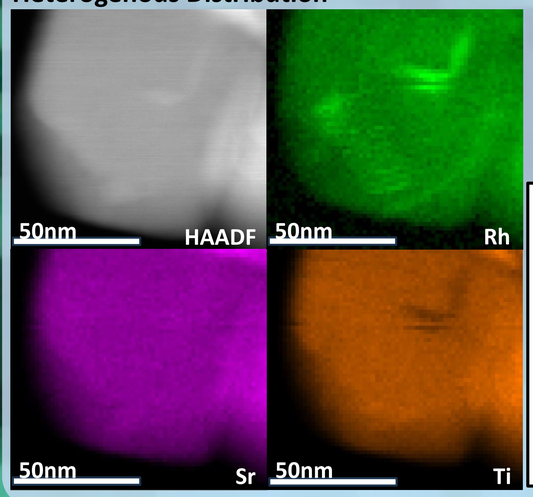
Uniform Distribution



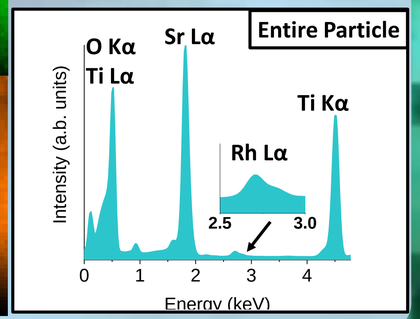
The summed EDS spectra shows how little Rh signal is generated due to the low doping concentration (.2at%).



Heterogenous Distribution



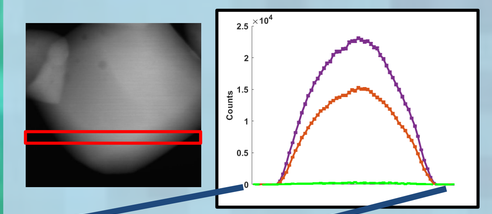
Rh & Ti element maps display a heterogenous site where Rh largely substitutes for Ti atoms in the lattice.

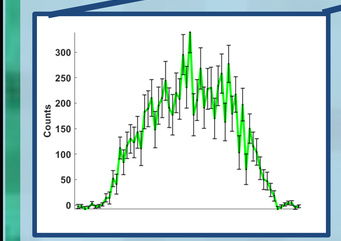


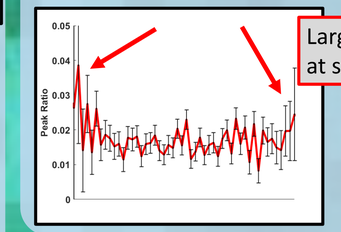
Quantifying Error

An error bar analysis performed on compositional line profiles quantifies the limitations of detecting variations in trace amounts of Rh near the surface and in the bulk of the particle.

Uniform Distribution

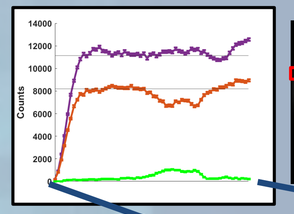


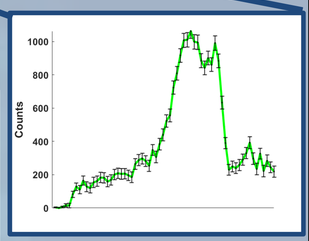


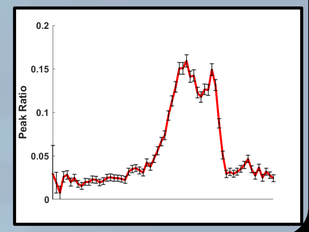


Large error bar at surfaces

Heterogenous Distribution



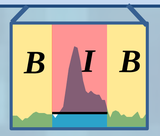




Sr Rh
Ti Rh:Ti

Primary source of error is a result of signal counting based on Poisson statistics.

Error Bar = $\pm\sqrt{I + 2B}$



Taking the ratio of Rh:Ti normalizes the Rh signal to reveal relative concentration.

Conclusions

- Within the one sample, individual nanoparticles of Rh-STO can possess uniform doping or exhibit heterogenous features on the nanoscale.
- Error analysis on the element profile displays sufficient precision to confidently identify the presence and composition of a secondary phase within a 25nm feature.
- An accurate assessment cannot be made on the Rh concentration at the surface of the particle due to large error bars in the Rh:Ti signal, a consequence of low doping concentration.

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Ira A. Fulton Schools of Engineering
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