Photoconductivity in Rare-earth Doped Nanocrystalline Titanium Dioxide

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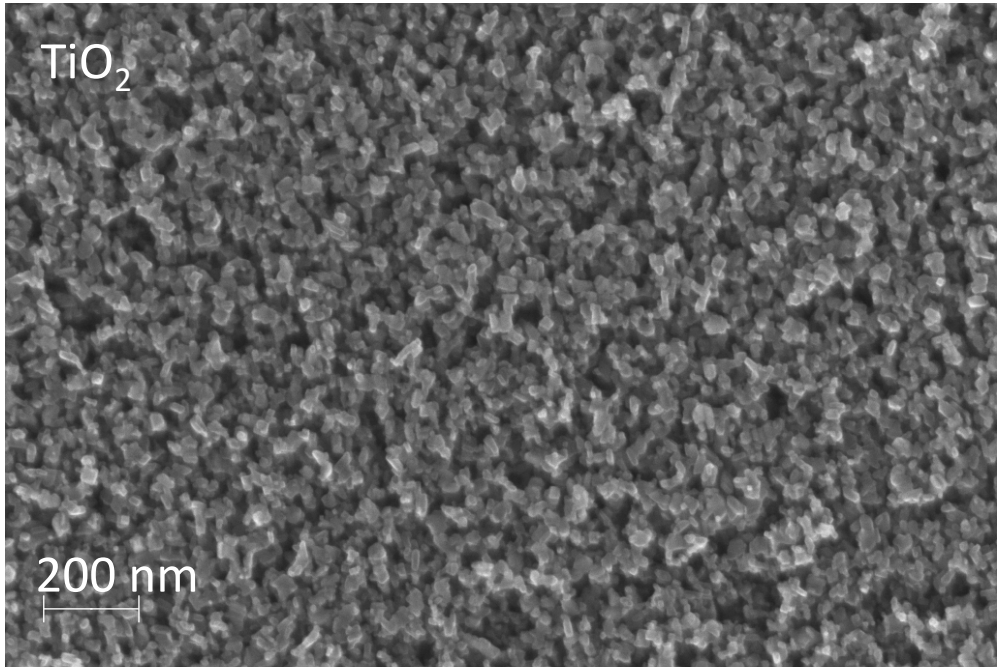
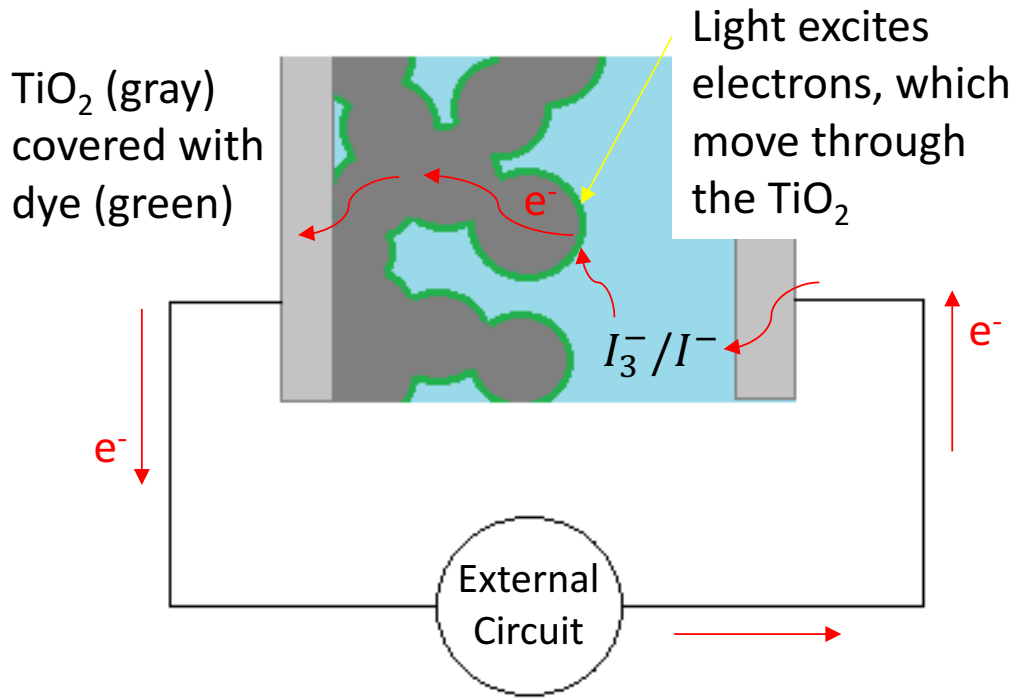
Applications of TiO_2

- Titanium dioxide (TiO_2, top) is commonly used in dye-sensitized solar cells (DSSC) as an electron transport layer
  1. Light excites electrons in dye
  2. Electrons move through TiO_2
  3. Electrons pass through external circuit to generate power
- Important to have fast, unimpeded electron transfer for high solar cell efficiencies
  - Avoid recombination

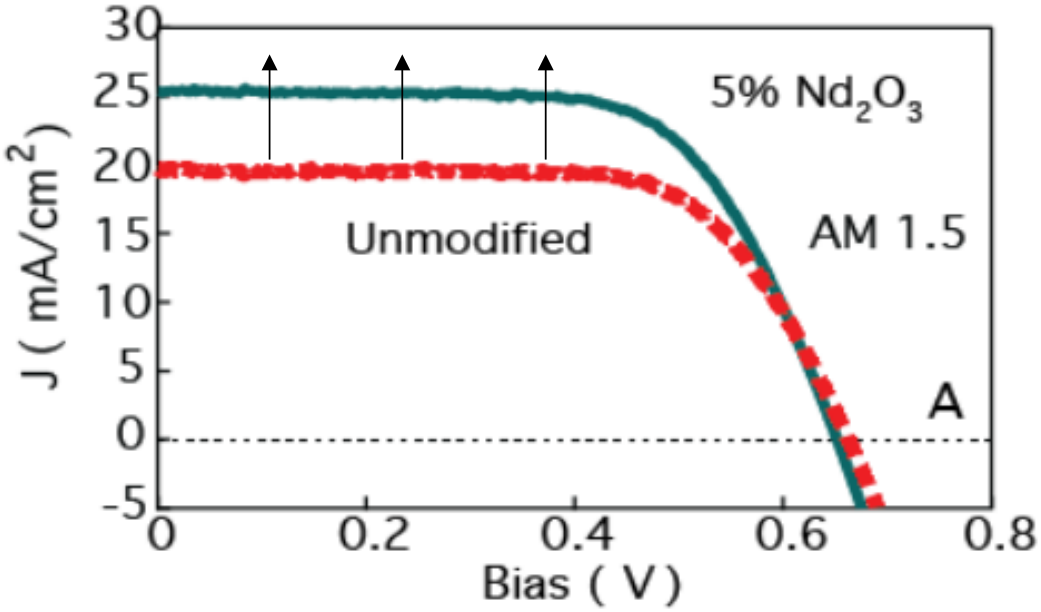




Doping TiO_2 with Rare-earth Oxides

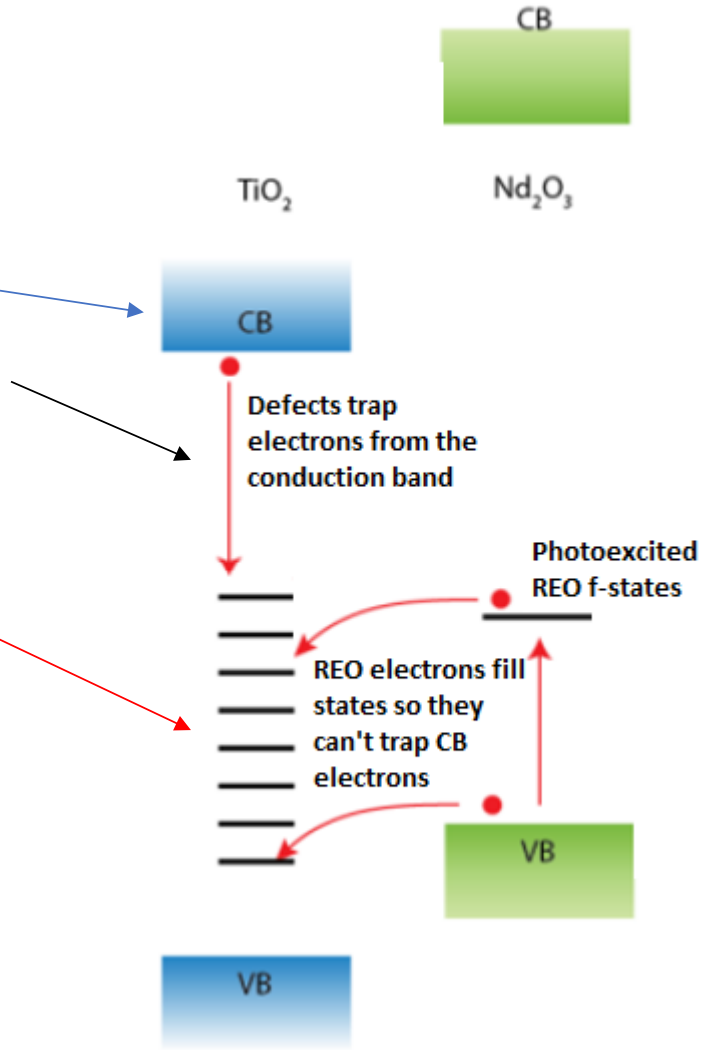
- Doping TiO_2 with rare-earth oxides improves:
  - DSSC efficiency by 20-30% (right) and
  - Conductivity by 40-50 times
    - Related to how fast electrons can travel
- The goal of this project is to understand why the conductivity increases
  - Optimize the doping process to achieve even higher efficiencies
  - Apply the process to similar materials and applications

Doping increases the current generated by the DSSC, leading to higher efficiencies



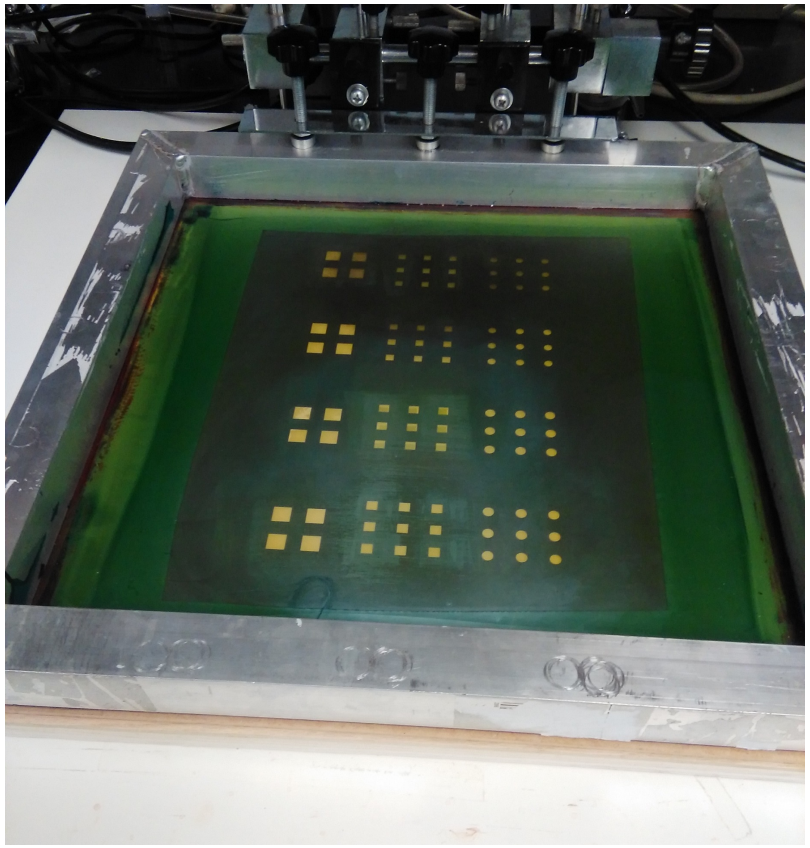
What Causes the Increase in Conductivity?

- For an electron to move freely though the TiO_2, it needs to stay in the conduction band (CB)
- Grain boundary and surface defects create available energy states that trap electrons from the CB, reducing conductivity and solar cell efficiency
- Rare-earth oxides may donate electrons to
  1. Fill trap states so they can't trap CB electrons
  2. Create new states with different properties
- Look for changes in trap state energies or kinetics
  - Cyclic voltammetry

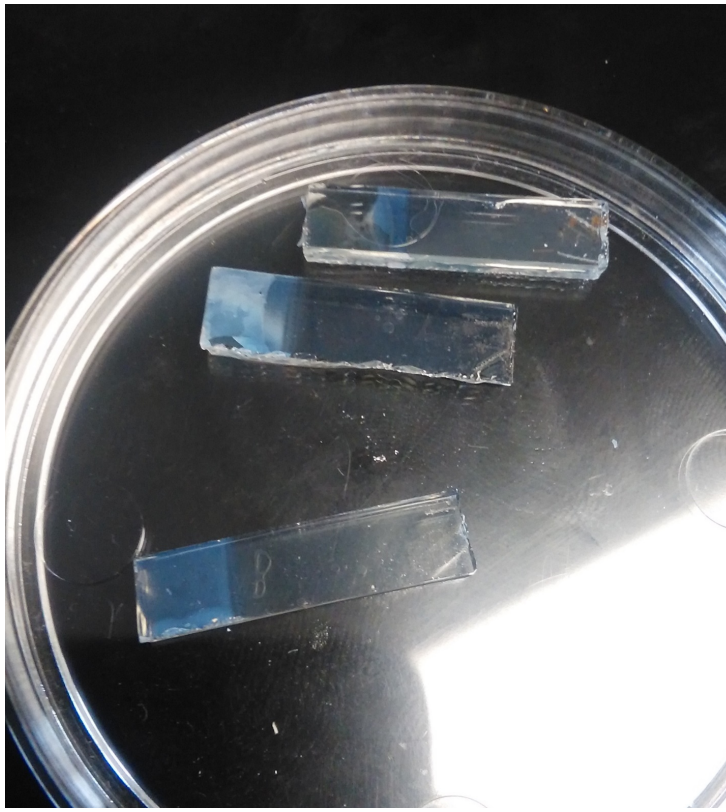


Sample Preparation

- Prepare TiO_2 thin film electrodes
- Screen print TiO_2 paste on FTO slides (left)
  - Mix in rare-earth oxide nanoparticle powders to create doped pastes
- Sinter at 500 °C



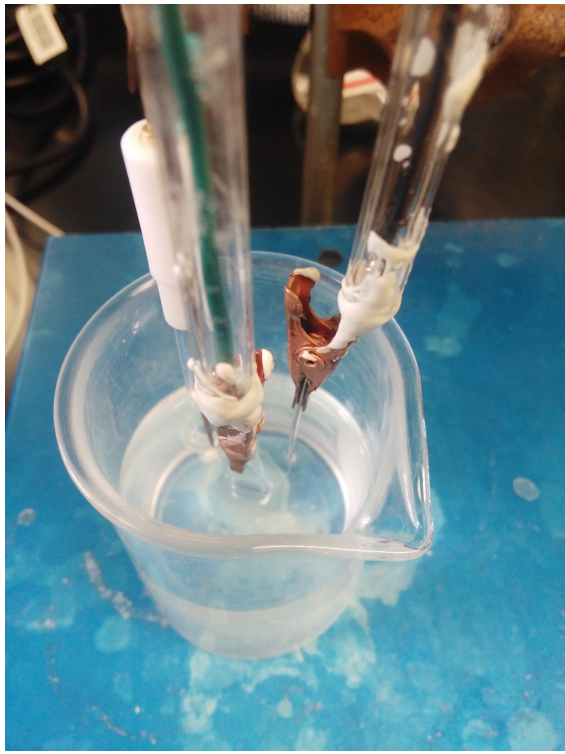
Screen printer

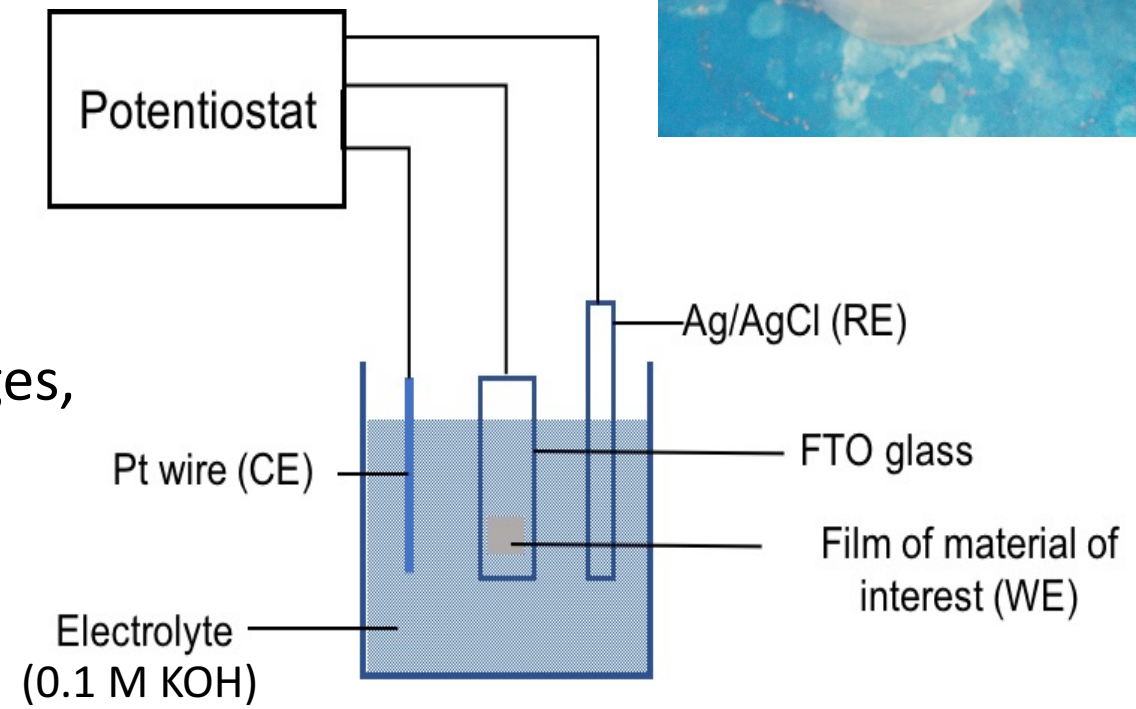


Prepared 2 x 0.5 cm samples

Cyclic Voltammetry Measurements

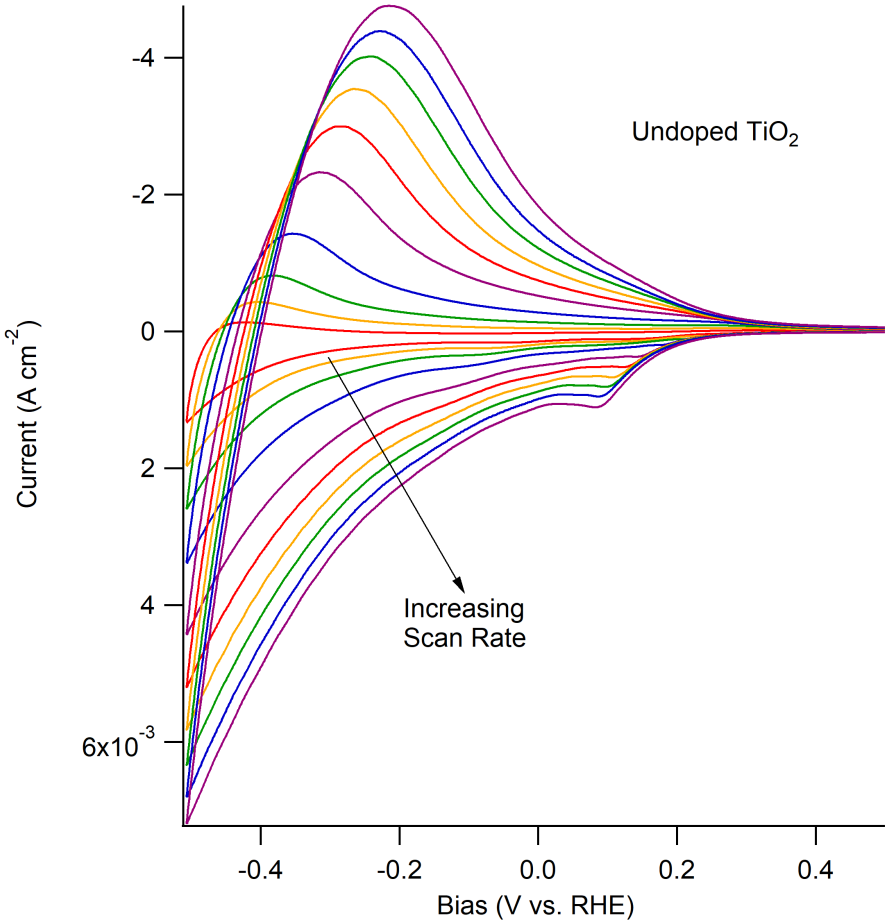
- 3-electrode setup
  1. Prepared sample as working electrode (WE)
  2. Ag/AgCl reference electrode (RE)
  3. Platinum wire counter electrode (CE)
  - 0.1 M KOH electrolyte
- Cyclic Voltammetry (CV)
  - Apply voltage across WE and RE
  - Measure current through WE to CE
  - Sweep from positive to negative voltages, then back again to reset the device for successive measurements



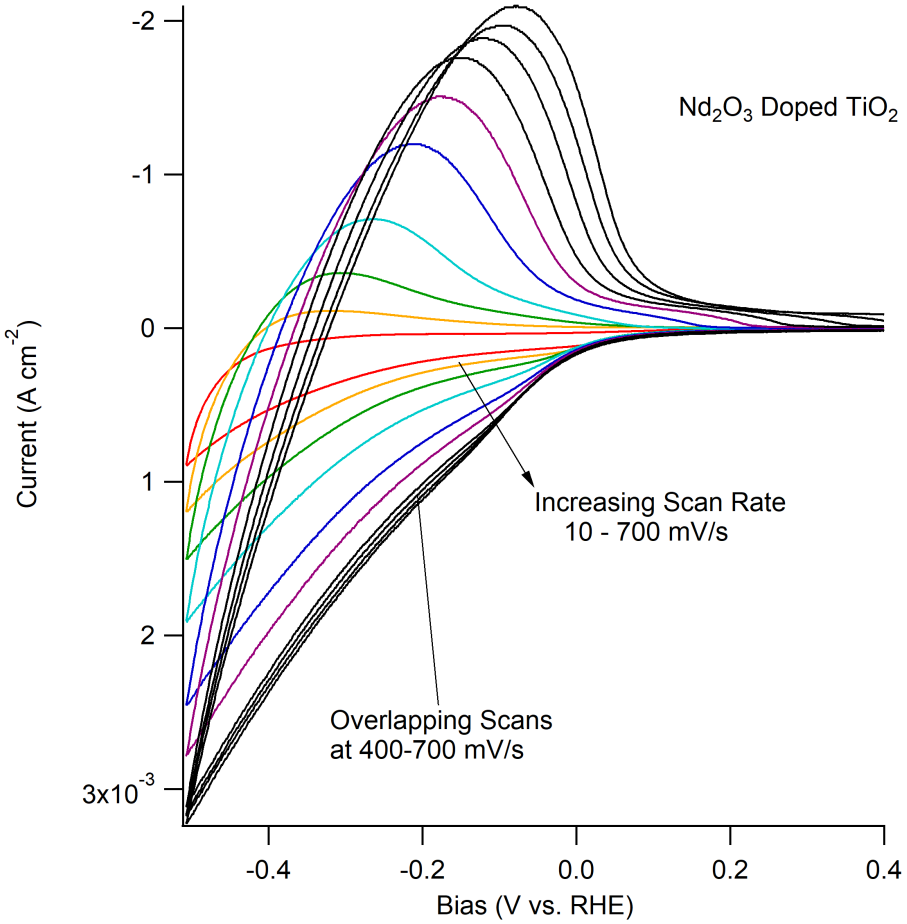


- Current should increase with faster scan rates
- In doped samples, current curves start to overlap at a scan rate of 400 mV/s
  - Happens because the scan rate is too fast for traps to completely fill
  - Doesn't occur in undoped TiO_2 until 800 mV/s
  - Suggests slower trapping rates

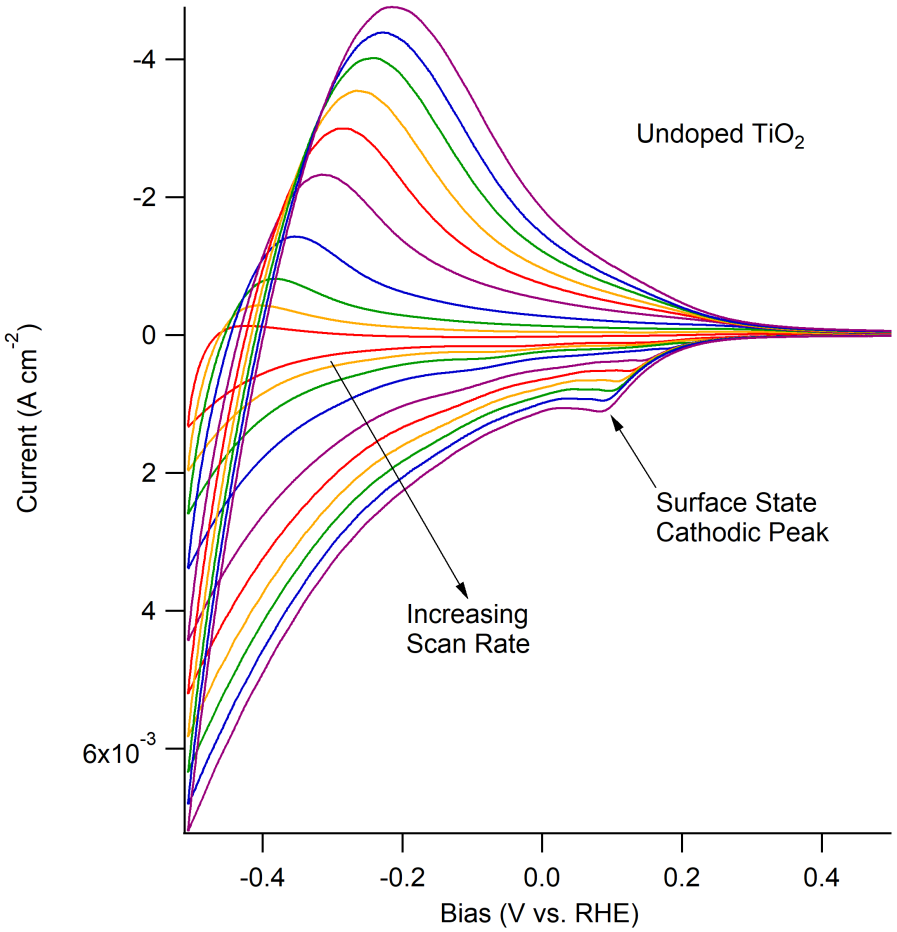
CV scans of undoped TiO_2, showing how the curves generally look as the scan rate is varied

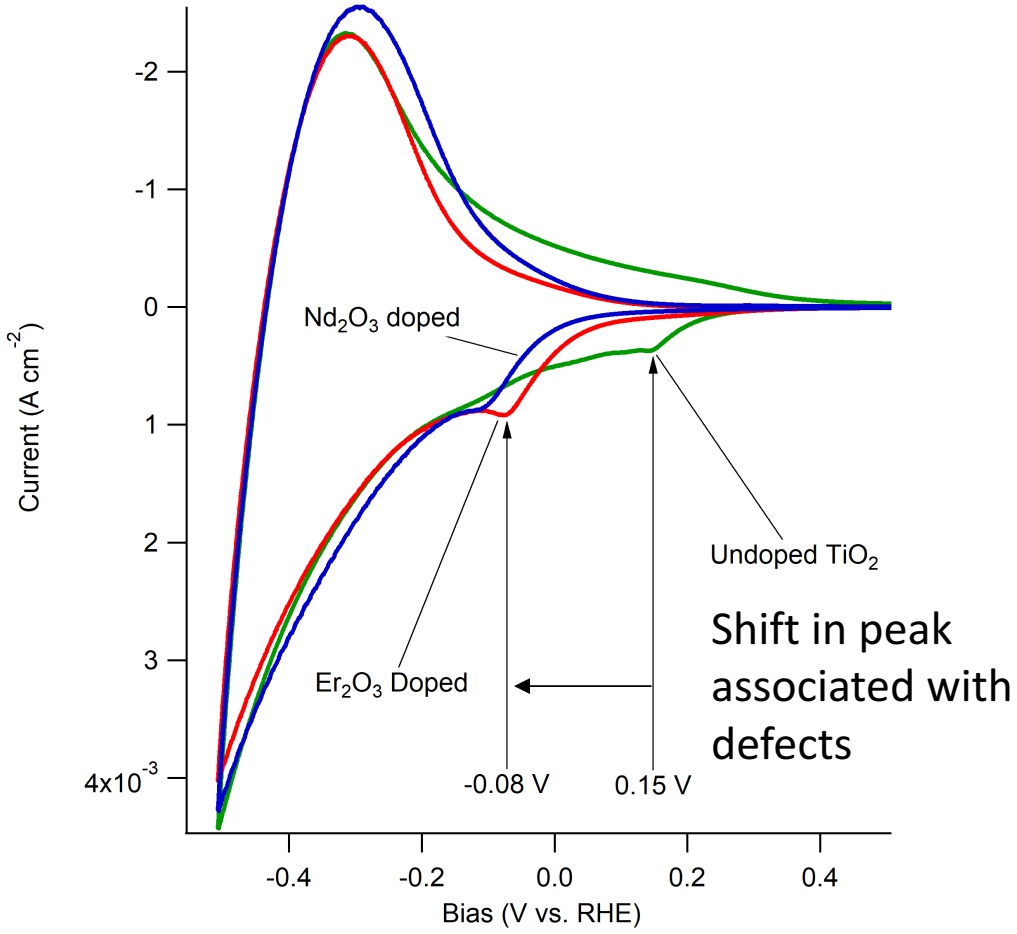


CV scans of REO doped TiO_2, showing overlapping scans that indicate slower trapping rates

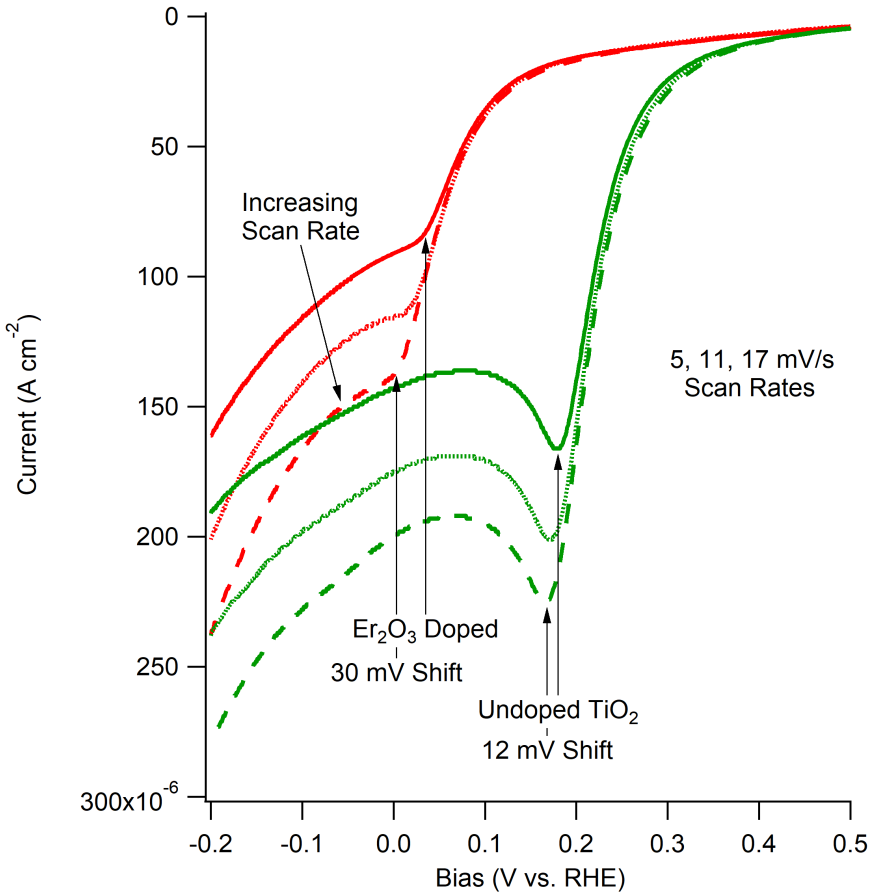


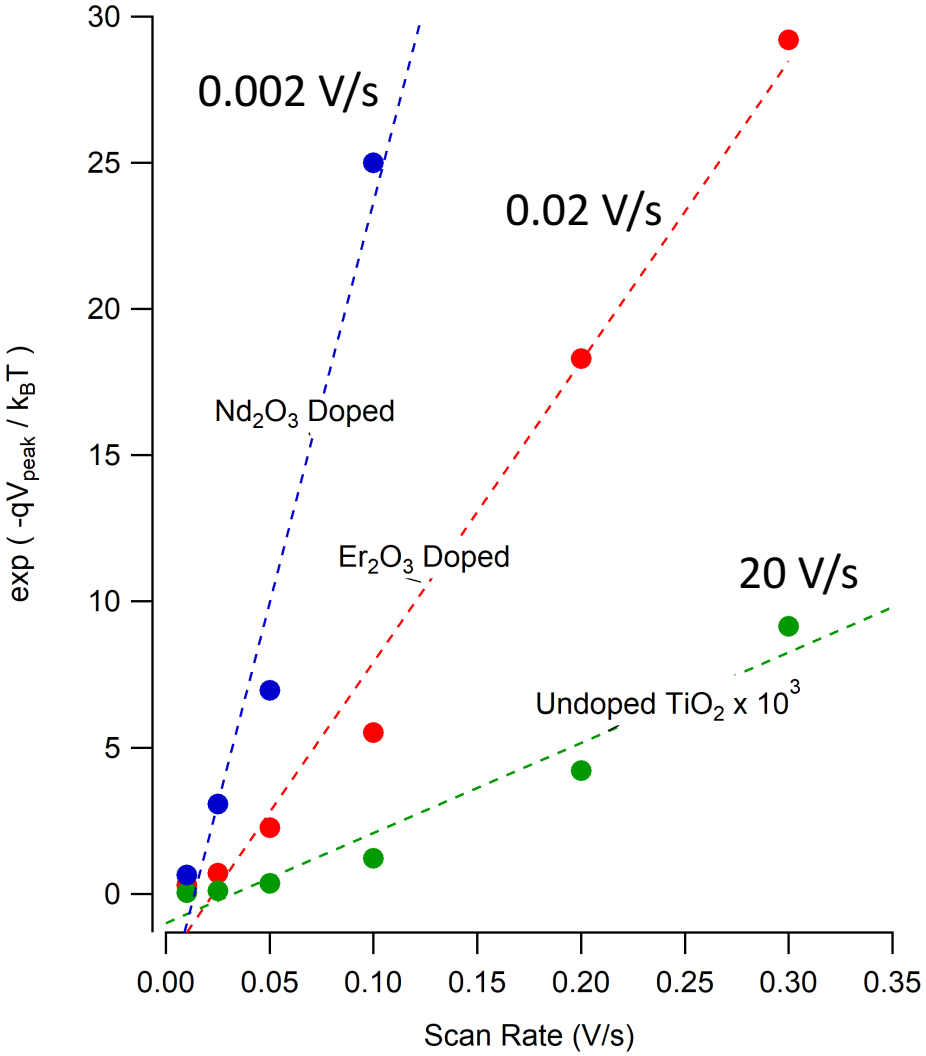
- Other feature of interest is the peak associated with surface defects
- The peak shifts after doping
  - Suggests average trap energy increases, i.e. traps are “shallower” and less likely to cause recombination





- Peak location also changes depending on the scan rate
- Peak location is more sensitive to changes in scan rate after doping (left)
  - Calculations show trapping rates are significantly slower (right)





Conclusions

- CV measurements suggest:
  - Trap states are at higher energies
    - Rare-earth oxide electrons fill traps below and create new vacancies at higher energies
  - Trapping rates are slower
    - New electron vacancies are less accessible
- Slower trapping rates would contribute to the observed higher conductivity and solar cell efficiency, since they give electrons more time to move through the TiO_2 without being trapped
- Use electrochemical impedance spectroscopy to verify our cyclic voltammetry results and correct for solution resistance

Acknowledgements

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