Role of Ultrafast Charge Dynamics in Photocatalytic Water Oxidation

Nanotek, December 2014

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Transient Optical, Infrared Spectroscopy

Heterogeneous Catalysts

Controlling Charge Flow

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{FUEL} + \text{O}_2 \]
Water Oxidation Catalysts: Transition Metal Oxides

\[ 4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \quad E_0 = 0.6 \text{ V vs. Ag/AgCl} \]

Hydroxilated Surfaces

Robust Catalysis

Bluhm, Salmeron, Nilsson et. al.,

- Efficient and Sustainable Catalysis on TM Oxide Surfaces
- Hydroxilated surfaces common to TM Oxide Surfaces
Heterogeneous Catalysis

Helmholtz Double Layer

Dynamic Catalytic Surface

Suggested First Hole Transfer (t=0):

\[ [h^+] + [OH^-] \longrightarrow [OH^*] \]

Activation Barrier thru Transient Spectroscopy
Challenges in Applying Ultrafast Spectroscopy to Catalysis

- Interplay of recombination and interfacial charge transfer
- Sensitivity to the surface
- Studying hetero-junctions (solid-solid, solid-liquid)
- Multi-electron transfer processes and “clocking” the cycle
Strategy and Techniques

Transverse Optical Reflectance
Transverse Diffraction Gratings
Transverse Infrared Spectroscopy

Light Pulses → Charge Injector + Catalyst

Counter Electrode

Reference electrode

Working electrode

Pump: Optical
Probe: Optical, Infrared

Detector

Charge Injector + Catalyst
### Catalysts & Devices Under Investigation

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![Diagram](image-url)
Photo-electrochemistry of n-SrTiO$_3$

High Quantum Efficiency with 1 kHz Laser ($W \sim \alpha$)

- Single 150 fs Pulse Triggers Multi-electron Transfer Water Oxidation
- Achieve high quantum efficiency (75%) under laser excitation
Transient Reflectance of n-SrTiO$_3$

Pump Band Gap, Probe Holes

Surface Sensitivity Thru Reflectivity

Experimental conditions needed to probe $k_{CT}$, [h] :

$$W = \alpha_{PUMP} = \alpha_{PROBE}$$

Width of Electric Field at High Q.E.:

$W \sim 25$ nm

Pump Band Gap (300 nm, 4 eV):

$$\alpha = \frac{\lambda}{4\pi k} \sim 24 \text{ nm}$$

Probe Hole Absorption (800 nm, 1.5 eV):

$$\alpha_{REFL} = \frac{\lambda}{4\pi n} \sim 27 \text{ nm}$$
Interfacial Charge Transfer

SrNb$_{0.001}$TiO$_3$ (0.1%)

SrNb$_{0.007}$TiO$_3$ (0.7%)

$W = 25$ nm \& $\alpha_{\text{pump}}, \alpha_{\text{probe}} \sim 24$ nm

$W = 9$ nm \& $\alpha_{\text{pump}}, \alpha_{\text{probe}} \sim 24$ nm

Change in kinetics reflects $k_{\text{CT}} [\text{h}]$
Manipulating Interfacial Charge Transfer

- Interfacial charge transfer rate increases with increasing oxidative voltages
- Rate changes while current and quantum efficiency constant
Kinetics (V)

- Kinetics are fit to a single exponential at early time scales
- Rate constant depends exponentially on applied V (Arrhenius Law)

Voltage Distribution at the Surface

- Since the solution potential is invariant, changes in $U_H$ are tied to changes in the valence band edge potential, $\phi_{BE}$

- Changes in $U_H$ (Helmholtz Voltage) by applied $U$ determined by capacitances at n-type SC/liquid interface

$$U_{FB} + U = U_H + U_{SC}$$

$\phi_{BE} =$ surface hole potential

$U =$ applied voltage
$U_H(V)$: Changing Surface Hole Potential

1. $U + U_{FB} = U_H + U_{SC}$

2. $U_H = (q_{sc} + q_{photo}) / C_H$

$U_H(0) = 0.65 \text{ V}$ give $C_H = 21 \mu\text{F/cm}^2$

$n$-SrTiO$_3$ | Electrolyte

$\phi_{O_2/\text{OH}^-}$ | $\eta(V)$

$U_H(V)$ | $\phi_{BE}(V)$

$C_H = 21 \mu\text{F/cm}^2$

$\eta(V)$

$0.045 \text{ mJ/cm}^2$
$0.065 \text{ mJ/cm}^2$

Brockeris, Bard, Bocarsly
Activation Barrier of First Hole Transfer

The diagram illustrates the reaction:

\[ [h^+] + [OH^-] \xrightarrow{k} [OH^*] \]

with the parameters:

- \( \alpha = 0.2 \pm 0.05 \)
- \( k_0 = 7 \times 10^{-7} \text{ ps}^{-1} \) (\( \mu \text{s} \))
- \( \phi_{OH^-/OH^*} = 1 \text{ V vs. SCE} \)
- \( e_0 \Delta U_H(V) = 1 \text{ V vs. SCE} \)

[From Photoemission, 1.2 V]

Quantifies barrier to localizing VB hole onto a molecular O2p bond.
Conclusions

• Quantified interfacial charge transfer at n-type semiconductor/liquid interface

• Activation barrier ($\alpha, k_0$) for first hole transfer of water oxidation reaction in n-SrTiO$_3$

Next Steps

• Next step on n-SrTiO$_3$: concomitant intermediates using ultrafast infrared spectroscopy

• Investigate lower over-potential catalysts, and other n-type semiconductors stable in aqueous solutions (e.g. GaN)
Acknowledgements

**Graduate Students**
Hoang Doan
Stephanie Choing
Kevin Pollack
David Herlihy
Xihan Chen
Jonathon Radberg
Aayush Singh (Undergraduate)
Joseph Mosley (Volunteer)

**Postdoc**
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**Funding**

[Image of U.S. Department of Energy logo]

CPIMS Program

AFOSR Young Investigator (Co₃O₄)
Possible Intermediate Species Formed

\[ [h^+] + [\text{OH}^-] \rightarrow [\text{OH}^*] \rightarrow [-\text{OOH or -OOTi}] \]

- -OOH is a likely intermediate: ms-FTIR (Frei)
- Single rate constant \(k_1\) implies a highly populated –OOH surface?
- Probe nature of \(\text{OH}^*\) (or \(\text{O}^*\)) as surface trap (transient XAS)
Ultrafast Transient IRRAS

- Small molecule rotations/bindings (-SCN, -NCS)
- Reaction Intermediate Rise Times
- Effects of surface potential/electric field vs. charge transfer
Transient Grating Diffraction

\[ \Delta I/I = R(t)\cos(\varphi(t)) + TG(t)\cos [\Psi - \varphi(t)] \]

Recombination \( (t) = R(t)\cos(\varphi(t)) \)

Diffusion \( (t) = \varepsilon(t) = TG(t)/R(t) = \exp\left(-Dq^2/t\right) \)

Heterodyne Detection: \( TG(t), R(t), \varphi(t) \) determined by varying \( \Psi \), probe-ref phase

(1) pump split into two pulses
(2) time-delayed probe split into two pulses
(3) Pulses are collimated between two lenses and focused onto sample
(4) Diffracted and reference pulses are reflected to detector
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**Transient Reflectivity on Hetero-junctions**

- Charge separation spatially separated from hole injection into catalyst
- Ultrafast charge injection (~ 10 ps) unimpeded by slow diffusion kinetics
- Can recombination kinetics in GaAs & hole kinetics in Co$_3$O$_4$ be separated in a transient reflectivity experiment?
• Surface sensitivity of $\Delta R$ w/ 400 nm probe
• Strong signal of surface holes with catalyst
• Time delay for hole injection (~10 ps)
• Kinetics vary w/ catalyst type
• Also with deposition technique
• Reproducibility for same batch

Kinetics of Holes in Catalyst Over-layer

- GaAs 800 nm, Bulk Recombination
- GaAs 400 nm, Surface Holes
- Co$_3$O$_4$ ALD 400 nm, Surface Holes

~0.5 mJ/cm$^2$

x 0.03
Hole Carriers as an antenna to THz?

- 0.8 THz (& w/ 0.4 THz) signal generated from catalyst over-layer, independent of catalyst type
- Strength and decay of THz signal depends on catalyst type and deposition technique
- Potentially, mobile holes responding to THz in GaAs that decay to surface trapped states

**THz Generation**

**THz Antenna**

Plasma frequency of p-dopants responding to $\Delta E$ field

Free Carriers Injected in Catalyst Responding to THz field

Effects of Electrolyte?
Conclusions

• Activation barrier ($\alpha, k_0$) for first hole transfer of water oxidation reaction in n-SrTiO$_3$

• Next steps n-SrTiO$_3$: (1) concomitant intermediates using ultrafast infrared spectroscopy, (2) transient diffraction gratings for interfacial hole diffusion

• Ultrafast photodiode for low over-potential catalysts: dynamics of charge-separated carriers at electrolyte interfaces
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AFOSR Young Investigator (Co$_3$O$_4$)
Reaction via surface hole (valance band oxygen)

\begin{align*}
\text{(1)} & \\
\text{(2)} & \\
\text{(3)} &
\end{align*}
Reaction via hot hole
(surface axial oxygen)
1. SrTiO₃ has a lattice constant of a=3.905Å
2. (1,0,0) surface for SrTiO₃ is cubic, which looks like the graph on the right
3. Each (1,0,0) lattice has 3 surface atoms (1 Ti, 2 O)
4. Therefore, each lattice has area of A=a²=1.525*10⁻¹⁵ cm²
5. Surface atom density=# of atoms on one lattice surface/lattice surface area
   So, surface atom density= 3/1.525*10⁻¹⁵ cm² = 1.967*10¹⁵ atoms/cm²
Voltage Distribution (Dark, Equilibrium)

Mott-Schottky: \( U_{\text{FB}} = 1.6 \text{ V} \)

Photo-Voltage: \( U_{\text{OC}} = U_{\text{SC}} = 0.85 \text{ V} \)

- Photo-voltage at open circuit roughly half of \( U_{\text{FB}} \)
- \( U_{\text{H}} = 0.65 \text{ V} \) in the dark, at equilibrium (no applied U)
• Photo-induced holes at interface create an interfacial p-type layer

• This interfacial “carrier inversion” changes $U_H$, even with no applied $U$
SEM images a)-d) show damage on 0.1% Nb doped SrTiO3 under laser and applied bias condition

1. SEM image shows laser burned holes on sample surface, most of the holes have 5um as diameter while some big holes have 10um as diameter
2. No damage is observed if only laser is applied to our sample, damage happens when current is running through the sample and laser is applied.
3. Laser spot size is 500um(FWHM) but the peak is narrow around 10um
4. One possible mechanism for the damage is coulomb explosion where high density of excitons generated by laser accumulate at sample surface causes explosion
Water Oxidation & Over-Potential

How do the surface dynamics modify the kinetic barriers and thermodynamics of each intermediate in the cycle?

Thermodynamic potential, High kinetic barriers
~ 0.01 O₂ /site-sec

High over-potential, Lower kinetic barriers
~10’s O₂ /site-sec

Reaction Coordinate