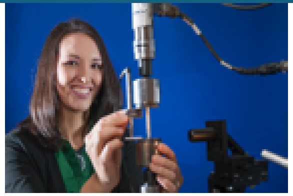
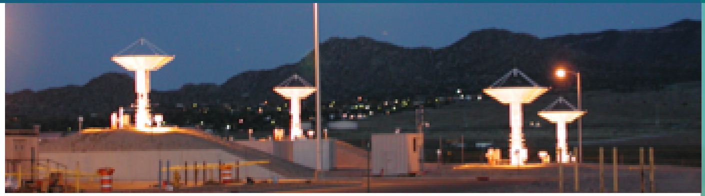
SAND2022-5518C

Sandia National Laboratories

Charge transport mechanisms in $SrTiO_3$:Rh nanoparticle photocatalysts for Z-scheme water splitting





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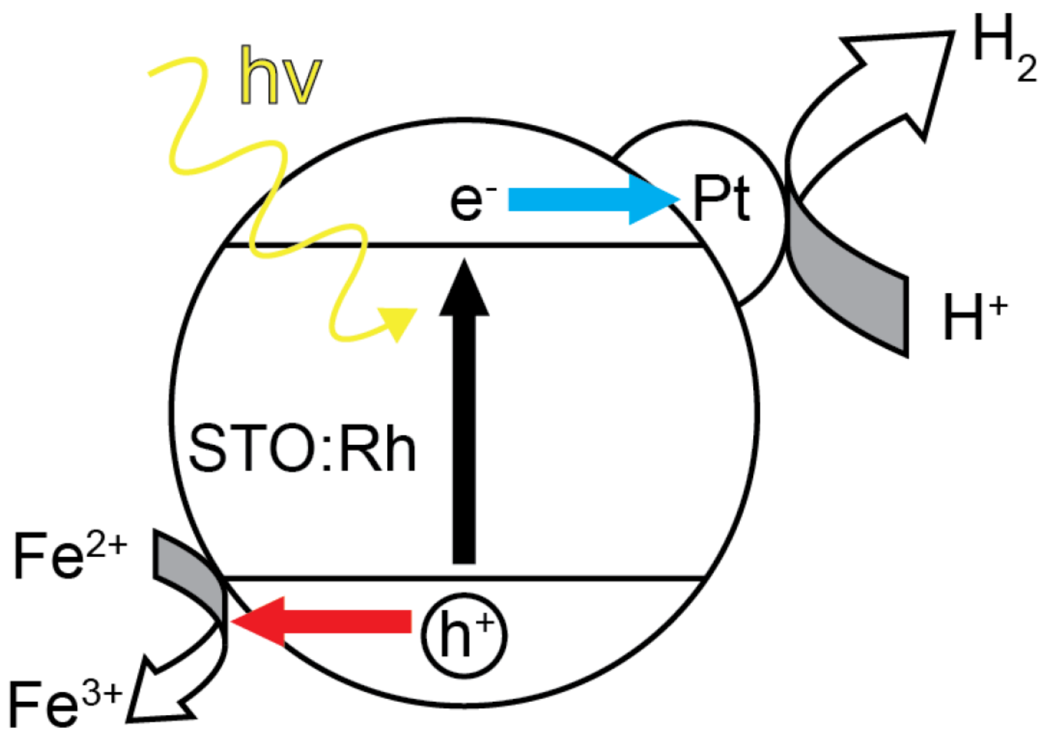
HER STO:Rh w/Pt cocatalyst nanoparticles in a Z-Scheme system

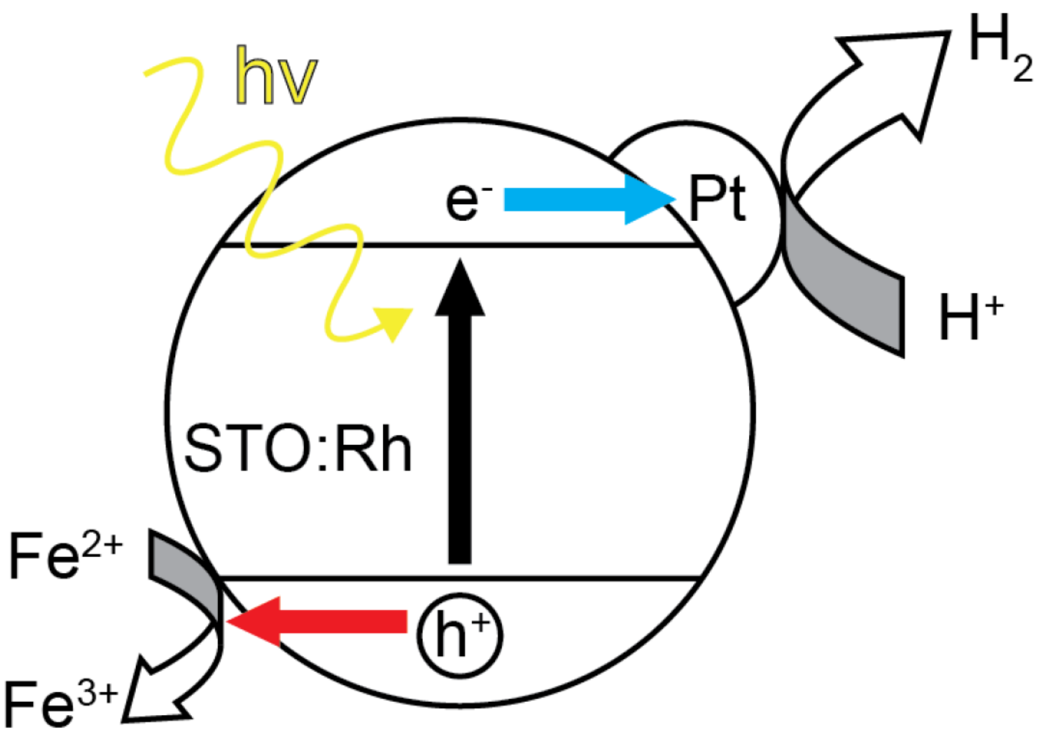


1) Light absorption

2) Transport of carriers to particle surface

3) Hydrogen evolution catalyzed by Pt & redox shuttle oxidation

HER STO:Rh w/Pt cocatalyst nanoparticles in a Z-Scheme system



Transport of carriers to particle surface

- Drift or diffusion?
- Measure photocarrier lifetime

Electrically probe individual STO:Rh nanoparticles to find limiting charge transport mechanism

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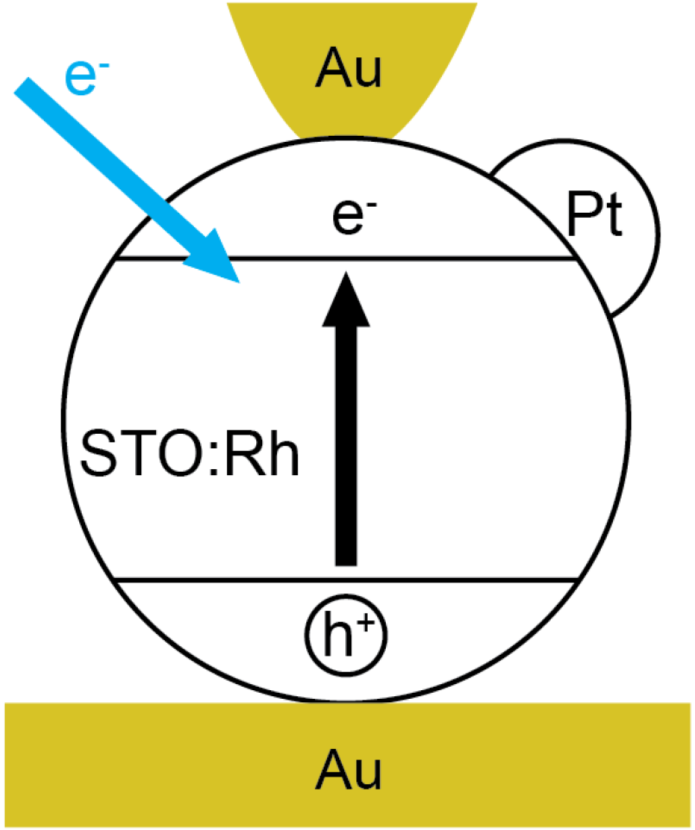
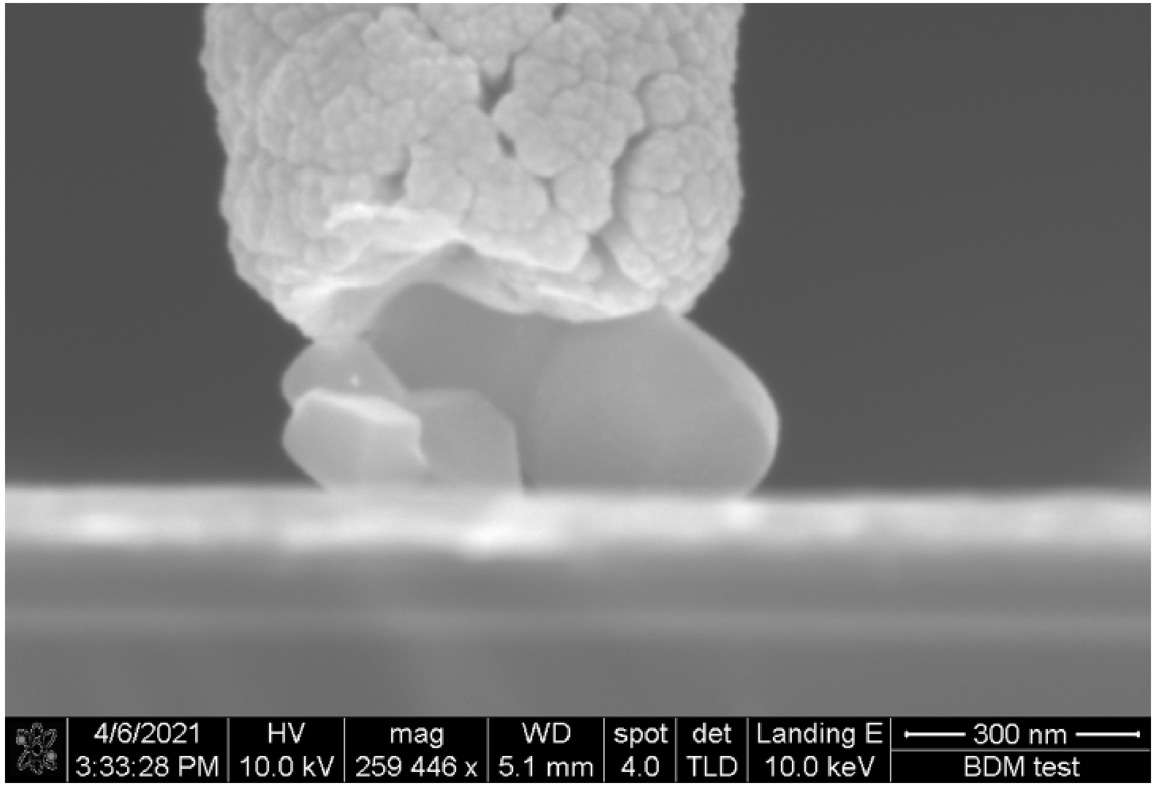
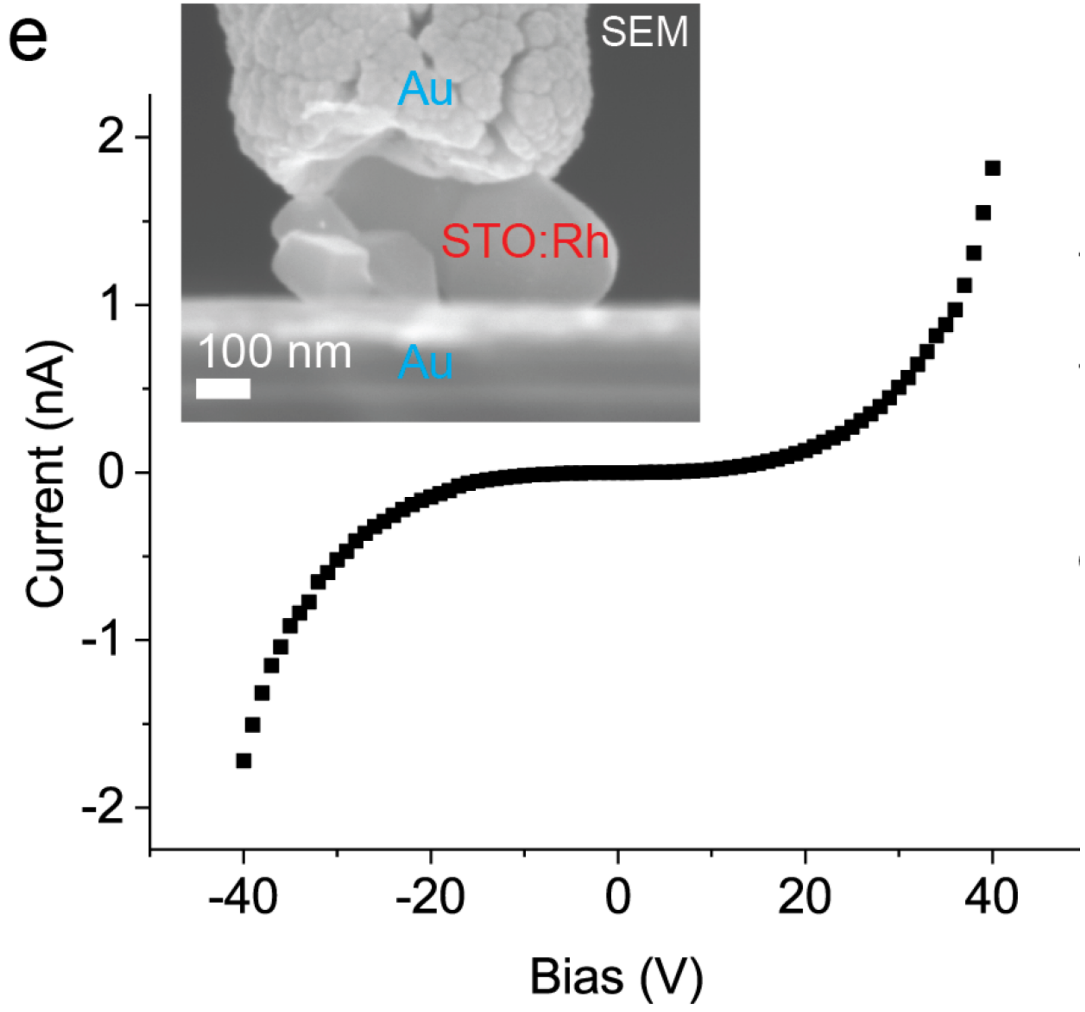




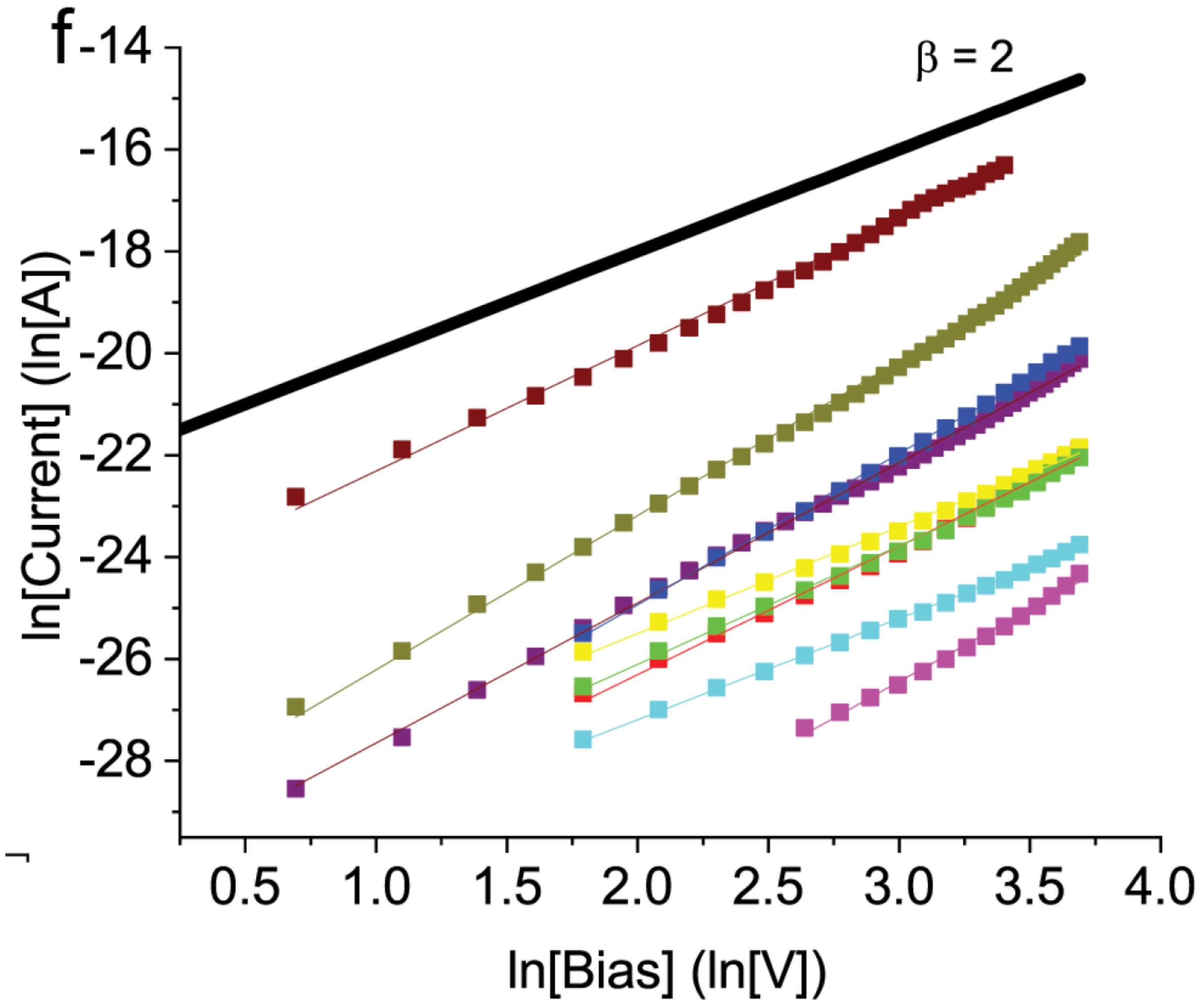
Trap-mediated space-charge limited current (SCLC)



$$I = \frac{9}{8} A\, \varepsilon \mu \frac{V^2}{D^3} \frac{N_c}{N_t} e^{-E_T/kT}$$

- Bulk –limited transport mechanism
- Nanoparticle has low free carrier concentration

Trap-mediated space-charge limited current (SCLC)

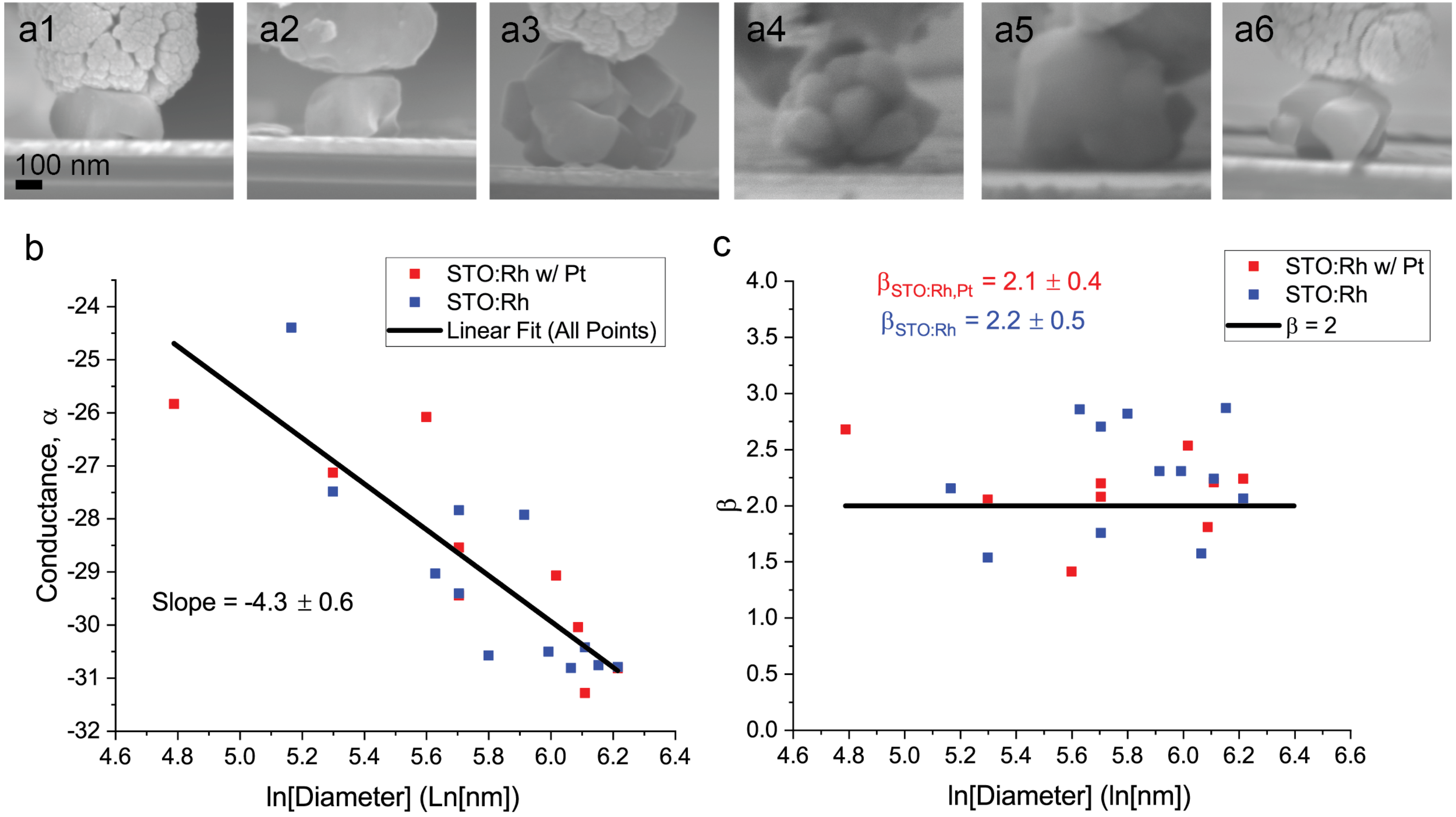


$$I = \frac{9}{8} A\, \varepsilon \mu \frac{V^2}{D^3} \frac{N_c}{N_t} e^{-W/kT}$$

$$\ln(I) = \alpha + \beta \ln(V)$$

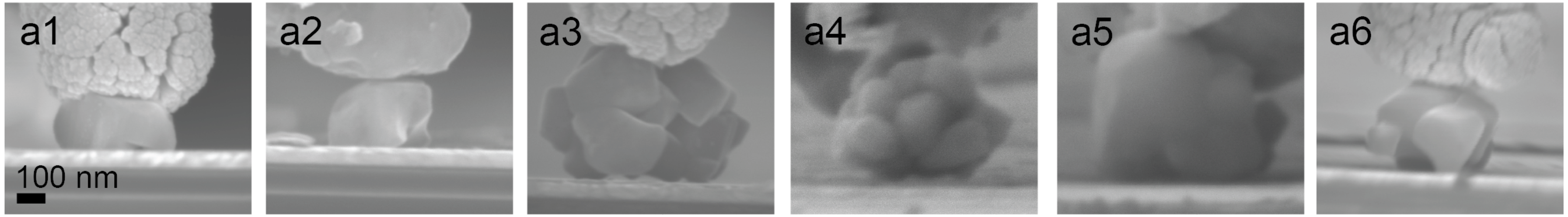
$$\alpha = \ln\left(\frac{9A\varepsilon\mu N_C}{8D^3 N_t}\right) - \frac{W}{kT} \qquad \beta = 2$$

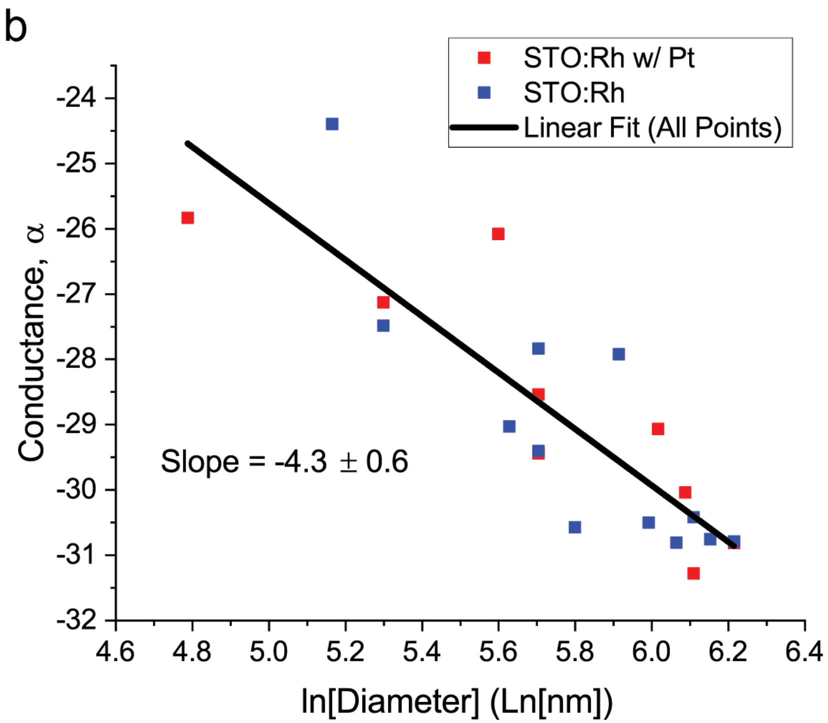
Impact of Pt co-catalysts on transport



Ideal SCLC	$\alpha = -3\ln(D) + C$	$\beta = 2$
Measured	$\alpha = -4.3\ln(D) + C$	$\beta = 2.2$

Impact of Pt co-catalysts on transport

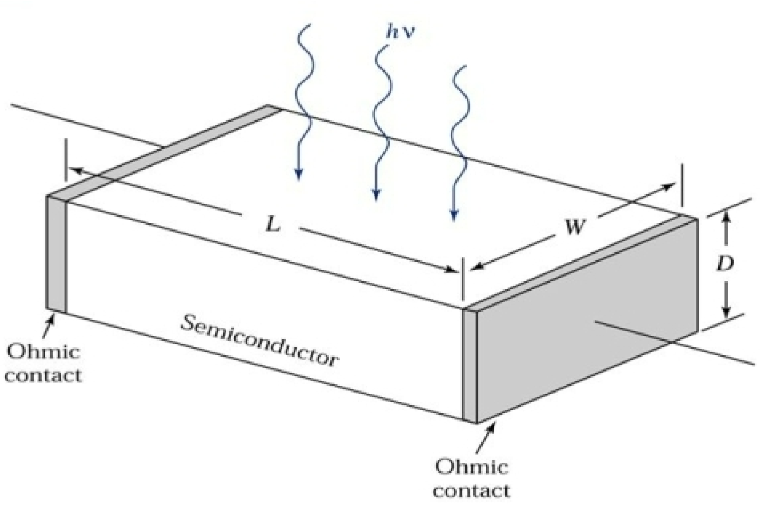




- Conductance (α) of particles is strongly dependent on particle size
- Pt co-catalysts have no impact on transport

Ideal SCLC	$\alpha = -3\ln(D) + C$	$\beta = 2$
Measured	$\alpha = -4.3\ln(D) + C$	$\beta = 2.2$

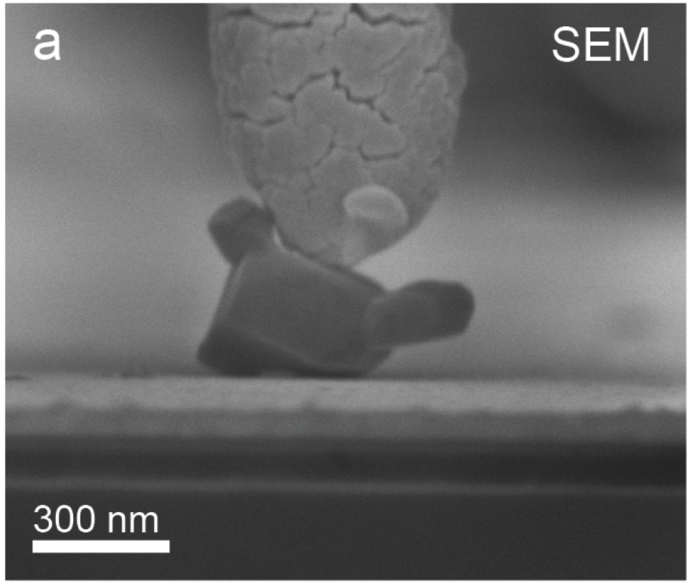
STO:Rh nanoparticles behave as photoconductors

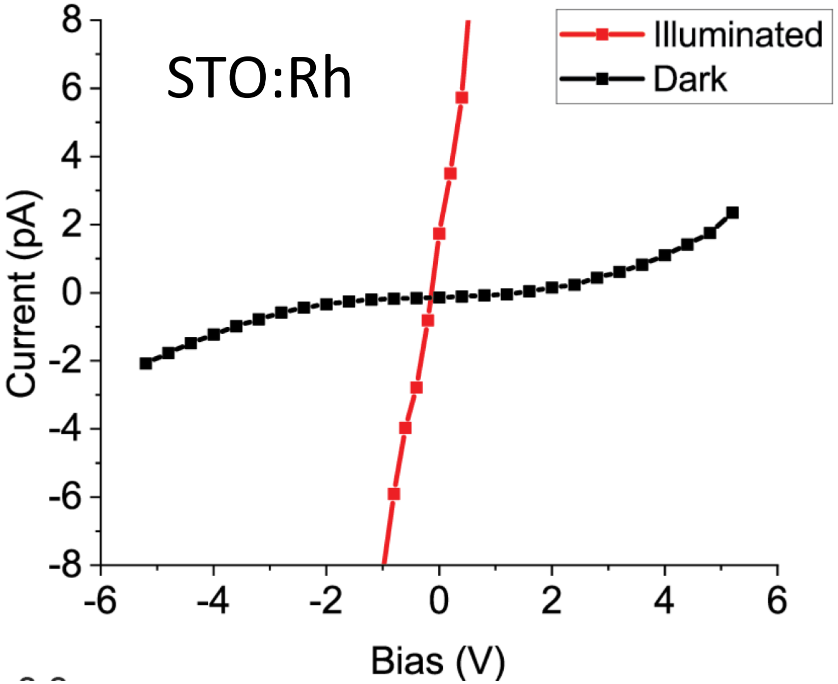


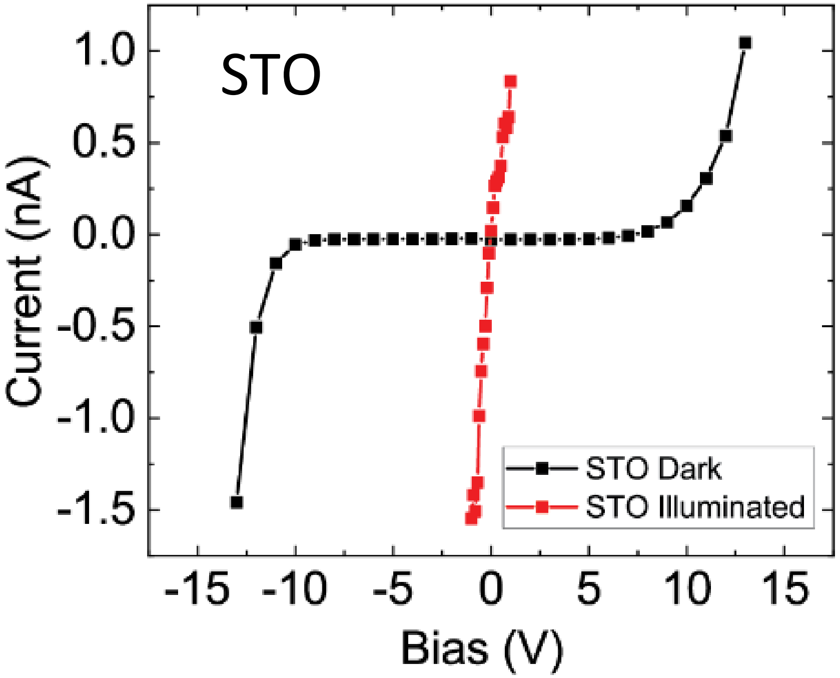
$$Gain = \mu \frac{V_0 \tau}{L^2}$$

$$\tau_{STO:Rh} = 1.2 \text{ ps}$$

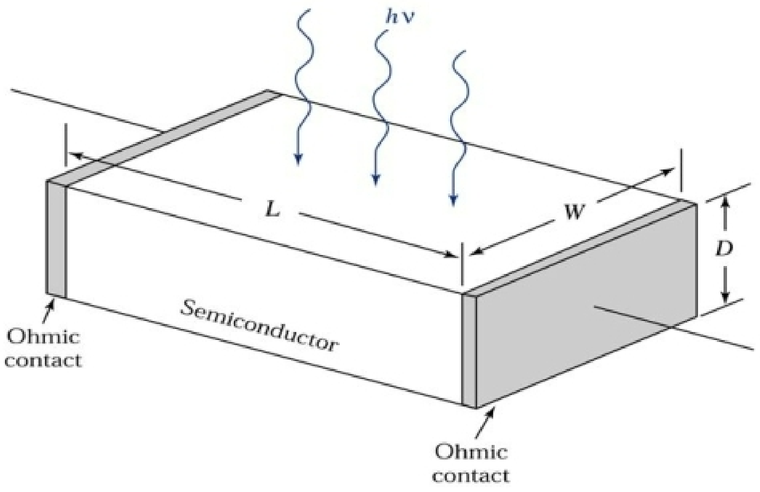
$$\tau_{STO} = 90 \text{ ps}$$







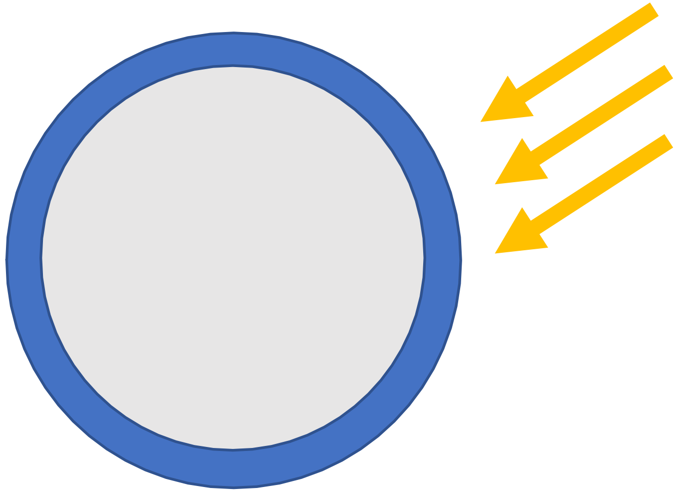
STO:Rh nanoparticles behave as photoconductors



$$Gain = \mu \frac{V_0 \tau}{L^2}$$

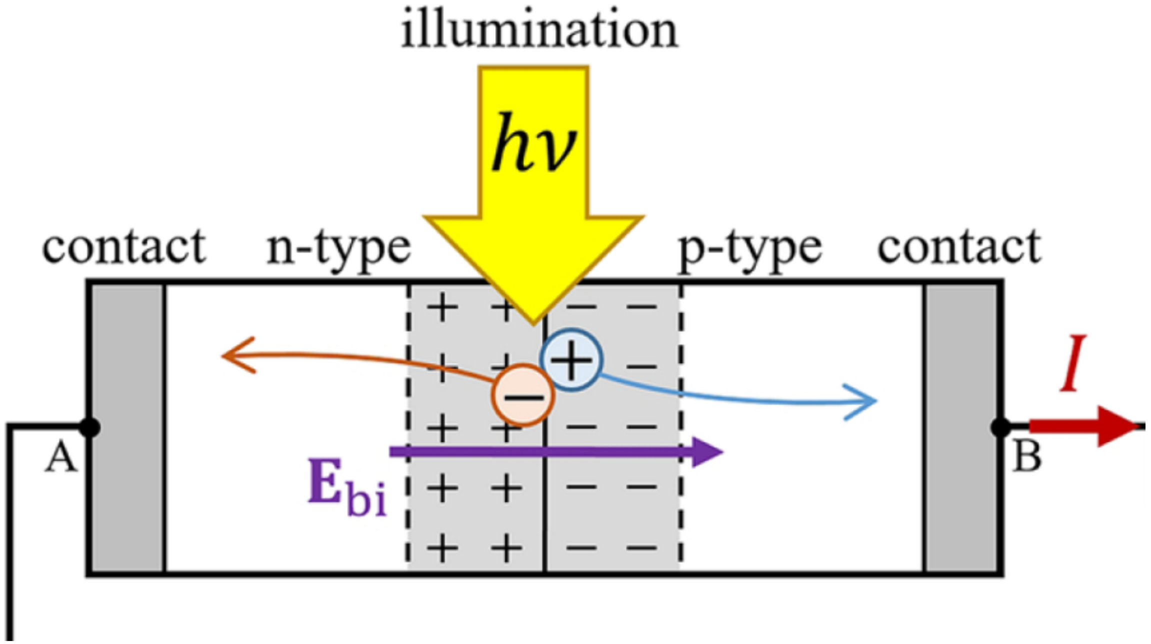
$$\tau_{STO:Rh} = 1.2\ \text{ps}$$

Diffusion Length = 6 nm



In 170-nm radius particle only 10% of volume is active

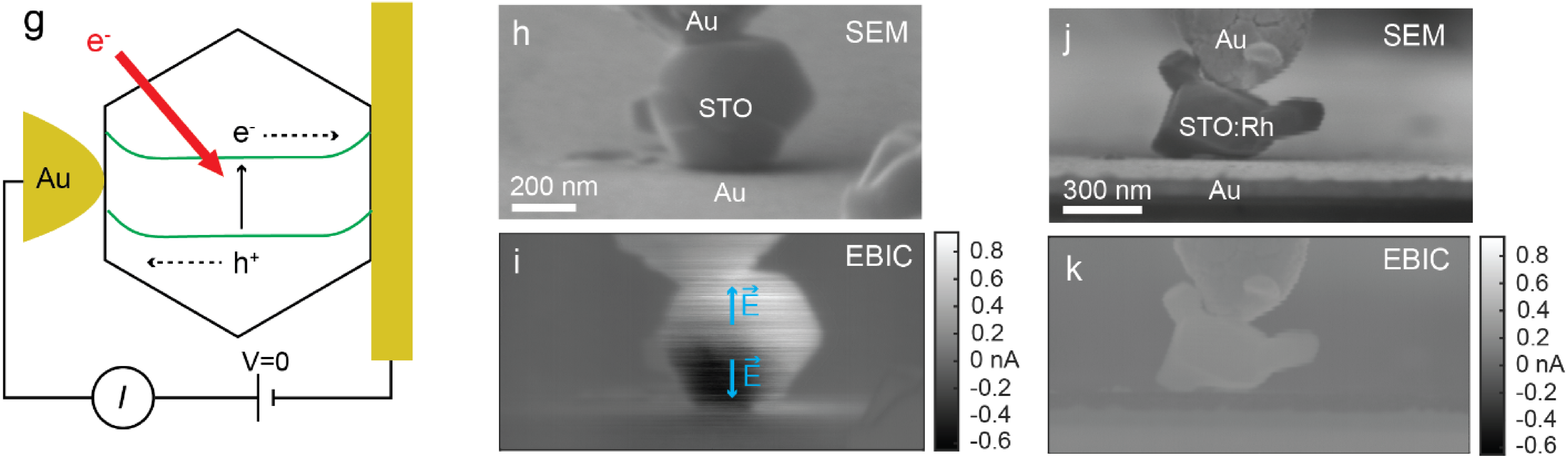
Built-in E fields increase e-h separation efficiency



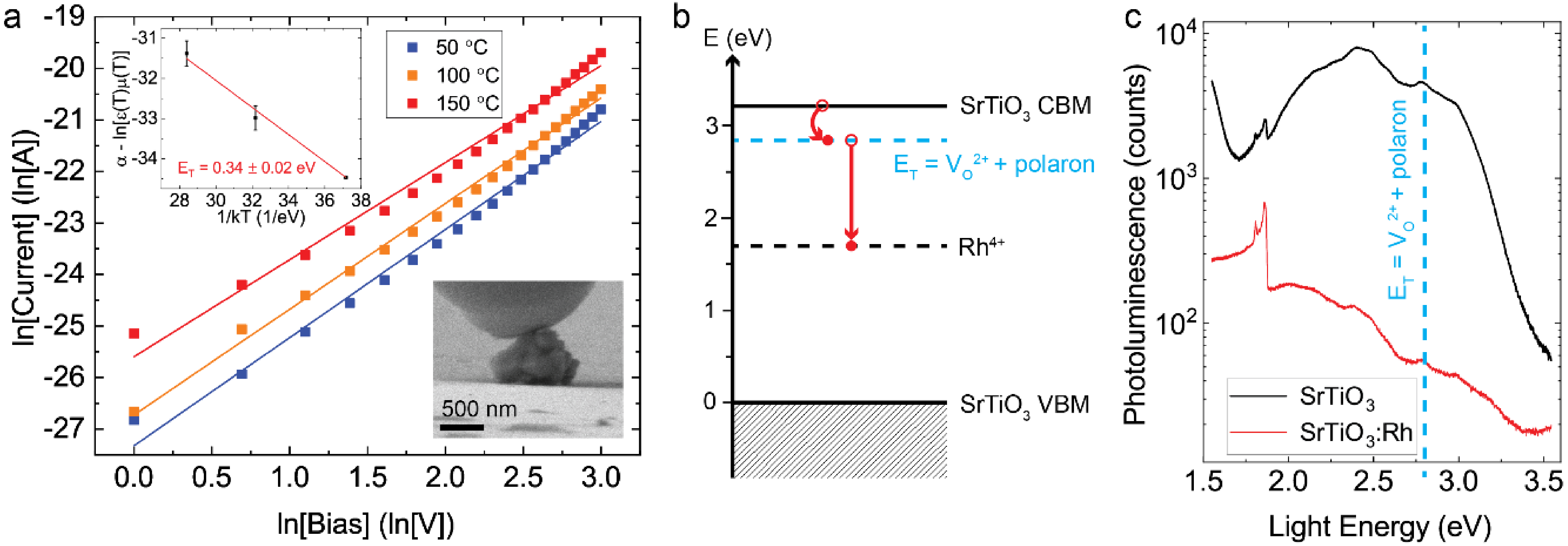
Lipovsek et al. AIP Advances 2019

Free carriers within a semiconductor can move to screen changes in work function

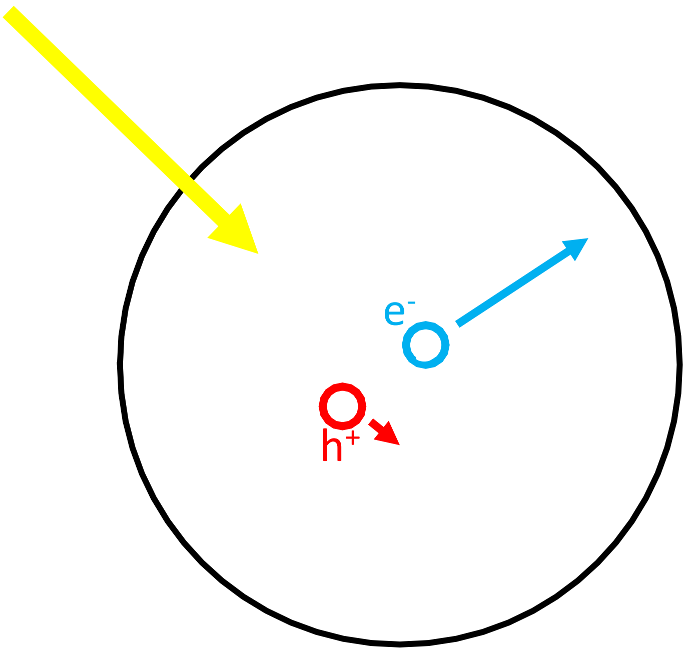
Imaging E fields with electron-beam induced current (EBIC)



No significant built-in E field, no free carriers to screen changes in work function



Free electrons donated by oxygen vacancies are trapped by rhodium acceptor states



- Solar irradiation will generate one e-h pair every 2 ns
  - 1 ps carrier lifetime in STO:Rh
  - 90 ps lifetime in STO
- Negligible chance of multiple e-h pairs interacting
  - Drift-diffusion model will not apply unless carrier lifetime is well in excess of 2 ns
- Difference in electron (10 cm^2/Vs) and hole (.005 cm^2/Vs) mobility may explain separation in STO

Charge transport in STO:Rh PC Nanoparticles

Few free carriers and trap-dominated charge transport

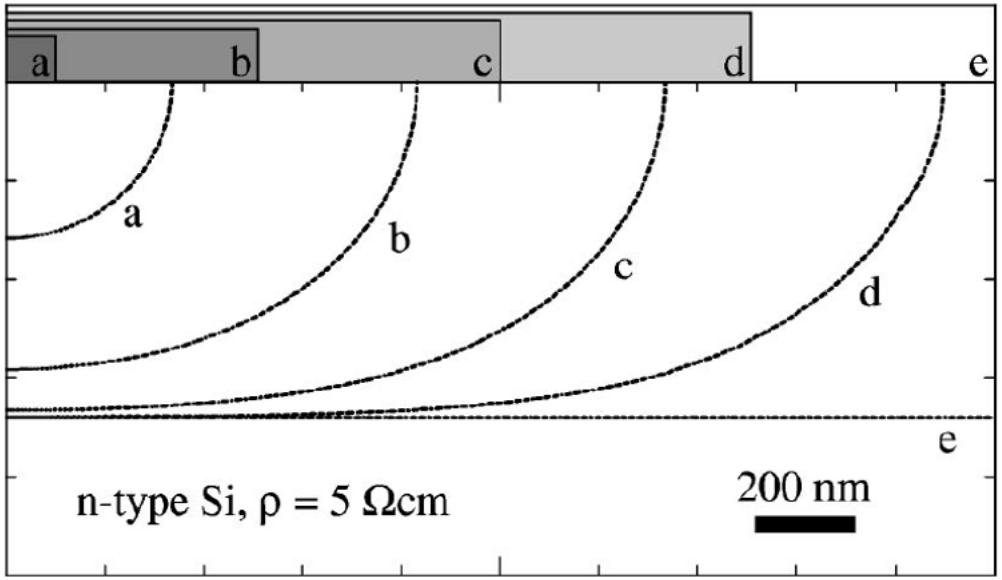
- 1 ps recombination lifetime, 6 nm carrier diffusion length limit active volume
- Free electrons donated by oxygen vacancies are trapped by rhodium acceptor states

No measured internal E fields to aid charge separation

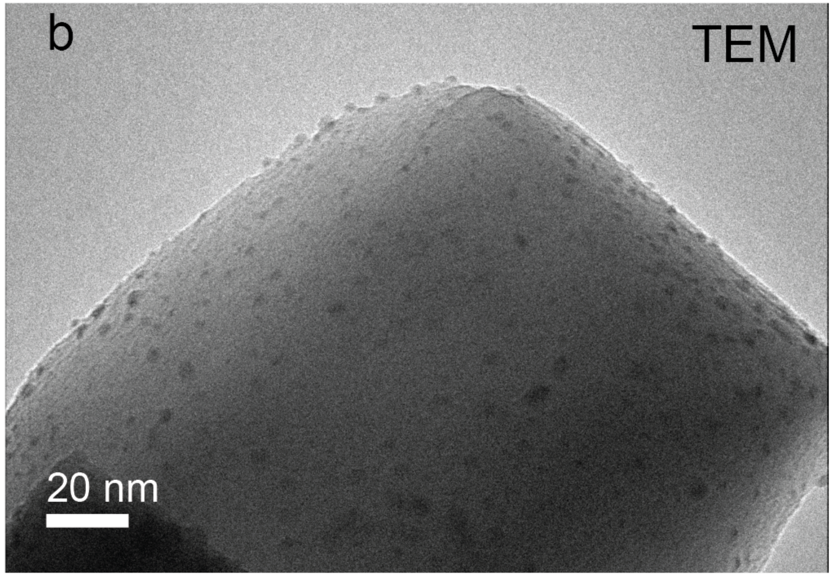
- High free carrier concentration (>> 10^{17} cm^{-3}) is required to screen changes in work function

Need a dopant (or co-dopant which increases light absorption without sacrificing carrier lifetime

Nanoscale Schottky contacts have different behavior than planar contacts



Smit, Rogge, Klapwijk. "Enhanced tunneling across nanometer-scale metal-semiconductor interfaces". Appl. Phys. Lett (2002)



Electrostatically, a Pt co-catalyst of 5 nm diameter can have a depletion region of, at most, 10-15 nm