Localized Imaging and Light-driven Enhancement of Water-splitting Catalysts

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Motivation

- Photovoltaic solar energy conversion alone only provides power while sun shines
- Instead, store solar energy in H₂ chemical bonds by splitting water on immersed semiconductor photoelectrodes
- Electrode/electrolyte interface details and surface features govern performance
- Traditional measurement techniques average reaction rate over all surface features

Goal: Image and enhance reactivity of various surface features on a water-splitting electrode surface.

Experimental method: Image bubbles formed during water photoelectrolysis to measure the local gas evolution rate. Alternatively, avoid bubbles and instead image pH across the electrode surface using fluorescence.

Possible interesting nanostructure:

**Plasmonic enhancement of water-splitting catalysts**

Collective oscillation of electron gas in metallic nanostructure (localized plasmon) gives rise to high local electric fields that could increase electrocatalytic activity.

**Plausible enhancement mechanisms:**
- Direct electron transfer of hot electrons excited by plasmon decay
- Localized heating to increase reaction rate
- Desorption or polarization of reaction intermediates

Experimental approach: Create plasmonic "antennas" to create high fields in gaps where catalyst resides.

Photoanode Bubble Analysis

Strontium titanate (SrTiO₃) used as a model semiconductor photoanode material due to favorable band edge positions, stability, and commercial availability of single-crystal (100) substrates.

- Dope crystal n-type by annealing in forming gas at 1000 °C
- Bubble evolution recorded on a video camera attached to microscope

Results on (100) Single-Crystal SrTiO₃

**Photovoltaic solar energy conversion** alone only provides power while sun shines. **Decouple plasmon resonance from catalyst choice.**

**Catalysts placed in gaps between Au squares may show increased activity when array illuminated at its resonance wavelength.**

**Simulation:** Using finite-difference time domain (FDTD) method.

**Field enhancement in gaps:**
- Average ~10
- Peak ~200

**Spectra:** Dip in reflectance indicates resonant wavelength with highest average field enhancement in gaps.

**Conclusions**

- Optical microscopy of photogenerated bubbles provides a quantitative measure of gas evolution.
- Presence of bubble could block possible sites of study due to gas/solid interface. Fluorescence method avoids bubble issues.
- Plasmonic antenna arrays show resonance with high fields in gap regions. Future work: test water-splitting catalysts with arrays.

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