Role of Ultrafast Charge Dynamics in Photocatalytic Water Oxidation

Nanotek, December 2014

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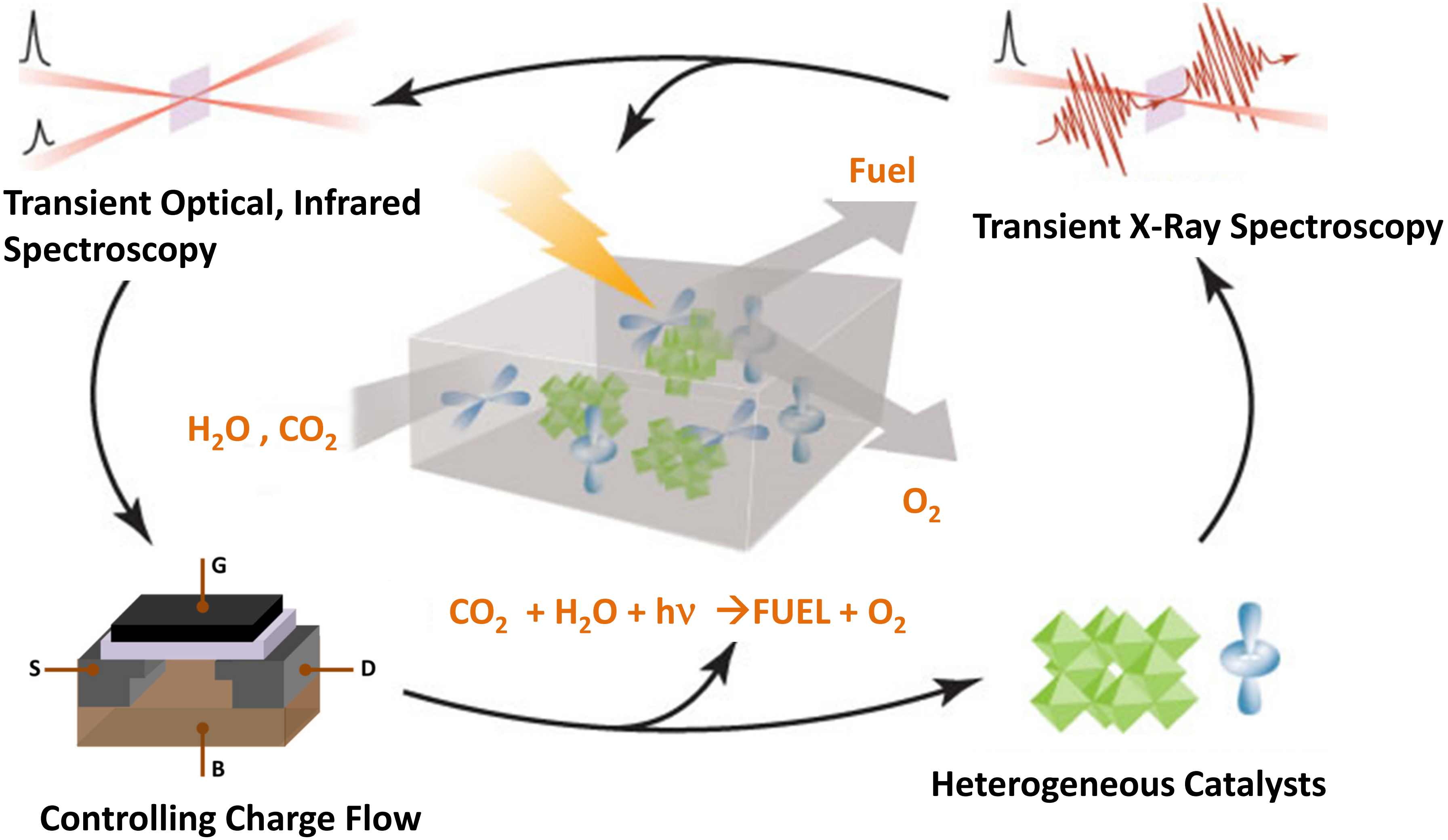
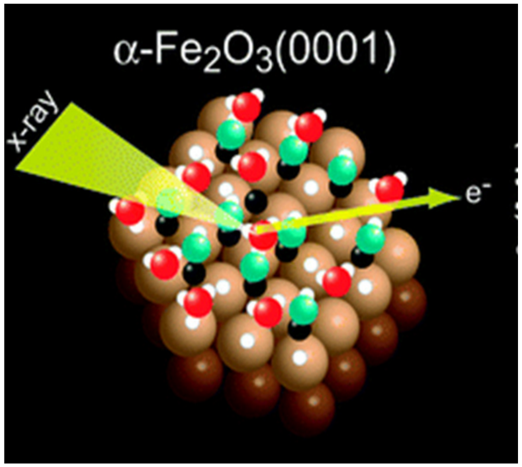

Transient Optical, Infrared Spectroscopy
Fuel
Transient X-Ray Spectroscopy
H_2O , CO_2
O_2
G
S
D
B
$CO_2 + H_2O + h\nu \rightarrow FUEL + O_2$
Controlling Charge Flow
Heterogeneous Catalysts

Water Oxidation Catalysts: Transition Metal Oxides

$4h^+ + 2H_2O \longrightarrow O_2 + 4H^+ \qquad E_0 = 0.6\ \text{V vs. Ag/AgCl}$

Hydroxilated Surfaces



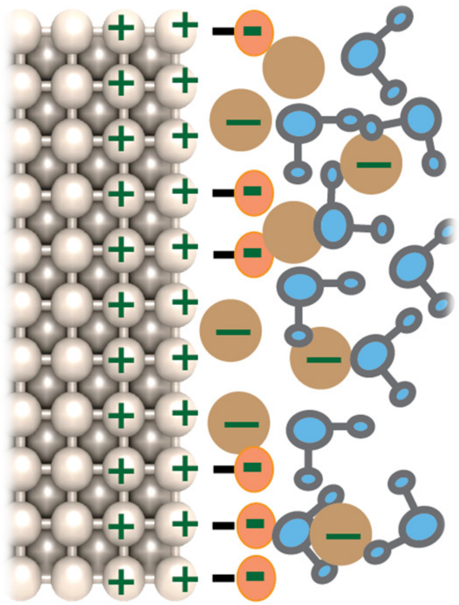
Bluhm, Salmeron, Nilsson *et. al.*,
J. Phys. Chem. C (2010)

Robust Catalysis

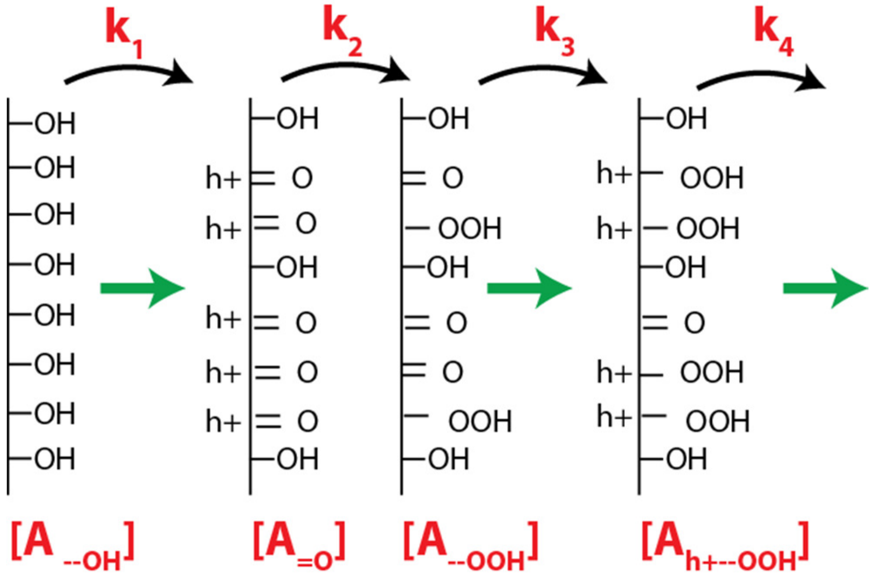
- Efficient and Sustainable Catalysis on TM Oxide Surfaces
- Hydroxilated surfaces common to TM Oxide Surfaces

Heterogeneous Catalysis

Helmholtz Double Layer



Dynamic Catalytic Surface



Suggested First Hole Transfer (t=0):

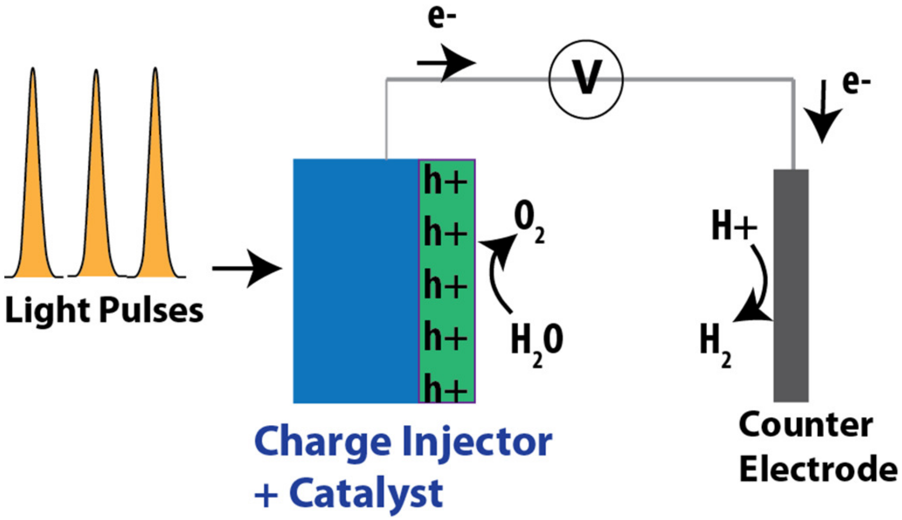
$$[h+] + [OH^-] \longrightarrow [OH^*]$$

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**

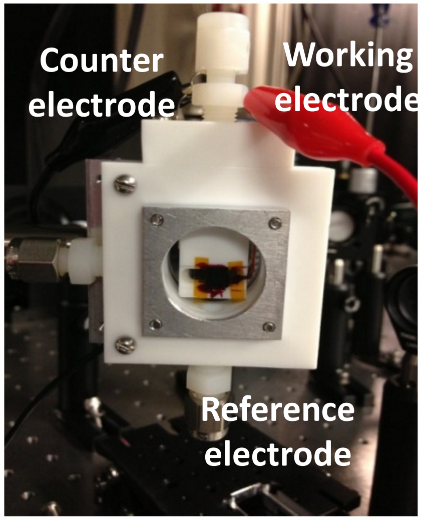
Strategy and Techniques

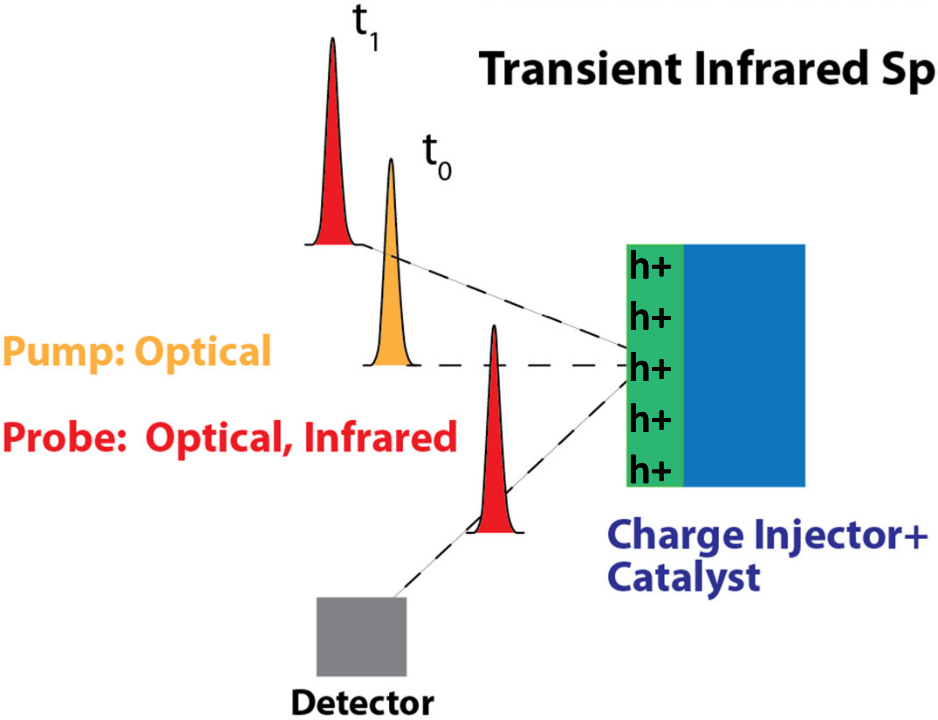


Transient Optical Reflectance

Transient Diffraction Gratings

Transient Infrared Spectroscopy

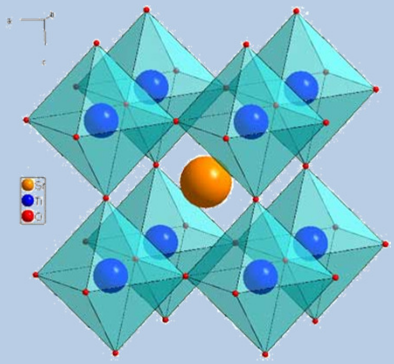




Catalysts & Devices Under Investigation

n-type SC/Liquid
Schottky Barrier

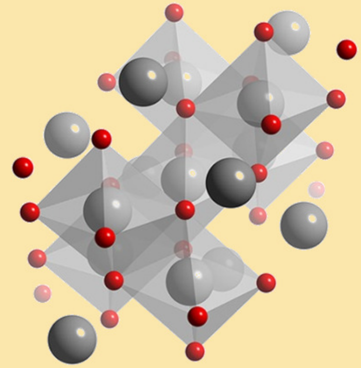
10 O_2/site-s



n-$SrTiO_3$, High Over-Potential

n-p GaAs photodiode/Co_3O_4
Hetero-junction

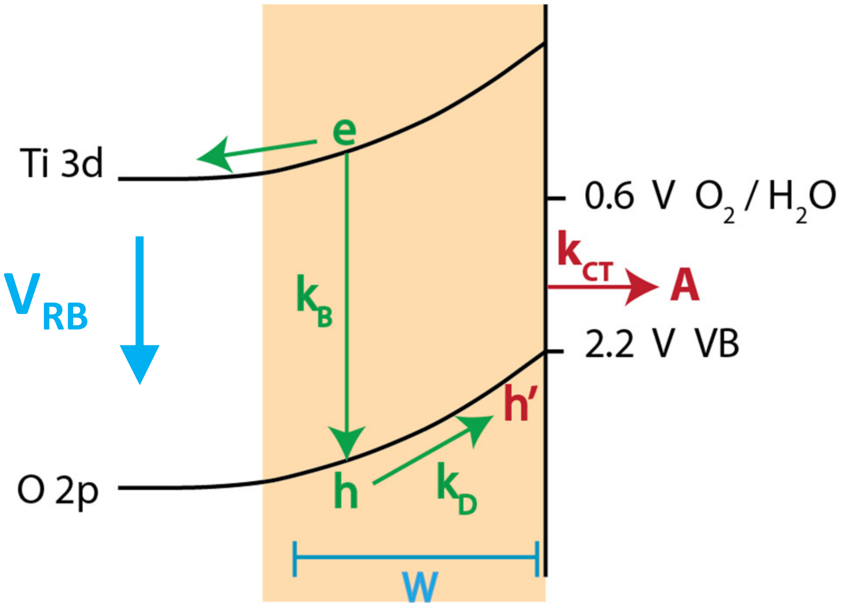
0.01 O_2/site-s

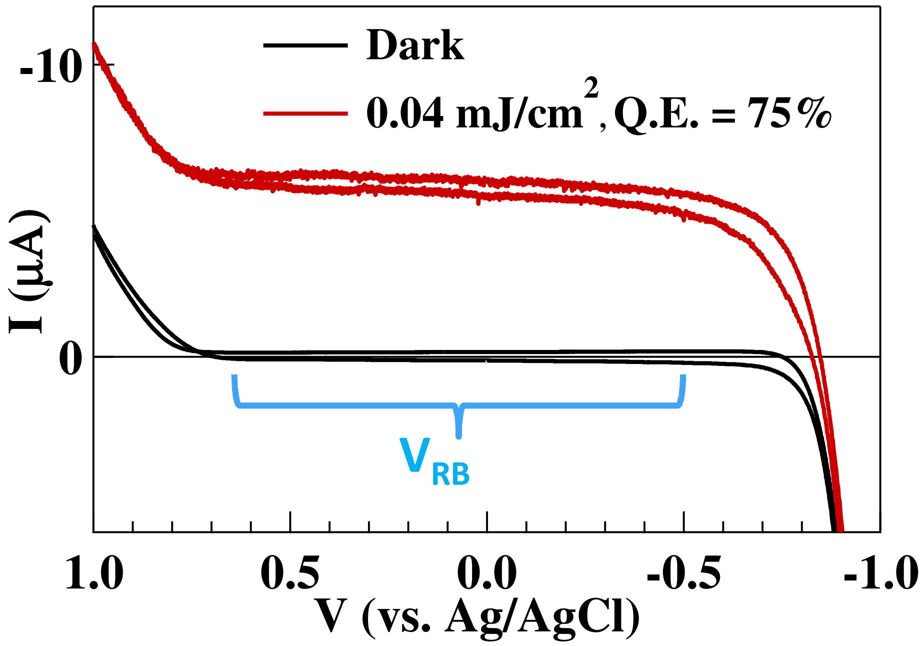


Co_3O_4 , Low Over-Potential

Photo-electrochemistry of n-$SrTiO_3$

High Quantum Efficiency with 1 kHz Laser (W ~ α)

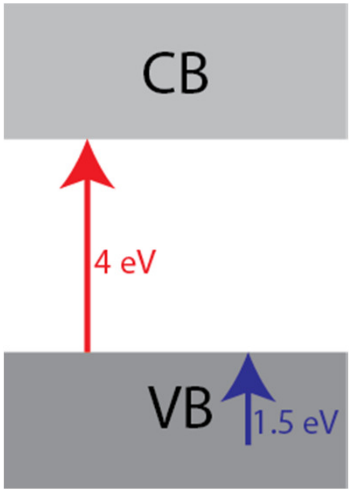




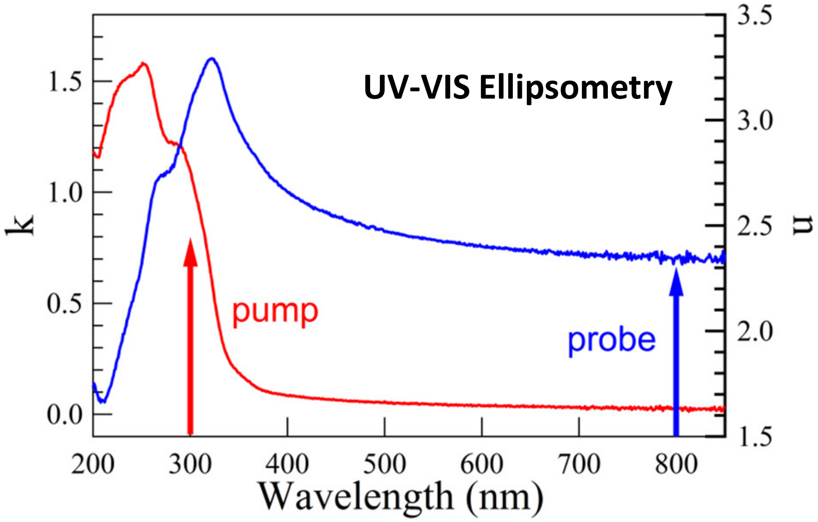
- Single 150 fs Pulse Triggers Multi-electron Transfer Water Oxidation
- Achieve high quantum efficiency (75%) under laser excitation

Transient Reflectance of n-$SrTiO_3$

Pump Band Gap, Probe Holes



Surface Sensitivity Thru Reflectivity



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

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

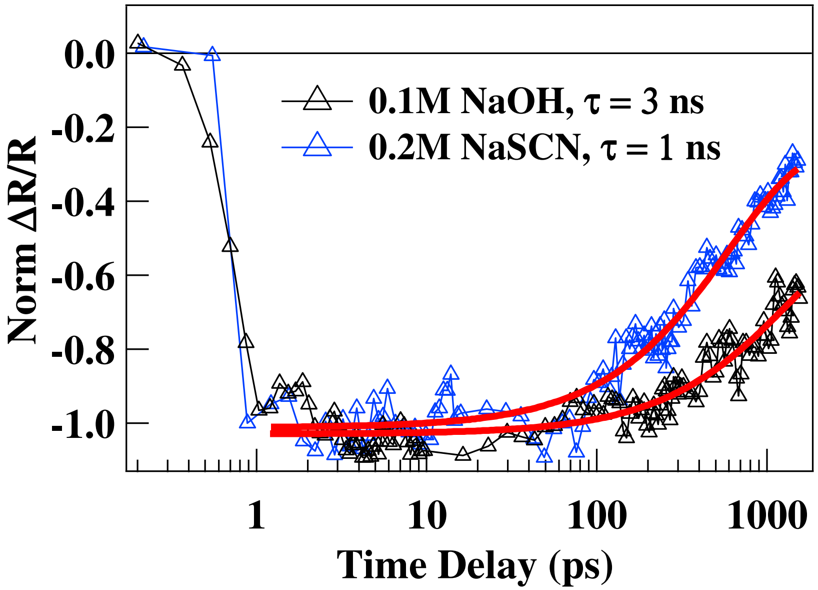
Width of Electric Field at High Q.E.:
W ~ 25 nm

Pump Band Gap (300 nm, 4 eV):
$\alpha = \lambda/4\pi k \sim 24$ nm

Probe Hole Absorption (800 nm, 1.5 eV):
$\alpha_{REFL} = \lambda/4\pi n \sim 27$ nm

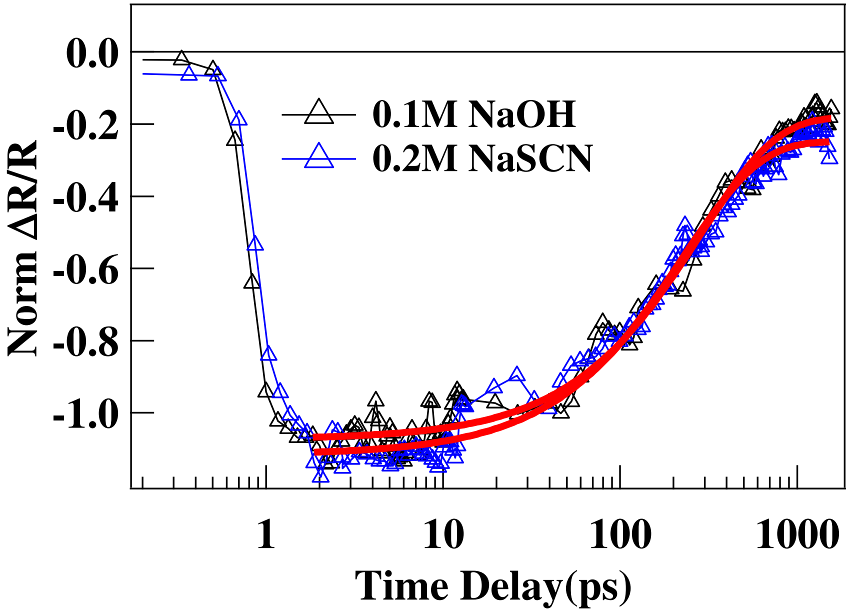
Interfacial Charge Transfer

$SrNb_{0.001}TiO_3$ (0.1%)



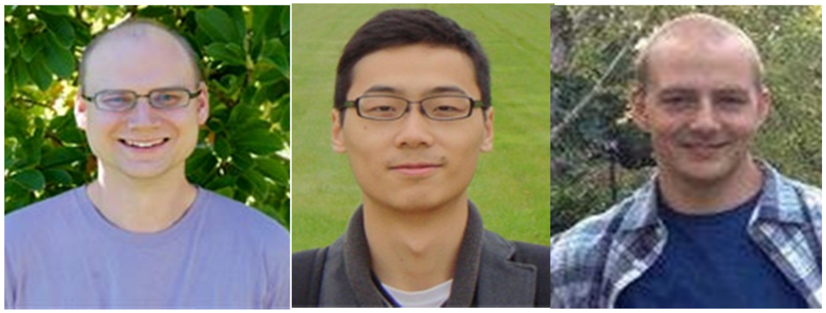
$W = 25$ nm & $\alpha_{pump}, \alpha_{probe} \sim 24$ nm

$SrNb_{0.007}TiO_3$ (0.7%)

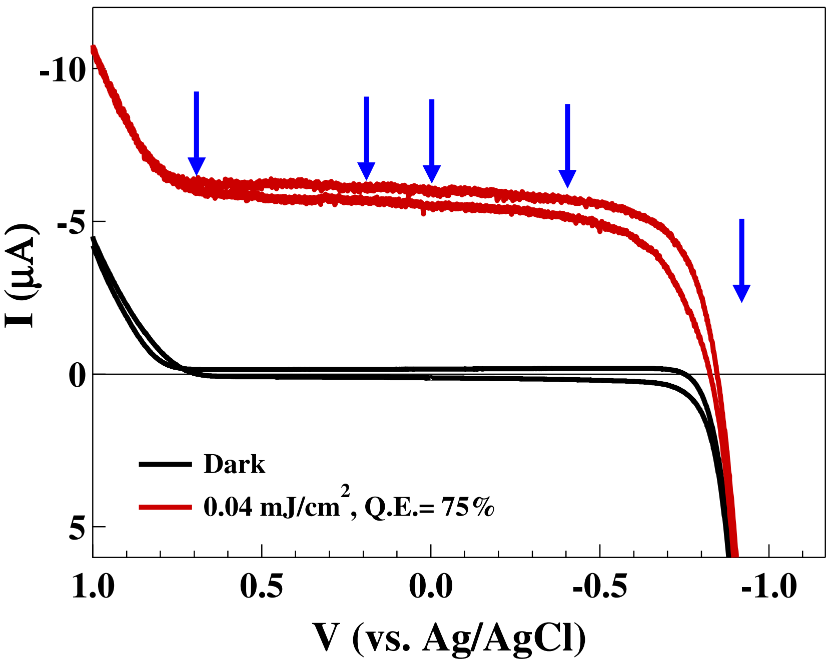


$W = 9$ nm & $\alpha_{pump}, \alpha_{probe} \sim 24$ nm

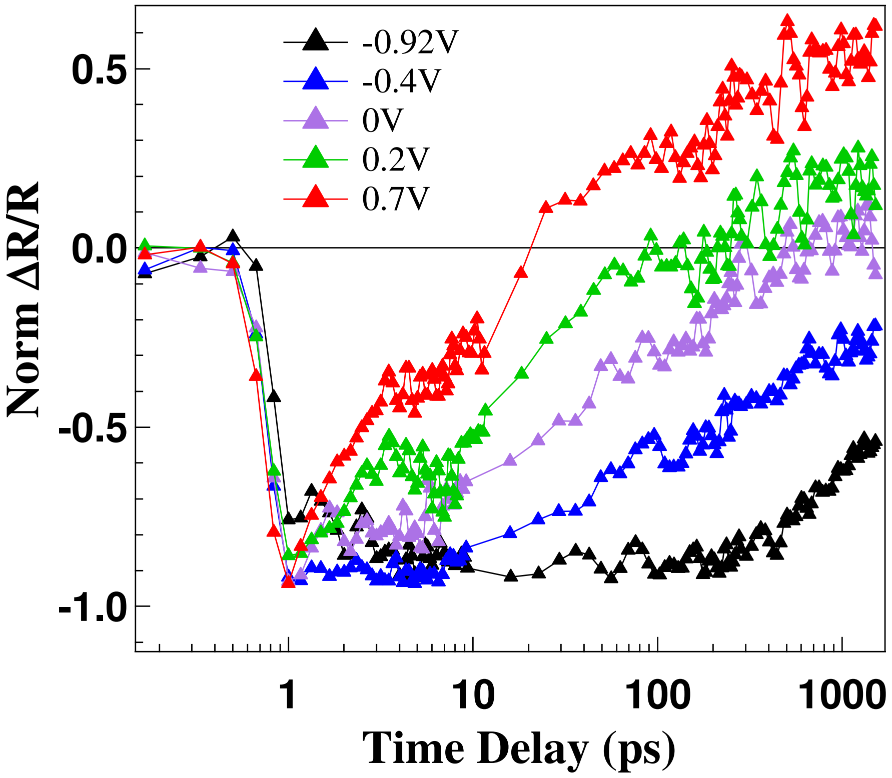
Change in kinetics reflects k_{CT}, [h]



Manipulating Interfacial Charge Transfer

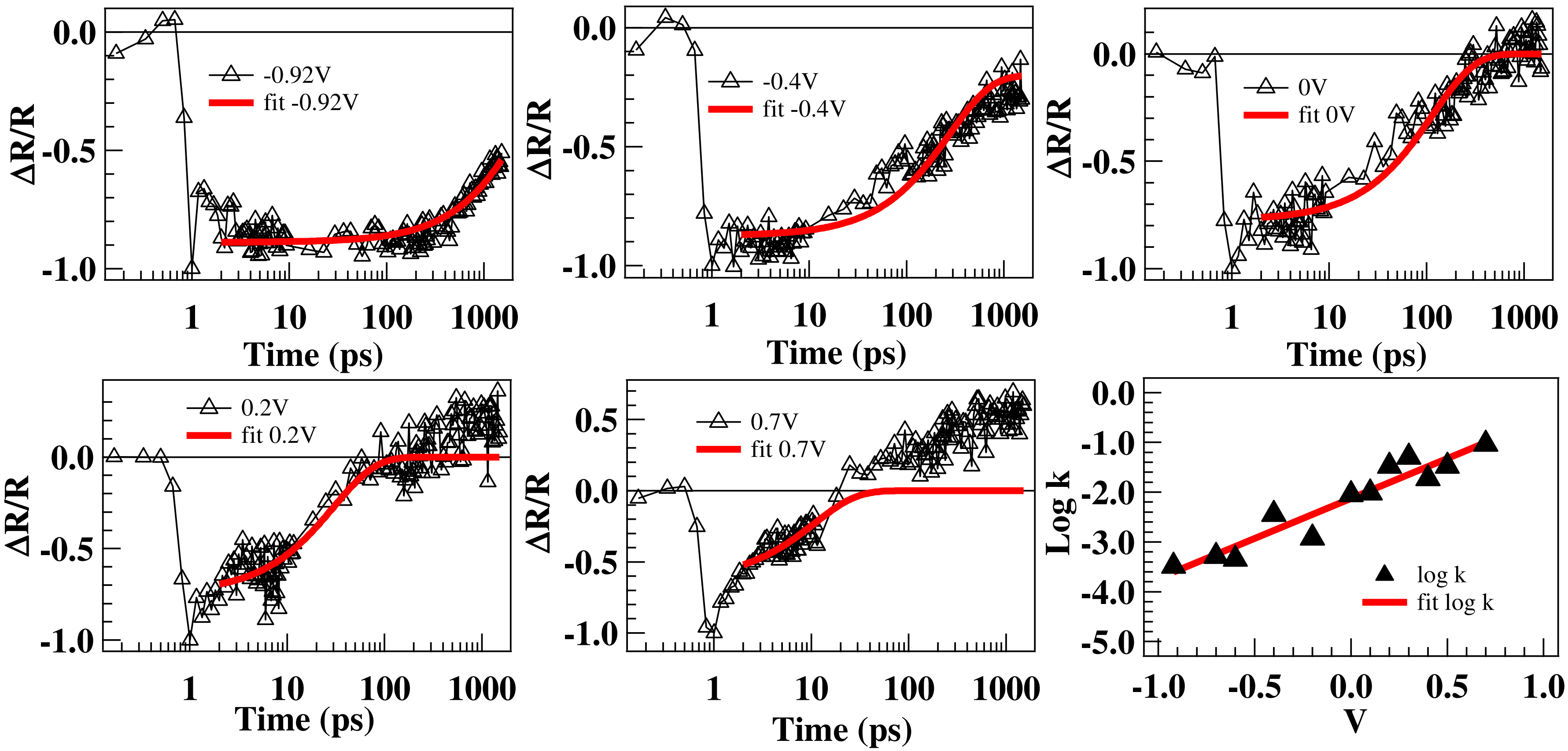


$SrNb_{0.001}TiO_3$ (0.1%)



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

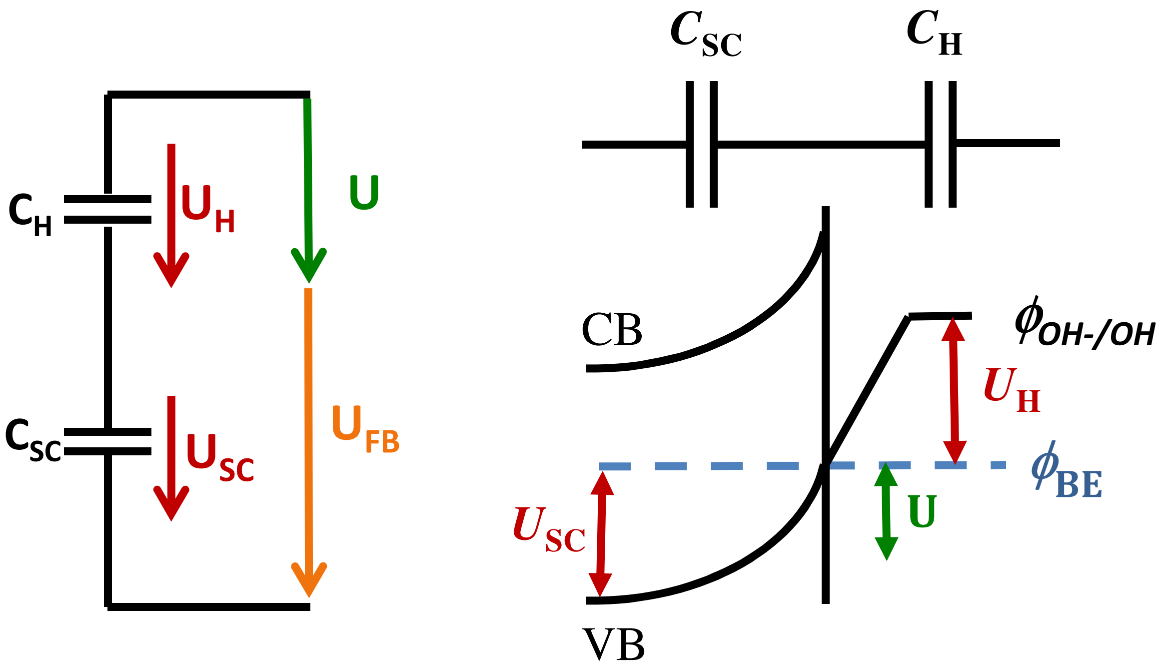
Kinetics (V)



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

M. Waegele, X. Chen, D. Herlihy, T. Cuk, JACS 2014

Voltage Distribution at the Surface



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

ϕ_{BE} =
surface hole potential

U = applied voltage

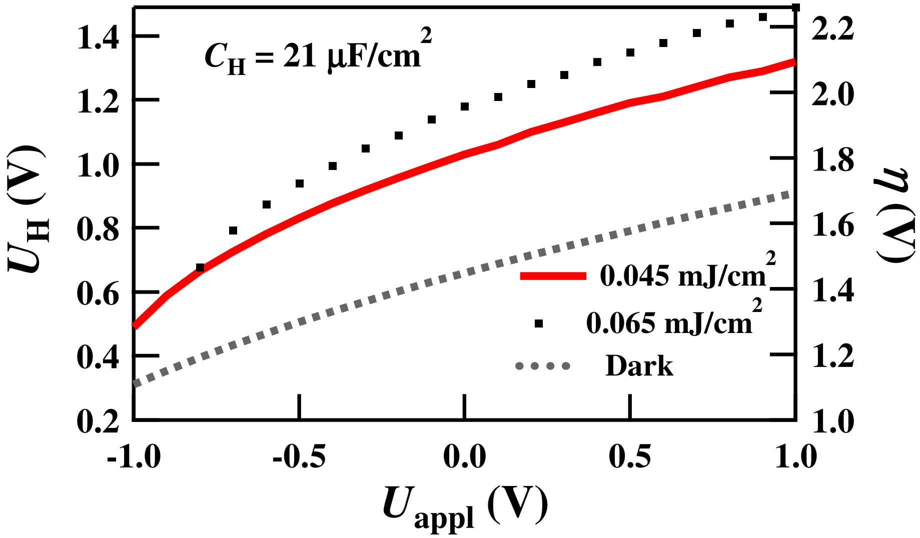
- **Since the solution potential is invariant, changes in U_H are tied to changes in the valence band edge potential, ϕ_{BE}**
- **Changes in U_H (Helmholtz Voltage) by applied U determined by capacitances at n-type SC/liquid interface**

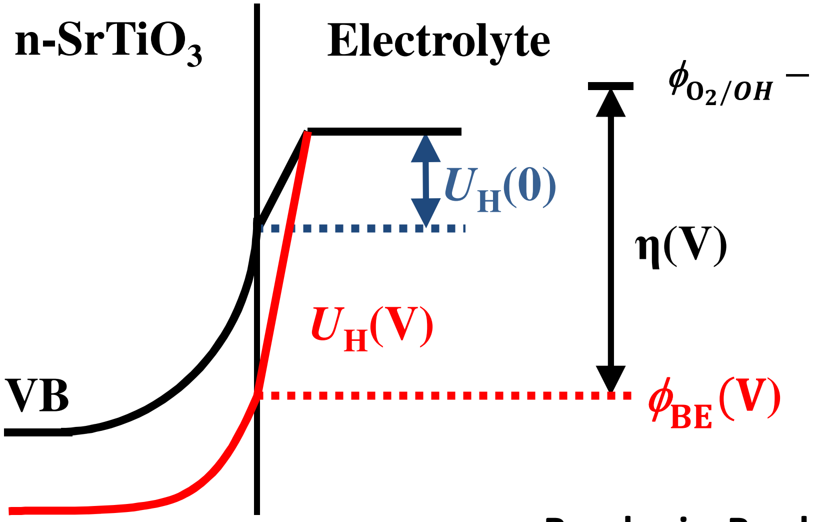
U_H(V): Changing Surface Hole Potential

(1) $U + U_{FB} = U_H + U_{SC}$

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

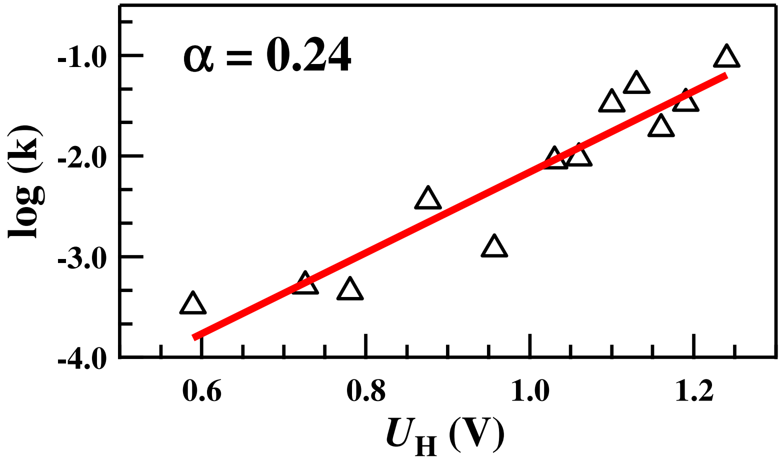
$U_H(0) = 0.65$ V give $C_H = 21$ uF/cm^2





Brockeris, Bard, Bocarsly

Activation Barrier of First Hole Transfer



$$k = k_0 \exp(\Delta G^*/4k_BT)$$

$$k = k_0 \exp(\alpha\, F U_H / RT)$$

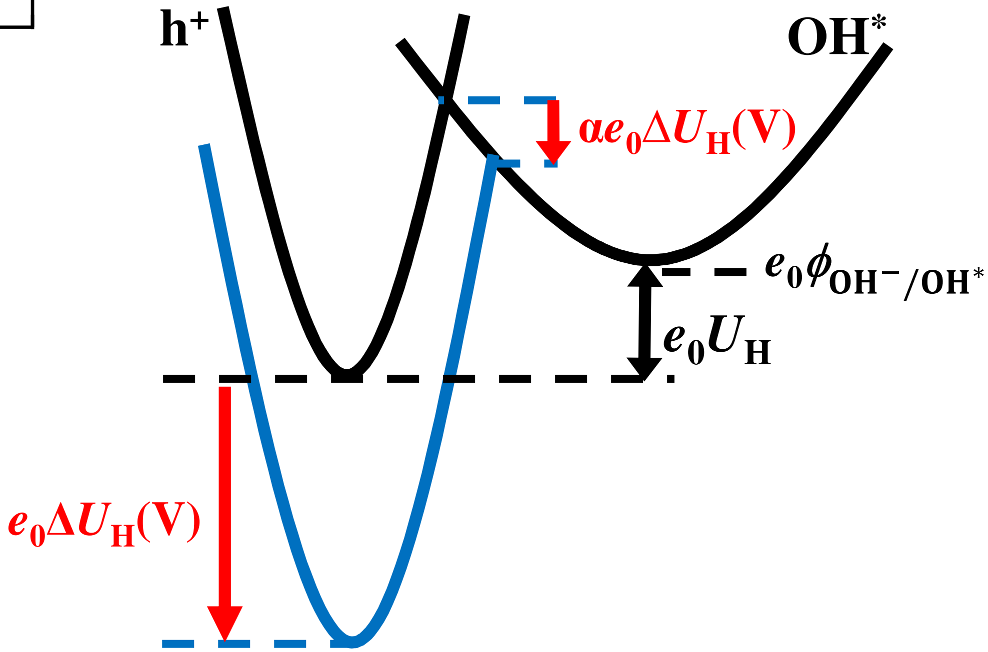
$$[h+] + [OH^-] \xrightarrow{k} [OH^*]$$

$\alpha = 0.2 \pm 0.05$

$k_0 = 7 \times 10^{-7}\ ps^{-1}$ (μs)

ϕ_{OH^-/OH^*} = 1 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 (α, 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
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Xihan Chen
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Michelle Chang

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U.S. DEPARTMENT OF
ENERGY

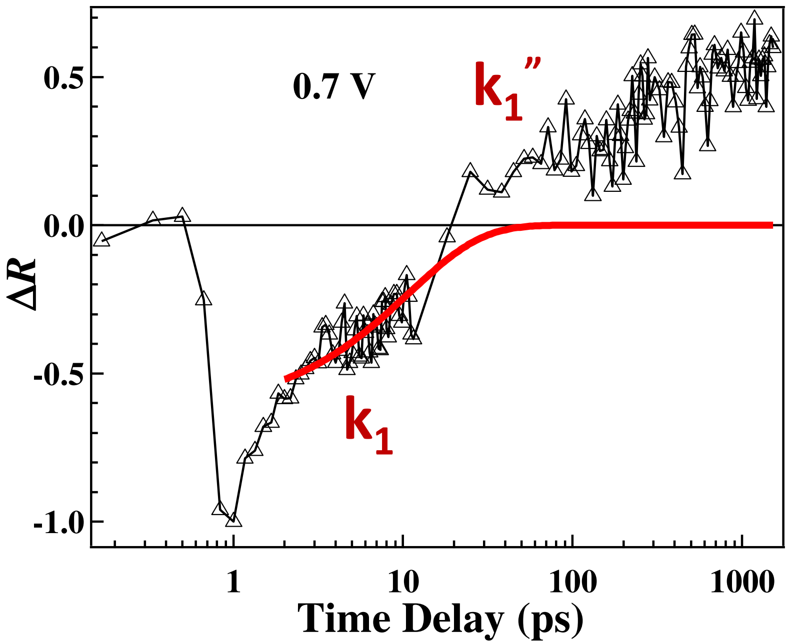
CPIMS Program

AFOSR Young Investigator (Co_3O_4)

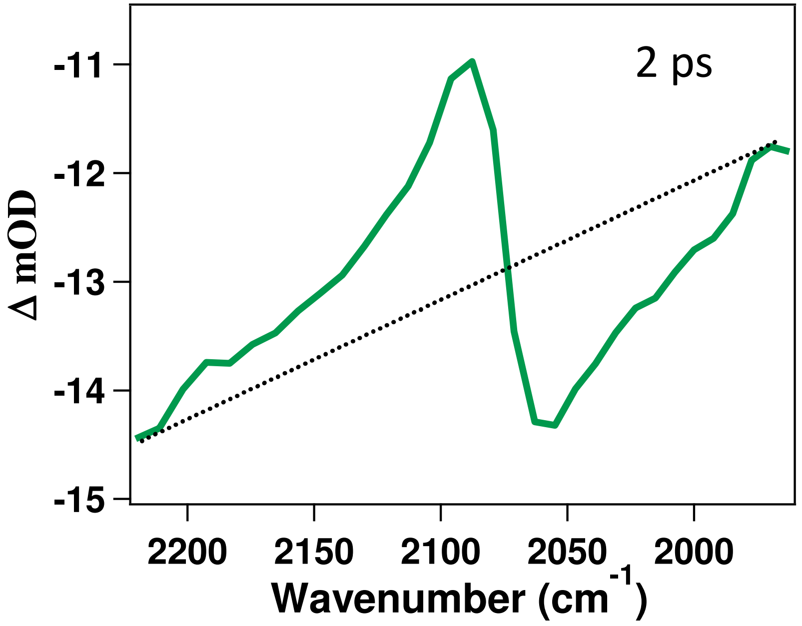
Possible Intermediate Species Formed

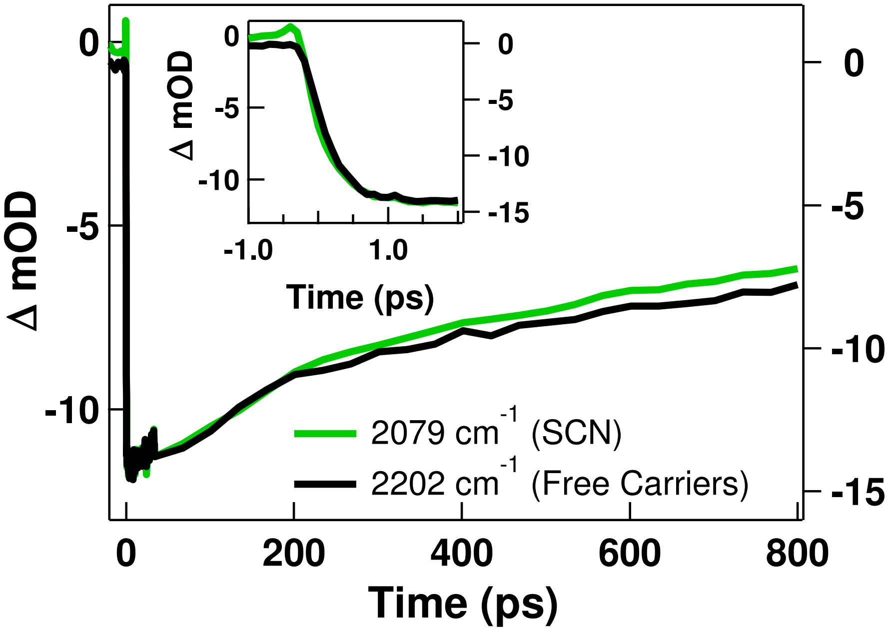
$$[h+] + [OH^-] \xrightarrow{k_1} [OH^*] \xrightarrow{k_1''} [\text{-OOH or -OOTi}]$$

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



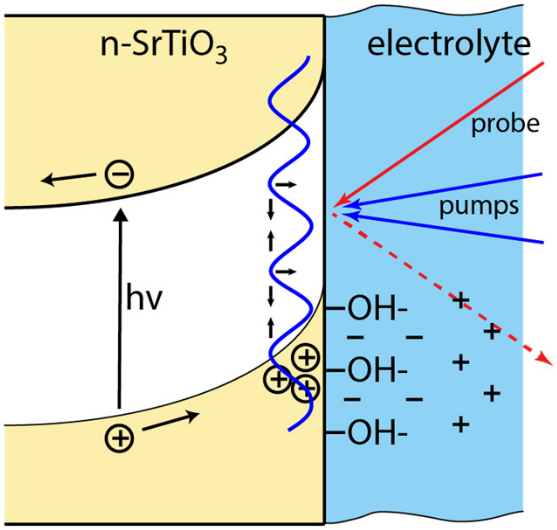
Ultrafast Transient IRRAS


Transient -SCN / -NSC at n-$SrTiO_3$


Decays with n-$SrTiO_3$ Free Carriers

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

Transient Grating Diffraction

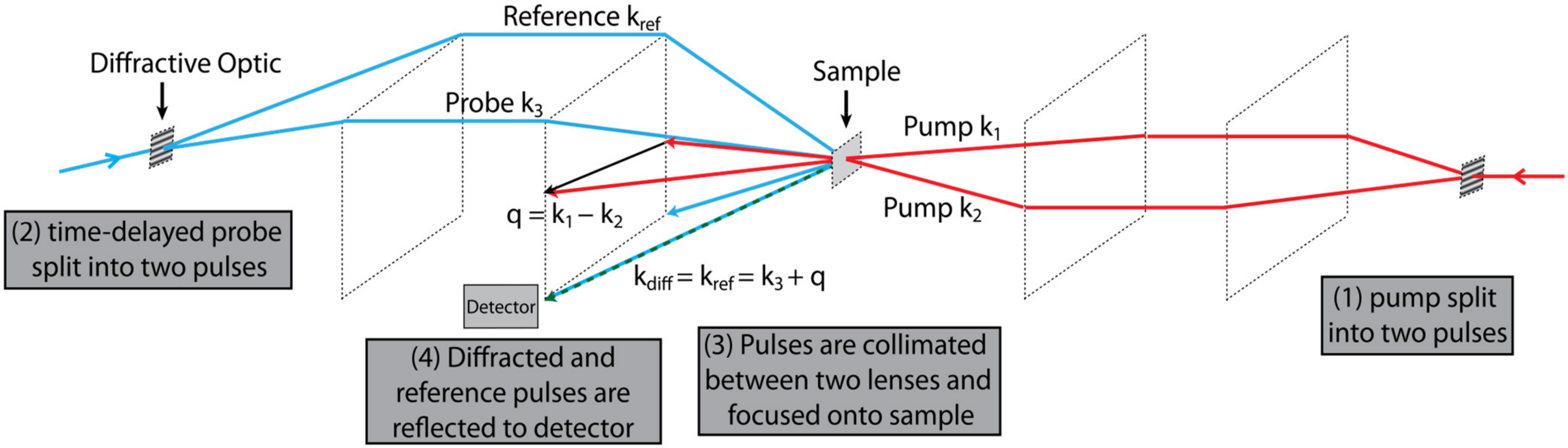


$$\Delta I/I = \mathbf{R(t)}\cos(\boldsymbol{\varphi}\mathbf{(t)}) + \mathbf{TG(t)}\cos\,[\Psi\ -\ \boldsymbol{\varphi}\,\mathbf{(t)}]$$

$$\textbf{Recombination (t)} = \mathbf{R(t)}\cos(\boldsymbol{\varphi}\mathbf{(t)})$$

$$\textbf{Diffusion (t)} = \boldsymbol{\varepsilon}\ \mathbf{(t)} = \mathbf{TG(t)}/\mathbf{R(t)} = \exp\,(-\mathbf{D}q^2/t)$$

Heterodyne Detection: **TG(t), R(t), φ (t)** determined by varying Ψ, probe-ref phase



(2) time-delayed probe split into two pulses

(4) Diffracted and reference pulses are reflected to detector

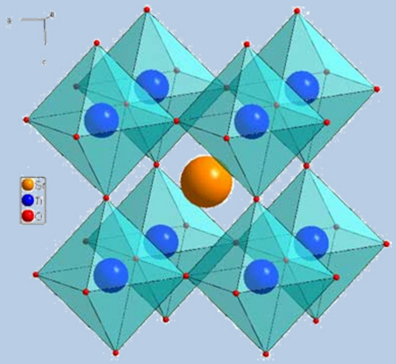
(3) Pulses are collimated between two lenses and focused onto sample

(1) pump split into two pulses

Catalysts & Devices Under Investigation

n-type SC/Liquid Schottky Barrier

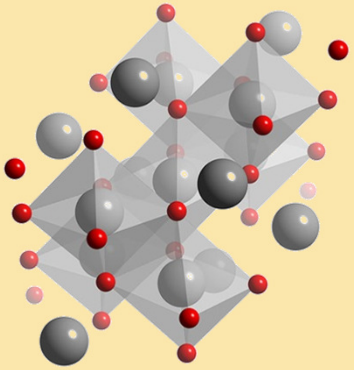
10 O_2/site-s



n-$SrTiO_3$, High Over-Potential

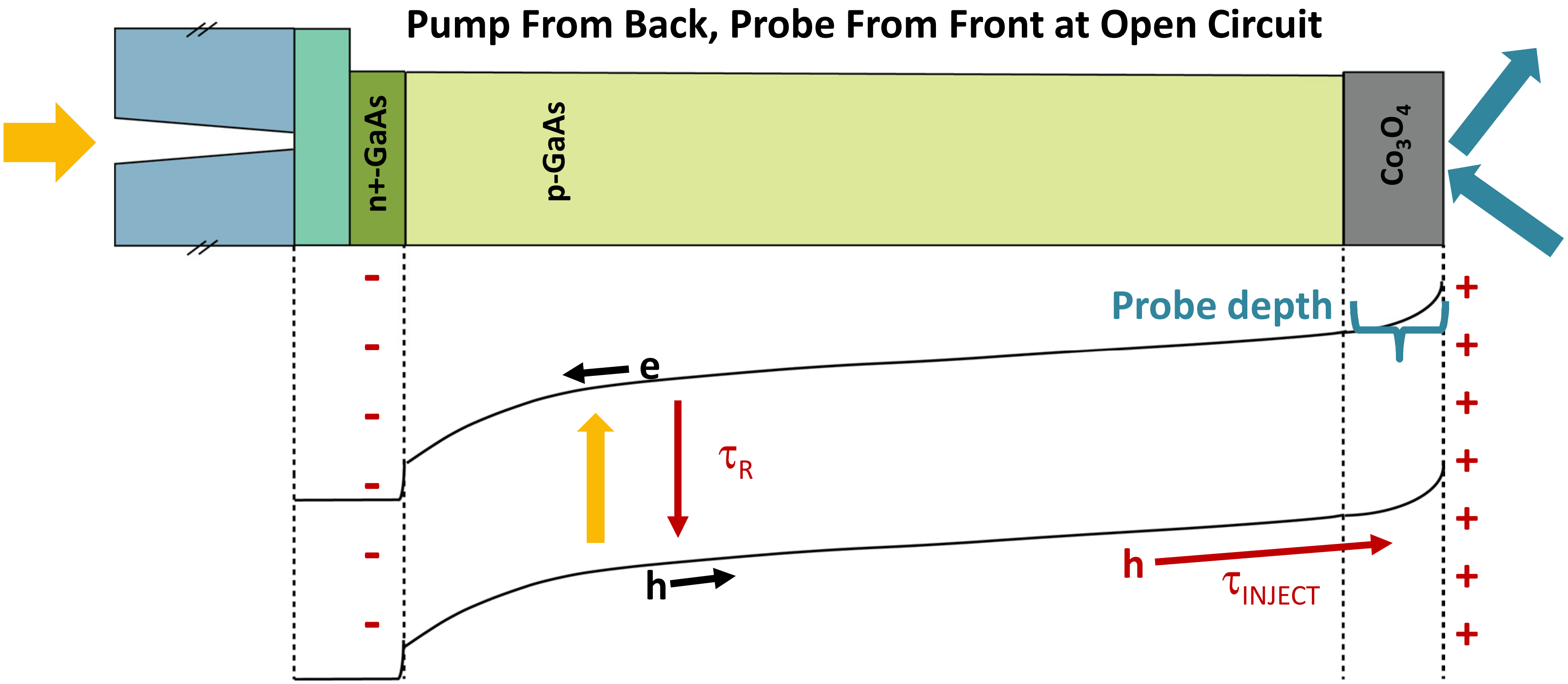
n-p GaAs photodiode/Co_3O_4 Hetero-junction

0.01 O_2/site-s



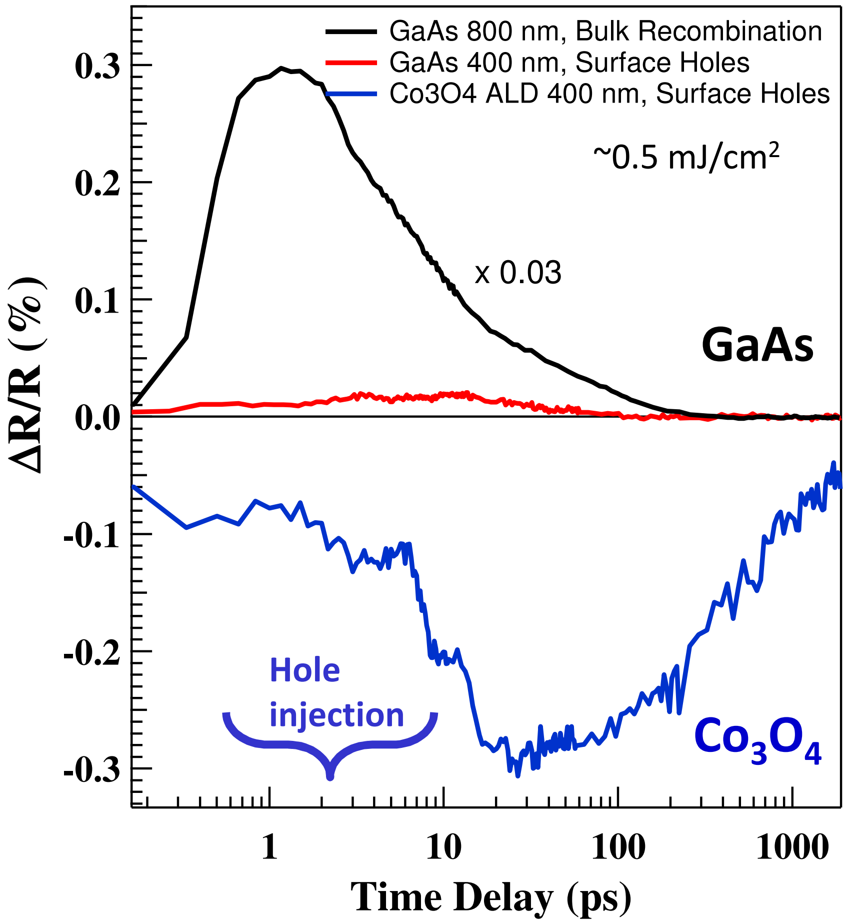
Co_3O_4 , Low Over-Potential

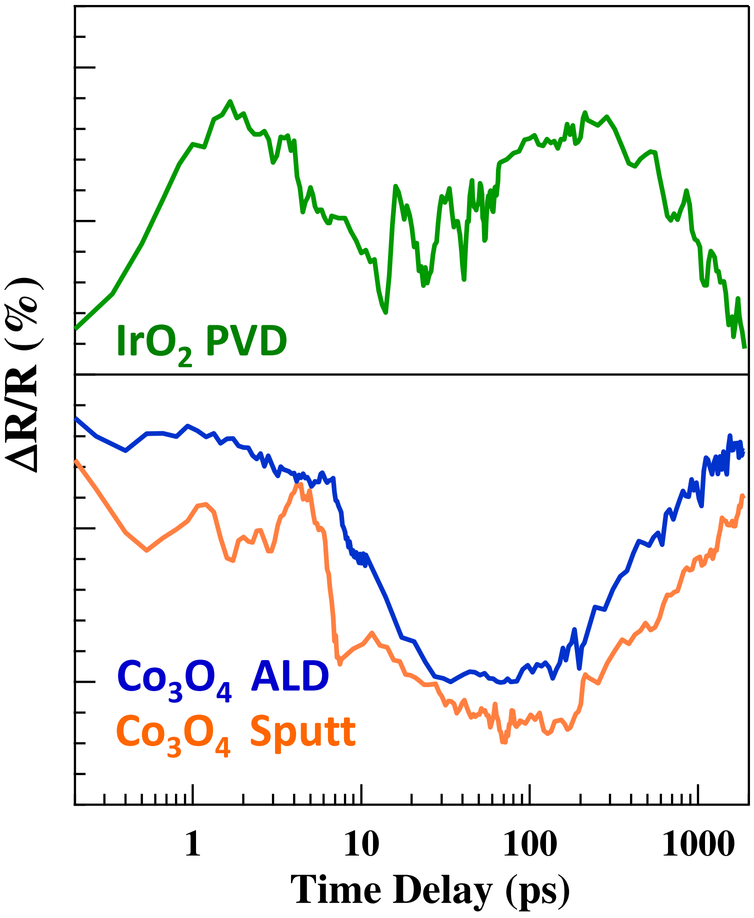
Transient Reflectivity on Hetero-junctions



- **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_3O_4 be separated in a transient reflectivity experiment?**

Kinetics of Holes in Catalyst Over-layer

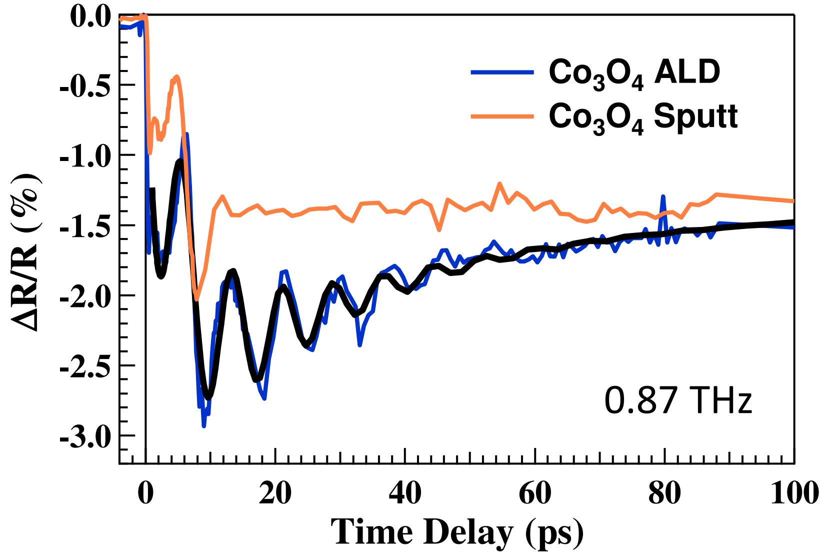


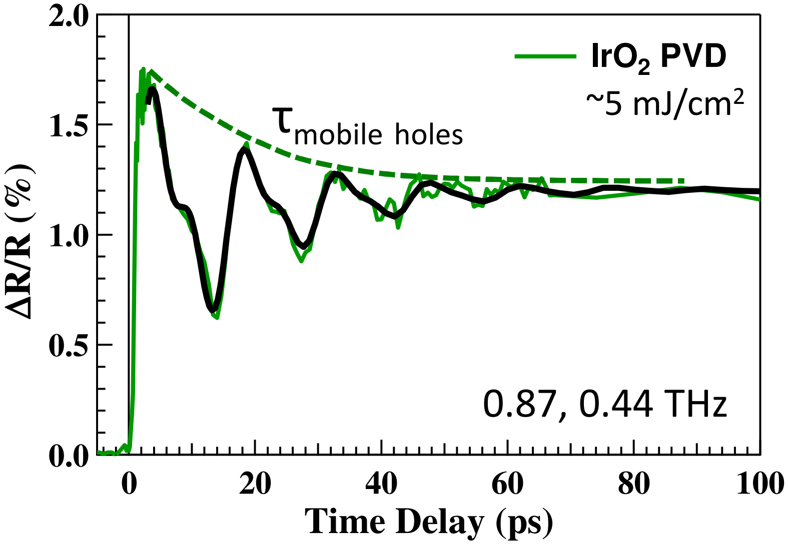


- Surface sensitivity of ΔR w/ 400 nm probe
- Strong signal of surface holes with catalyst
- Time delay for hole injection (~10 ps)

- Kinetics vary w/ catalyst type
- Also with deposition technique
- Reproducibility for same batch

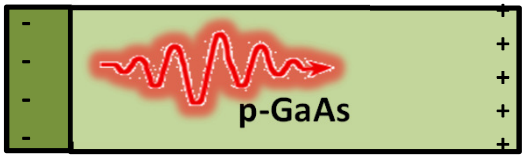
Hole Carriers as an antenna to THz?





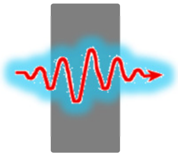
- 0.8 THz (& w/ 0.4 THz) signal generated from catalyst over-layer, independent of catalyst type
- Strength and decay of THz signal depends on catalyst type and deposition technique
- Potentially, mobile holes responding to THz in GaAs that decay to surface trapped states

THz Generation



Plasma frequency of p-dopants responding to ΔE field

THz Antenna



Effects of Electrolyte?

Free Carriers Injected in Catalyst Responding to THz field

Conclusions

- **Activation barrier (α, 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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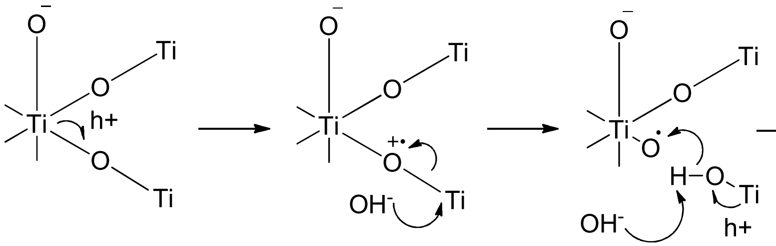
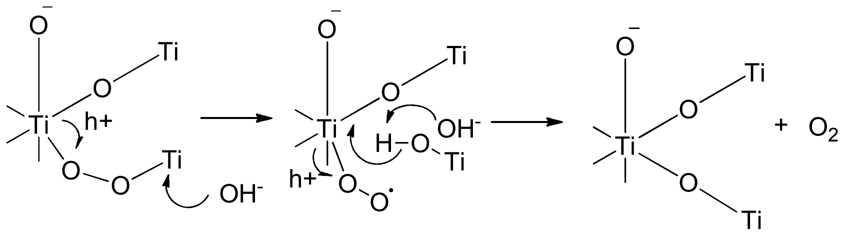
Reaction via surface hole (valance band oxygen)



(1)



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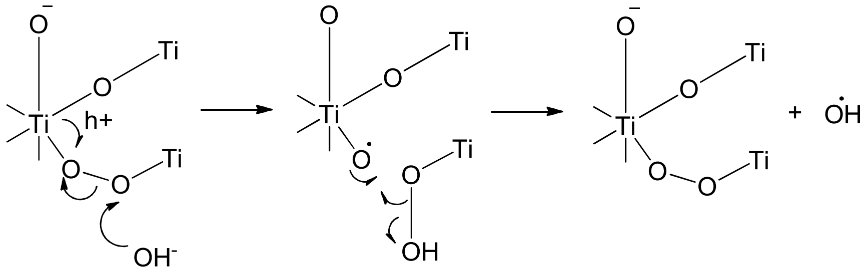
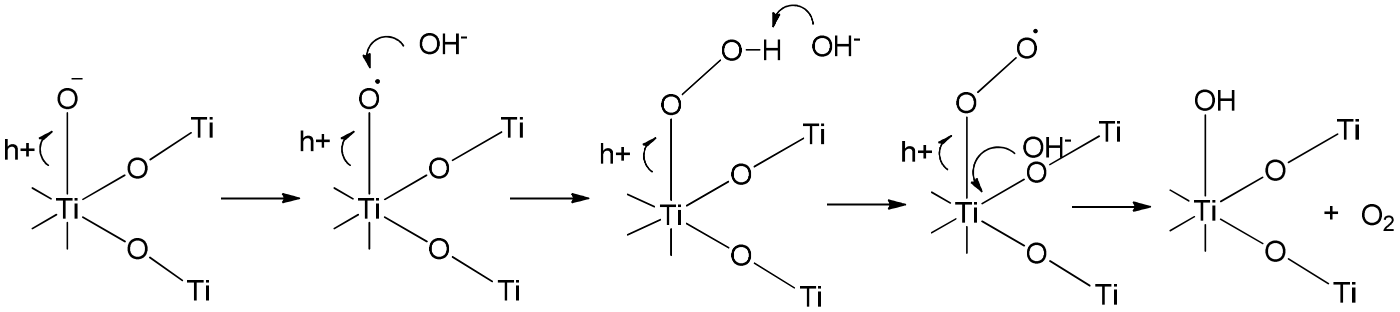
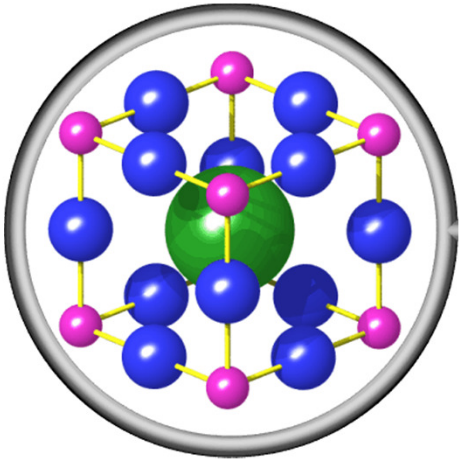


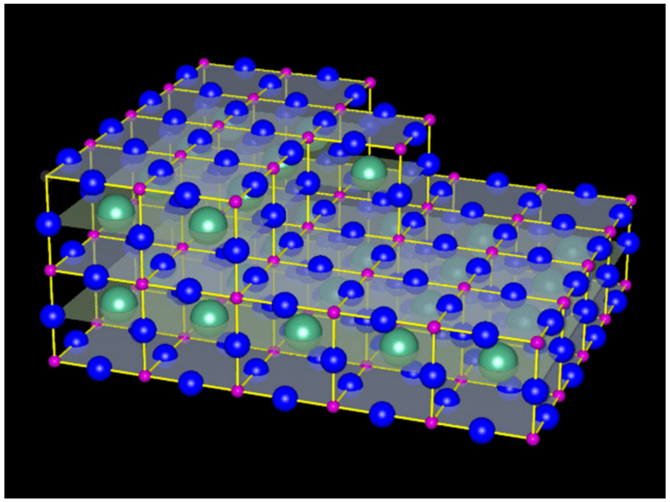
(3)

Reaction via hot hole
(surface axial oxygen)



Number of surface site calculation





1. $SrTiO_3$ has a lattice constant of a=3.905A
2. (1,0,0) surface for $SrTiO_3$ 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 $A=a^2=1.525*10^{-15}\ cm^2$
5. Surface atom density=# of atoms on one lattice surface/lattice surface area

   So, surface atom density= $3/1.525*10^{-15}cm^2 = 1.967*10^{15}$ atoms/cm^2

Voltage Distribution (Dark, Equilibrium)

Mott-Schottky: U_{FB} = 1.6 V

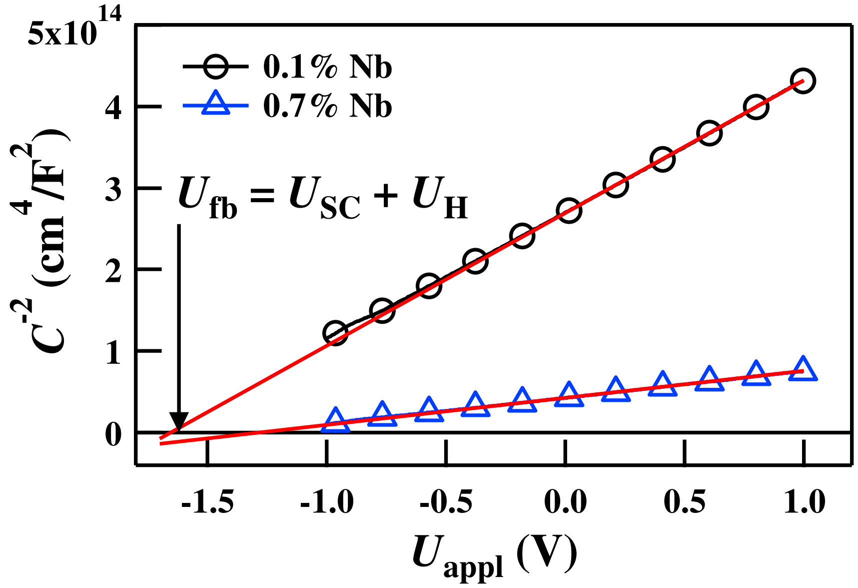
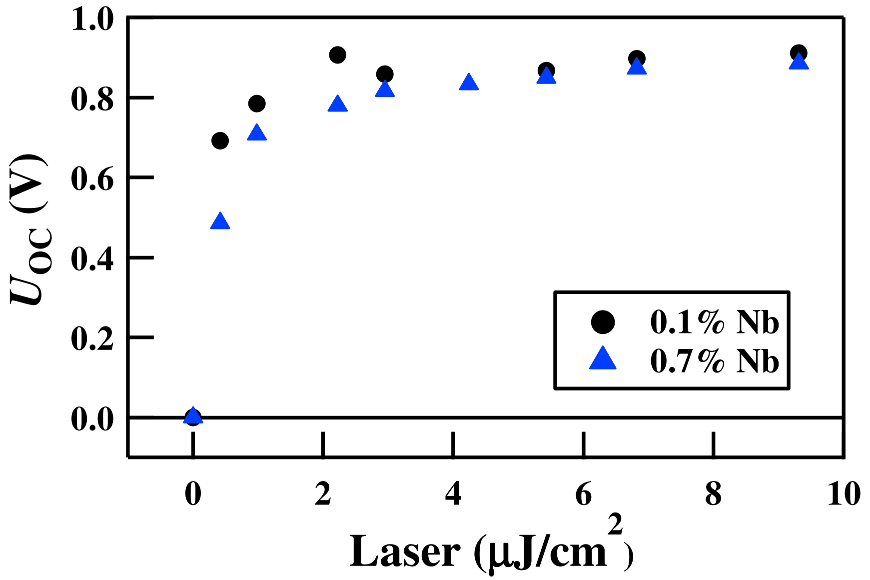


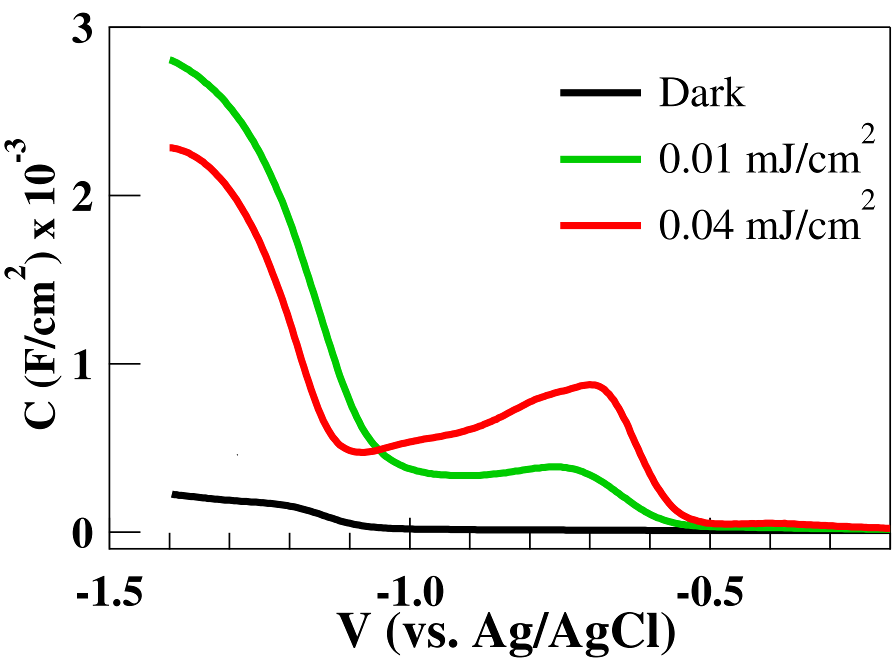
Photo-Voltage: $U_{OC} = U_{SC} = 0.85$ V



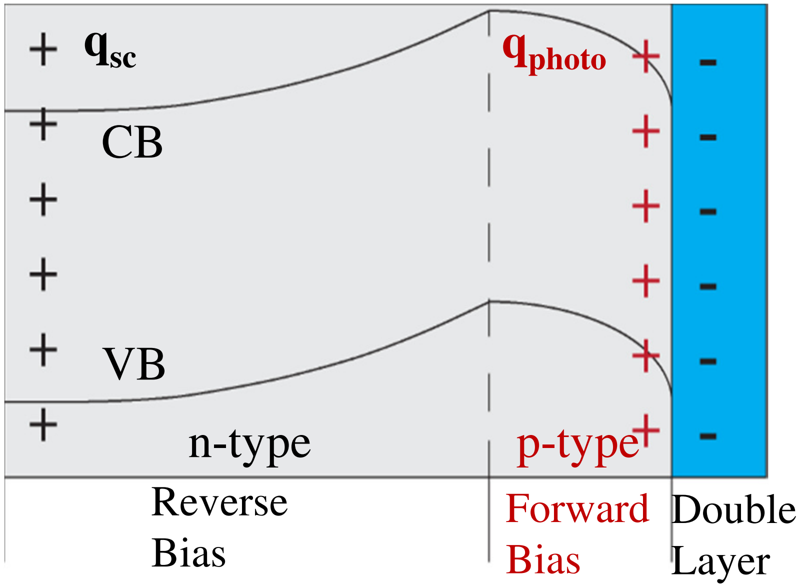
- Photo-voltage at open circuit roughly half of U_{FB}
- U_H= 0.65 V in the dark, at equilibrium (no applied U)

Voltage Distribution (Illumination)

Capacitance



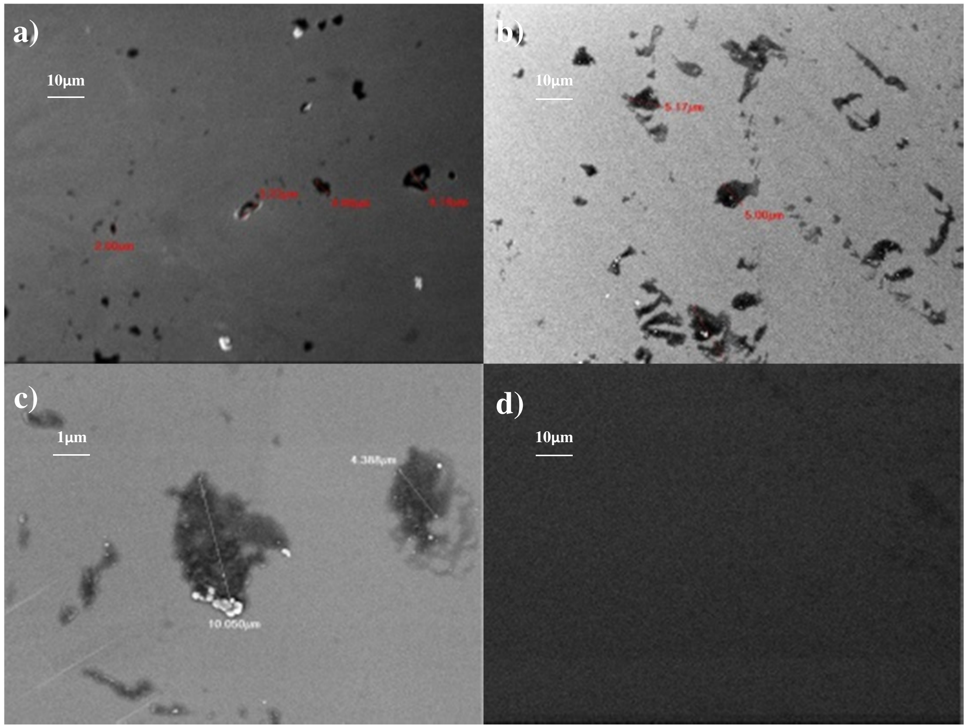
Illuminated Junction



Turner, Nozik APL **37** (1980)

- **Photo-induced holes at interface create an interfacial p-type layer**
- **This interfacial “carrier inversion” changes U_H, even with no applied U**

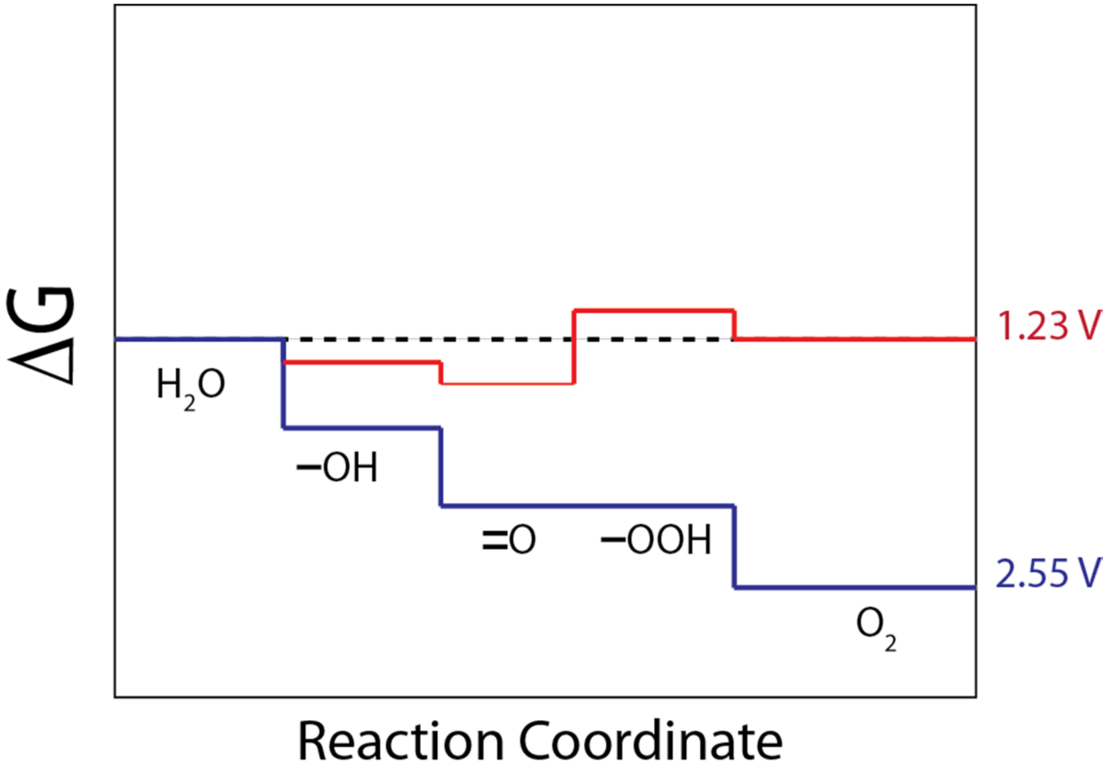
SEM images a)-d) show damage on 0.1% Nb doped SrTiO3 under laser and applied bias condition



a) Damaged sample at 1500× magnification
b) Damaged sample at 1500× magnification
c) Damaged sample at 3500× magnification
d) Undamaged sample at 1500× magnification

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



Thermodynamic potential,
High kinetic barriers
~ 0.01 O_2 /site-sec

High over-potential,
Lower kinetic barriers
~10's O_2 /site-sec

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