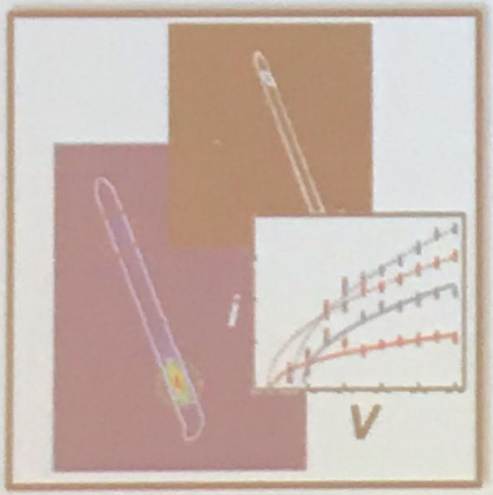
Single-molecule Catalysis

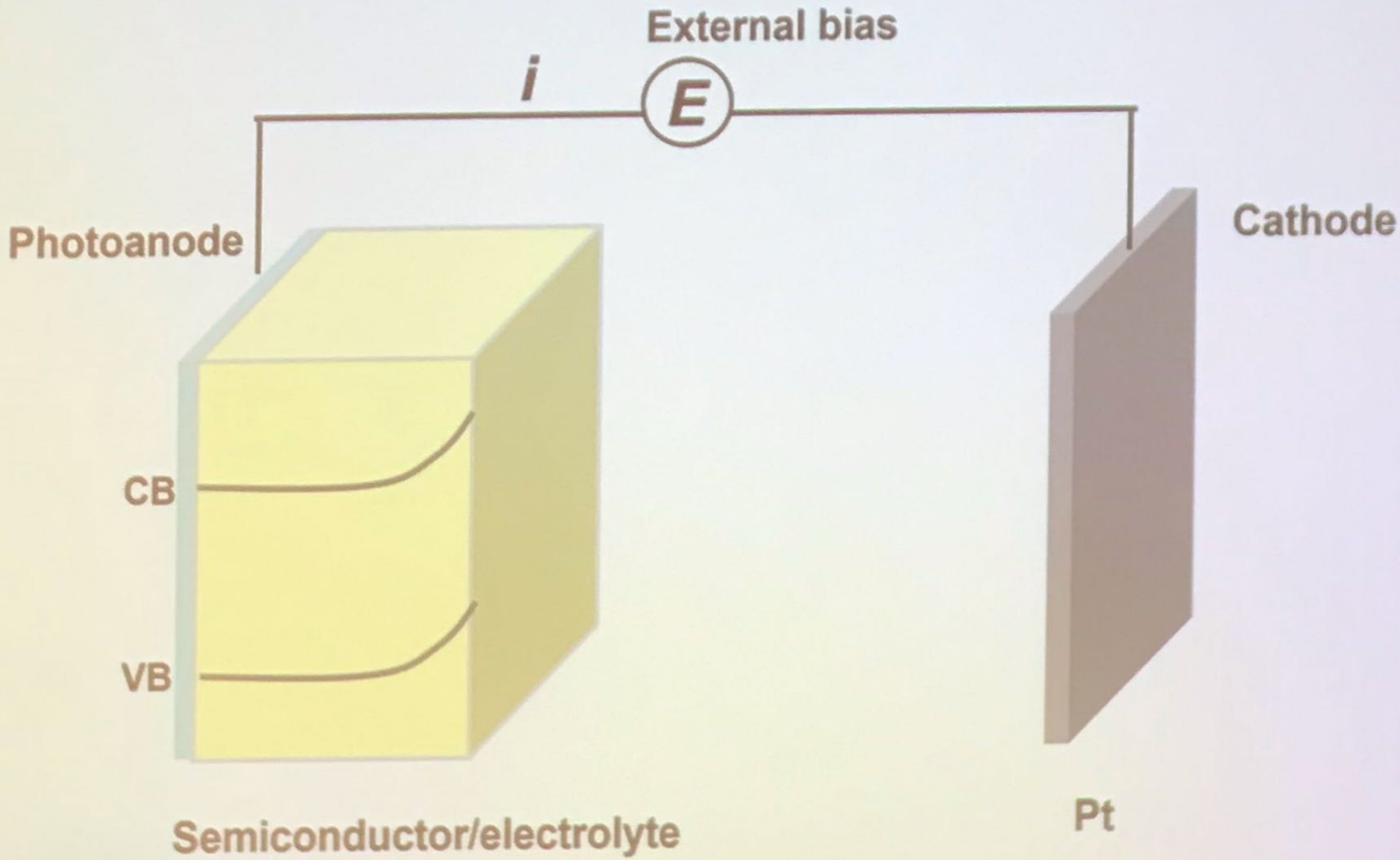
Photoelectrodes



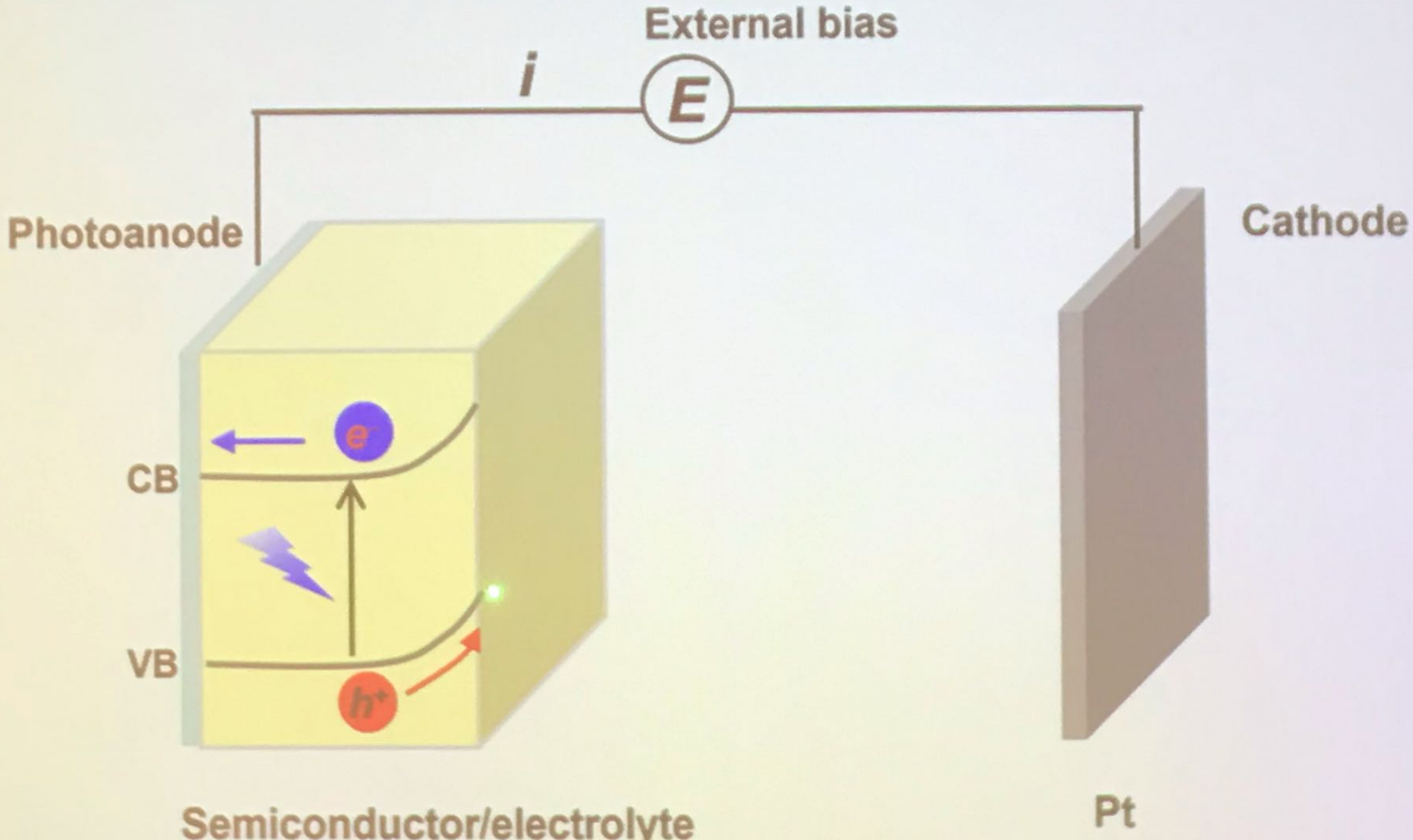
Polymers

Peng Chen
Cornell University
Department of Chemistry and Chemical Biology

Photoelectrochemical Water Splitting for Solar Energy Conversion



Photoelectrochemical Water Splitting for Solar Energy Conversion



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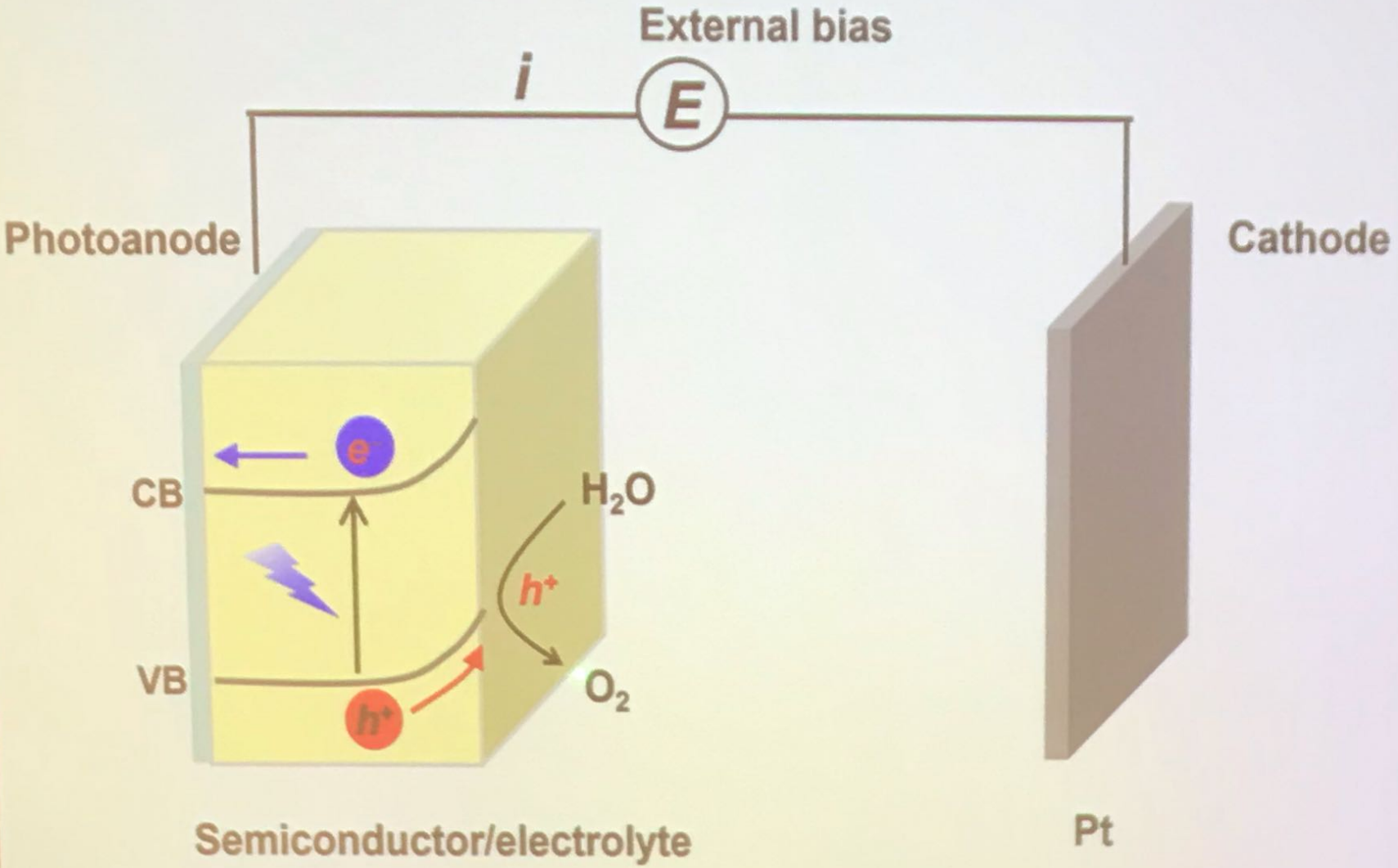
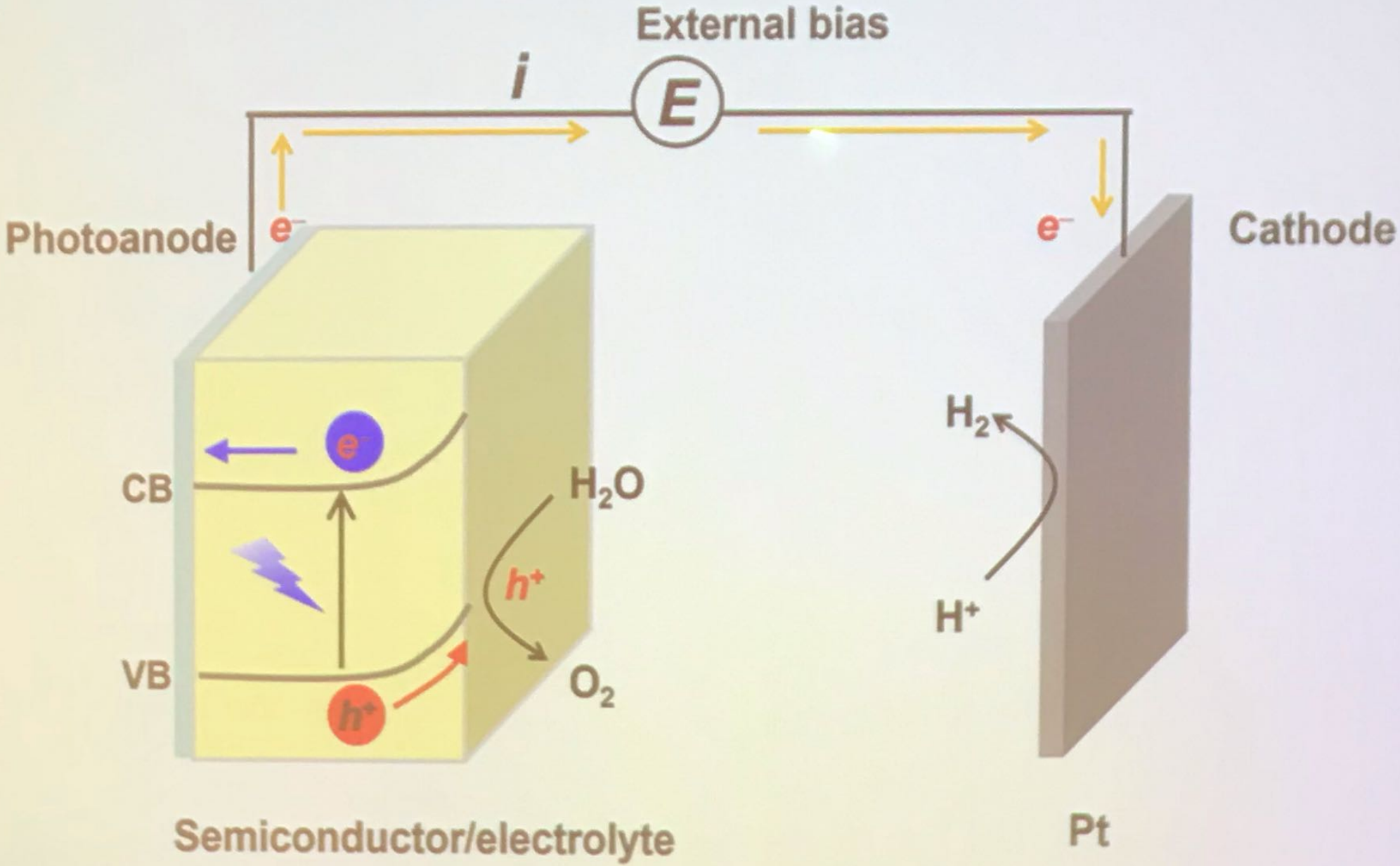


Photoelectrochemical Water Splitting for Solar Energy Conversion



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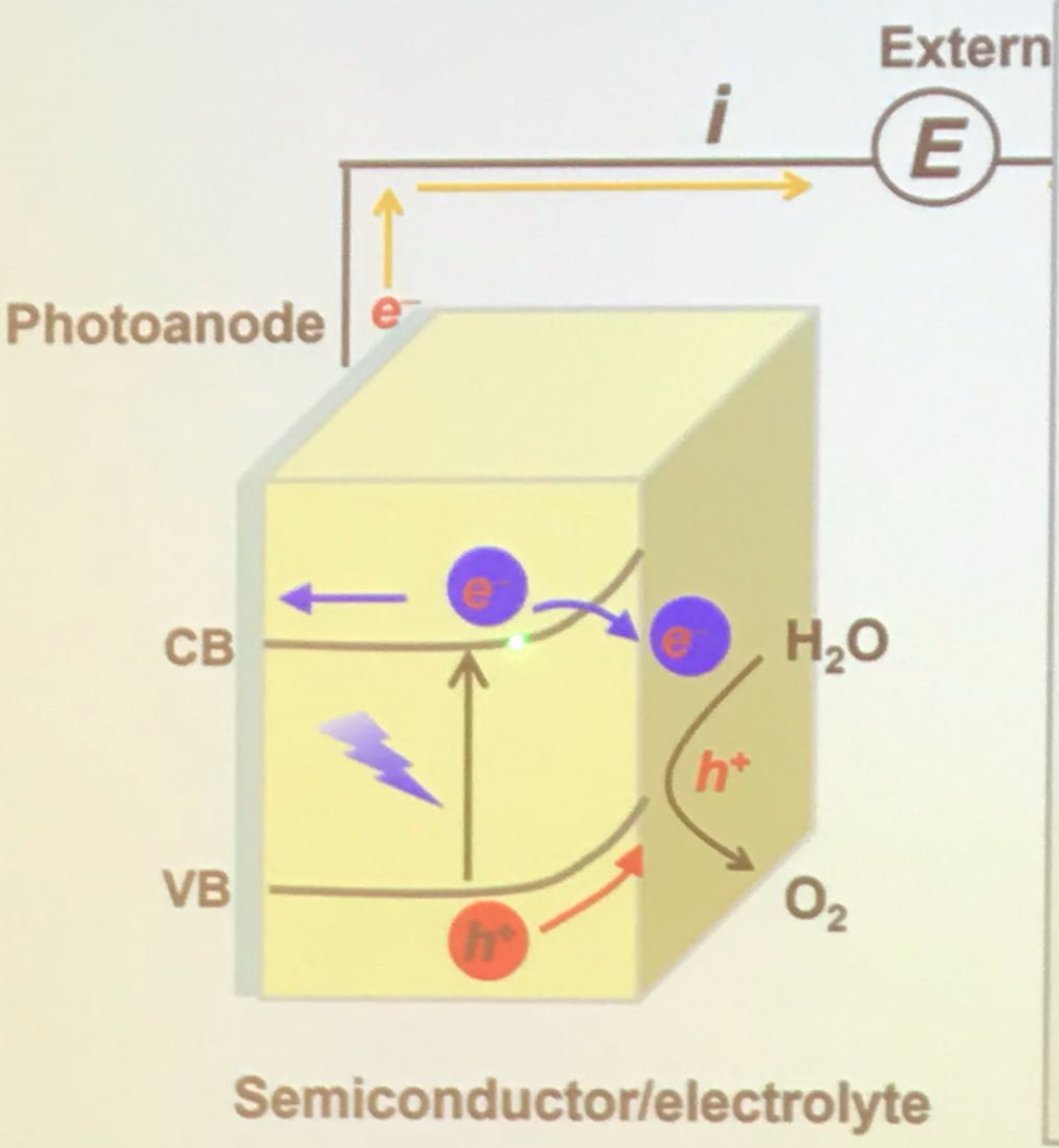
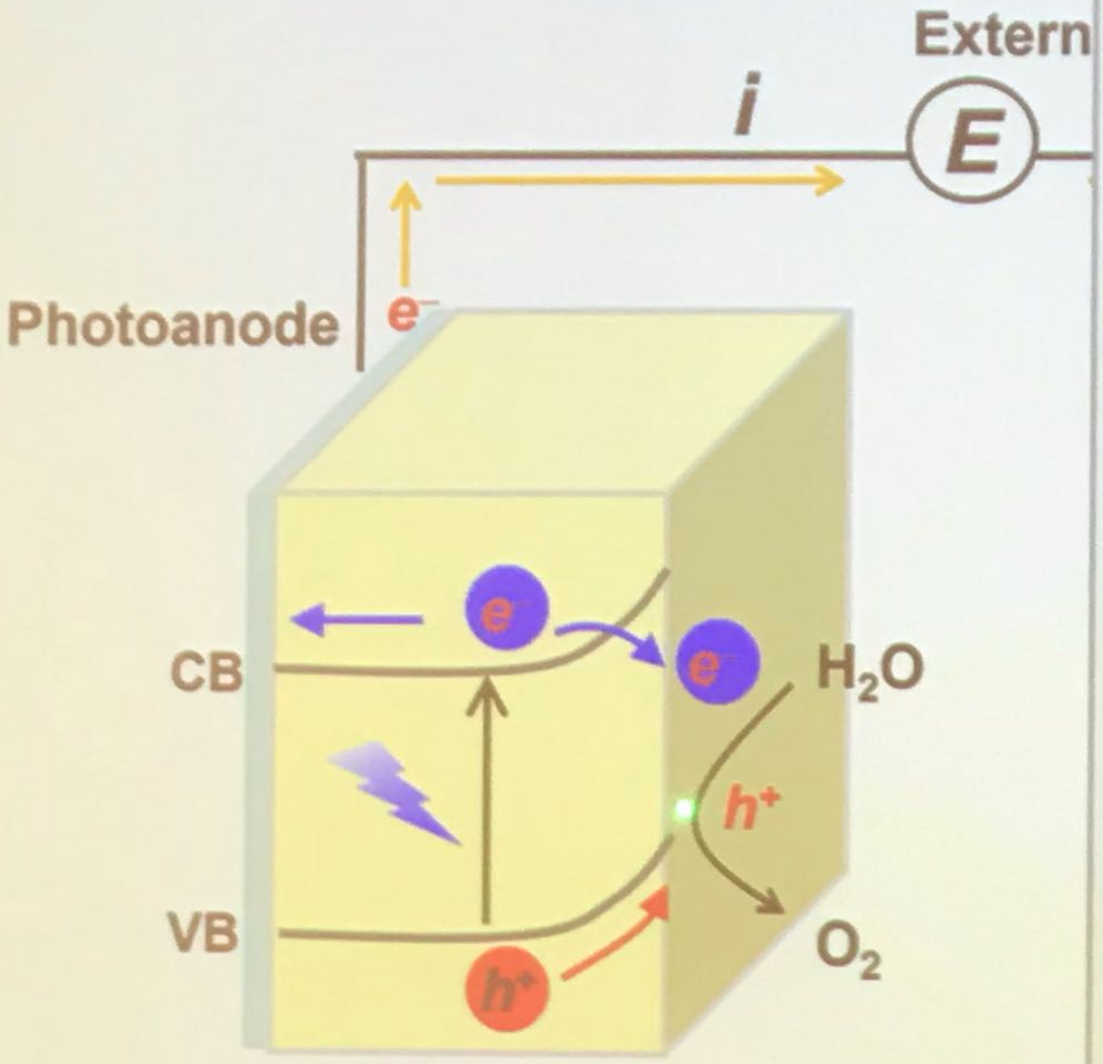


Fundamental questions:

1. **Surface e^-: recombination**
   - → Where preferentially?
   - → At water oxidation sites?

Photoelectrochemical Water Splitting



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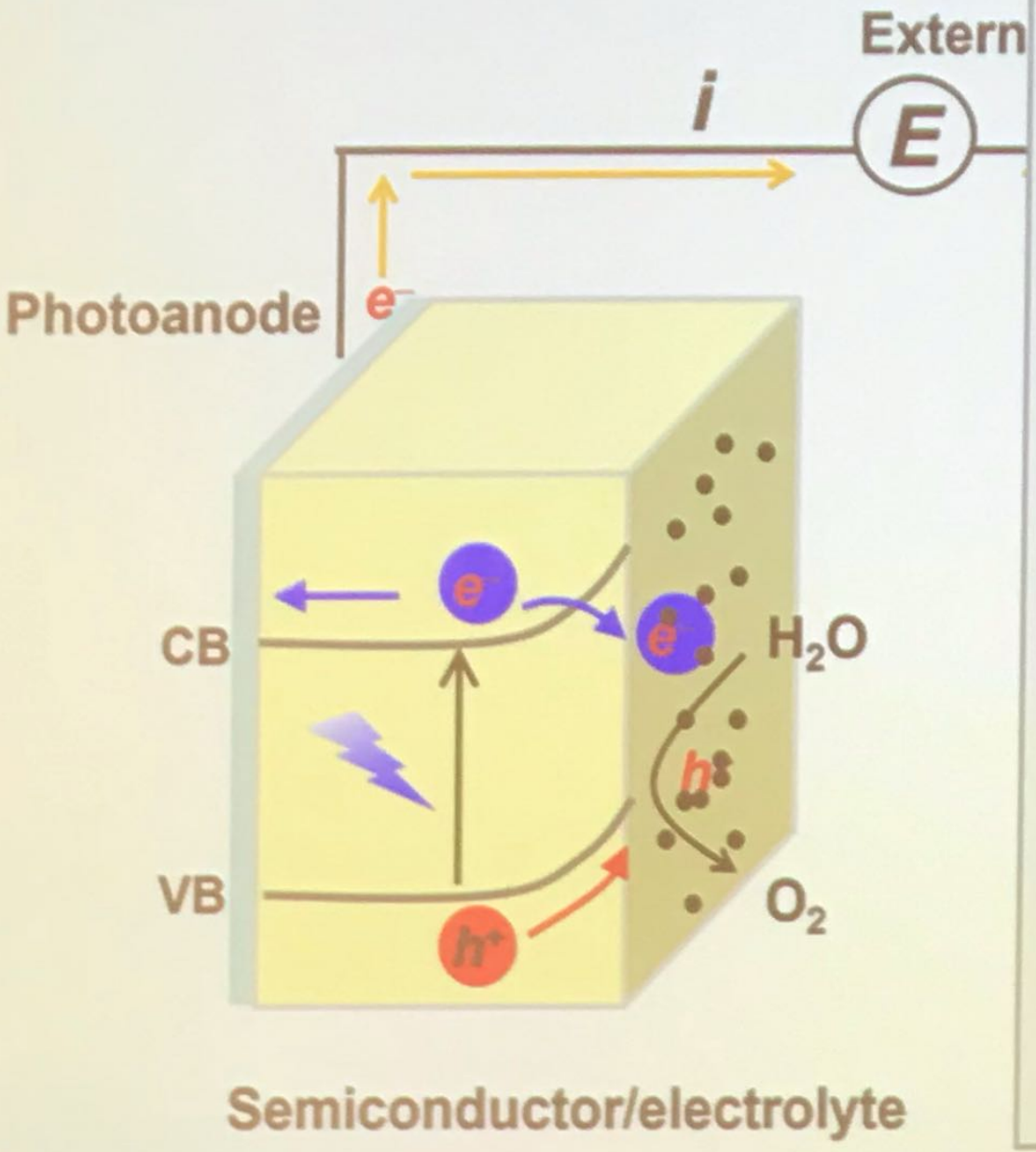
Photoelectrochemical Water Splitting



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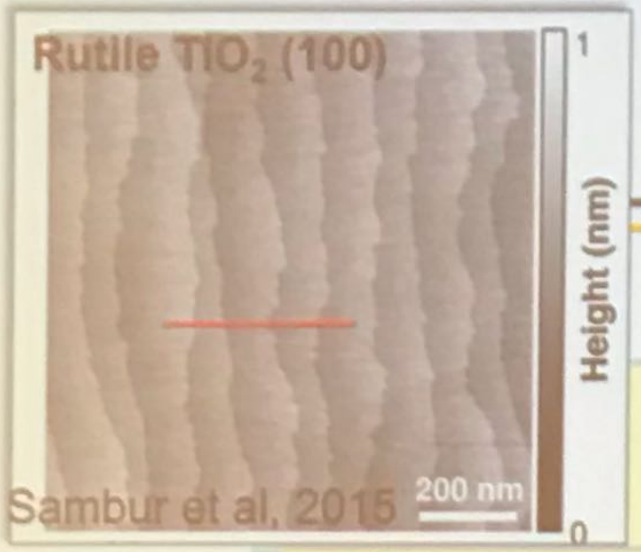

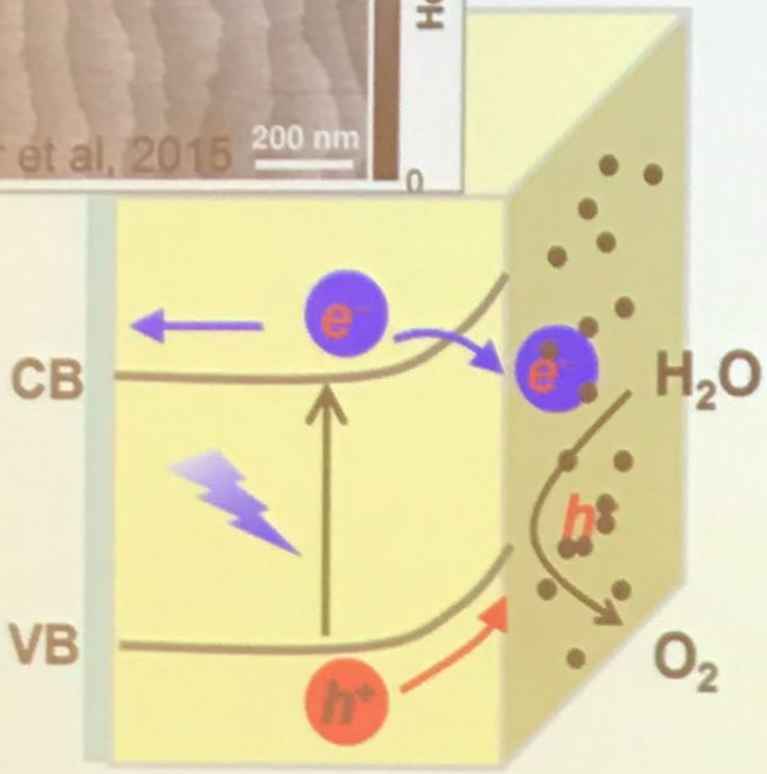

Semiconductor/electrolyte

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2. **Surface h^+ & e^- activity ↔ water oxidation efficiency?**
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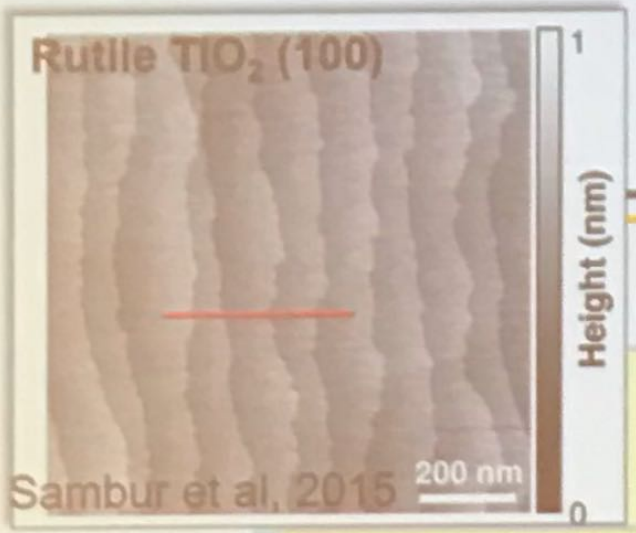
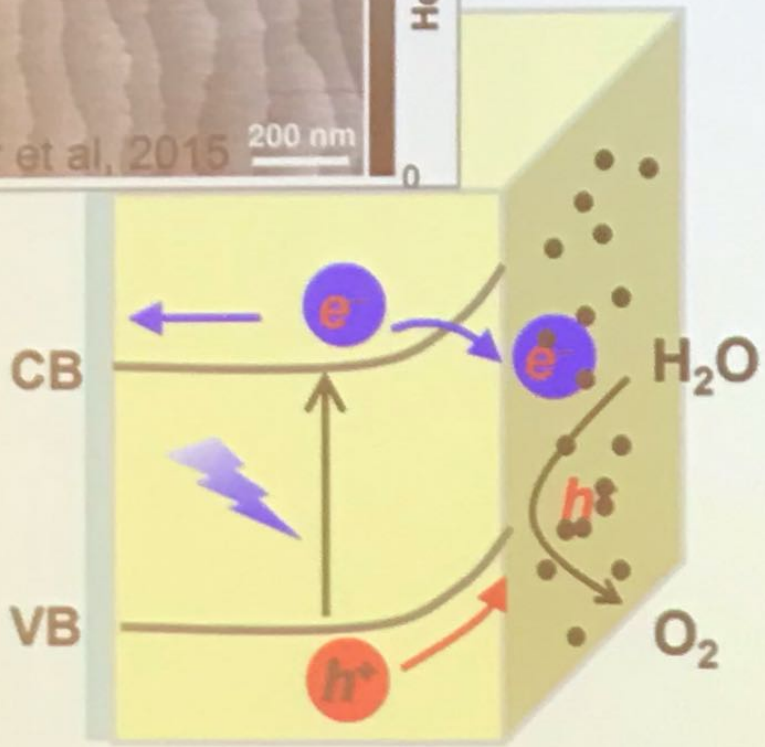
   - → Surface heterogeneity
   - → Worse for *nanoscale* photoanodes → preferred materials

Photoelectrochemical Water Splitting





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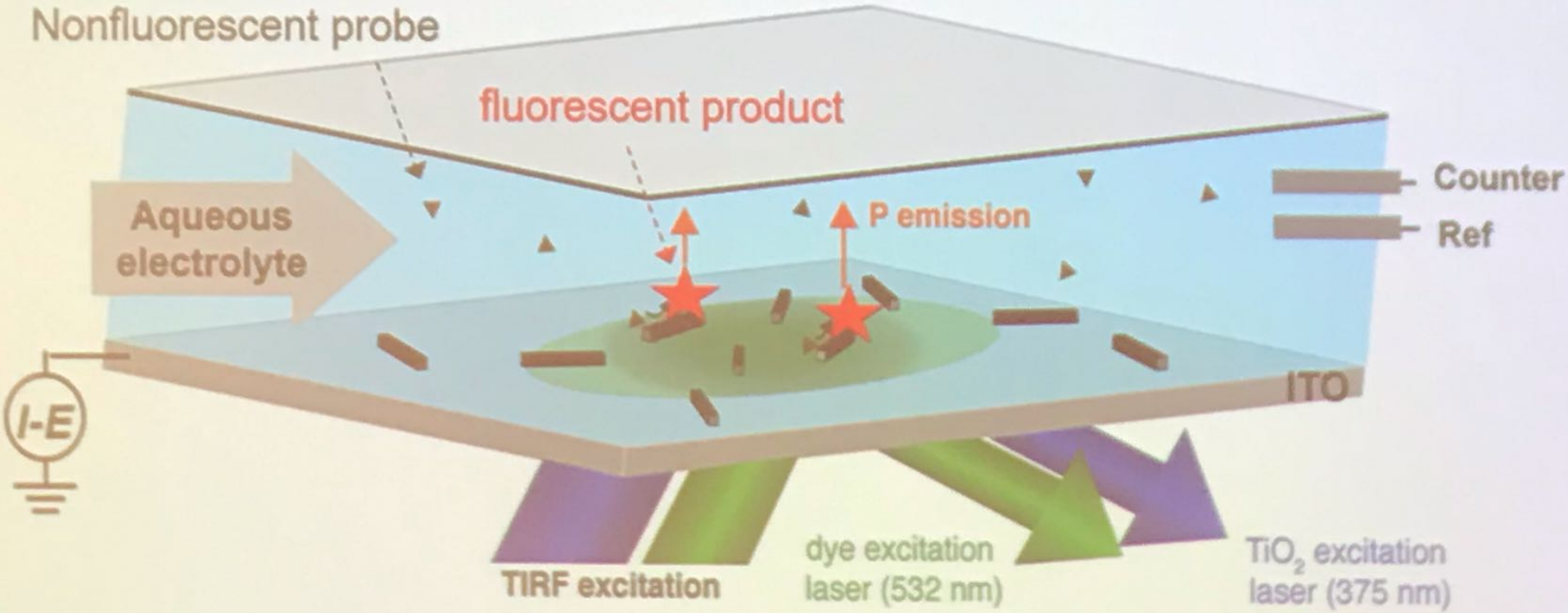
⇒ **Need to define correlation b/w: 1) carrier surface activity at nanoscale ↔ 2) water oxidation ↔ 3) catalyst deposition**

Carrier Activity: Single-Molecule Imaging of Fluorogenic Probe Reactions



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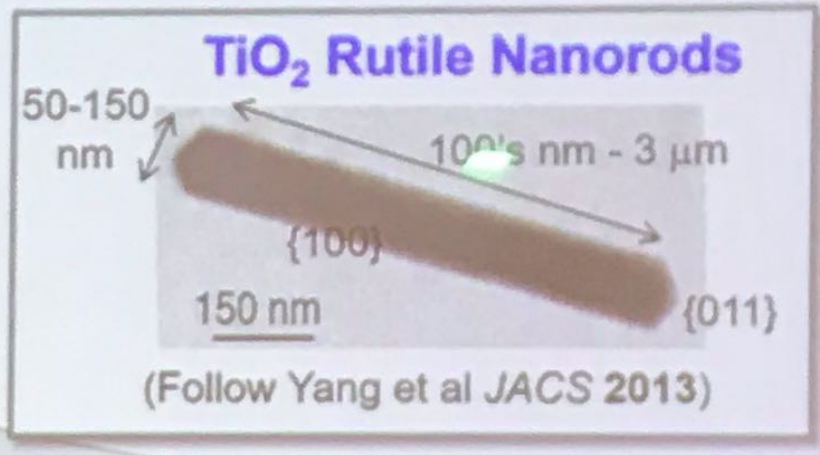

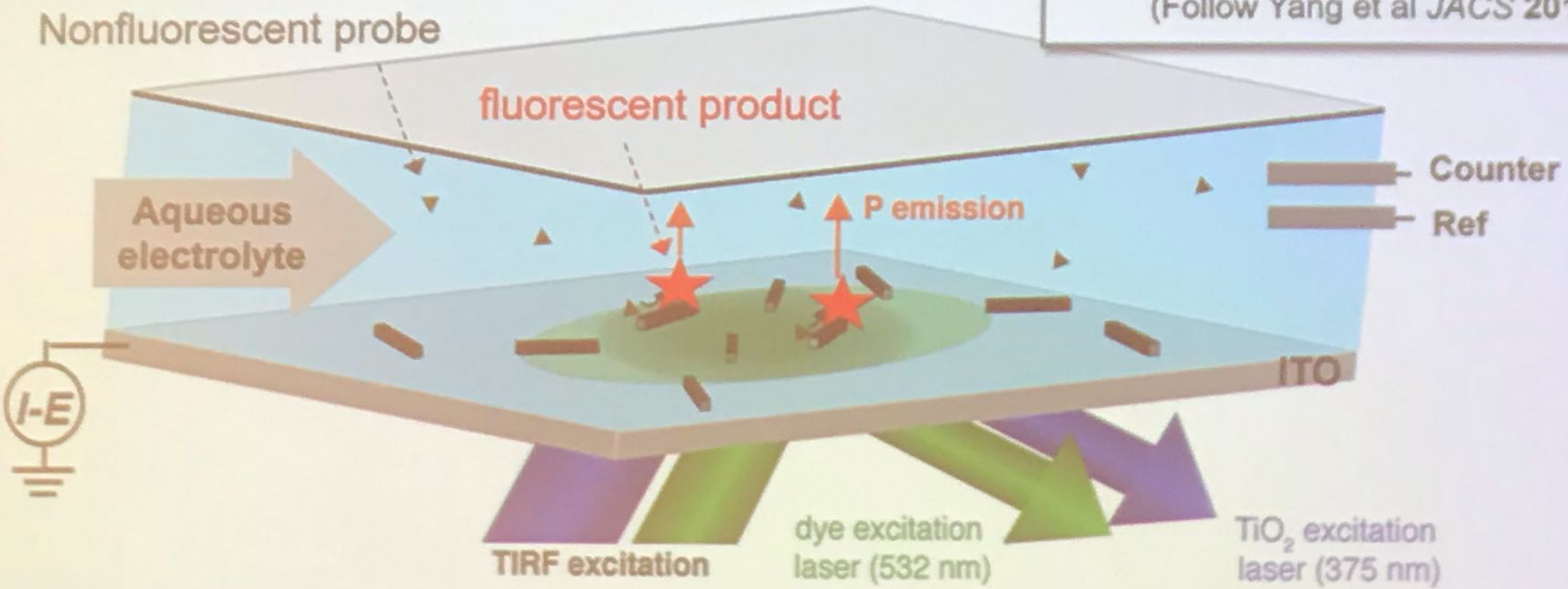

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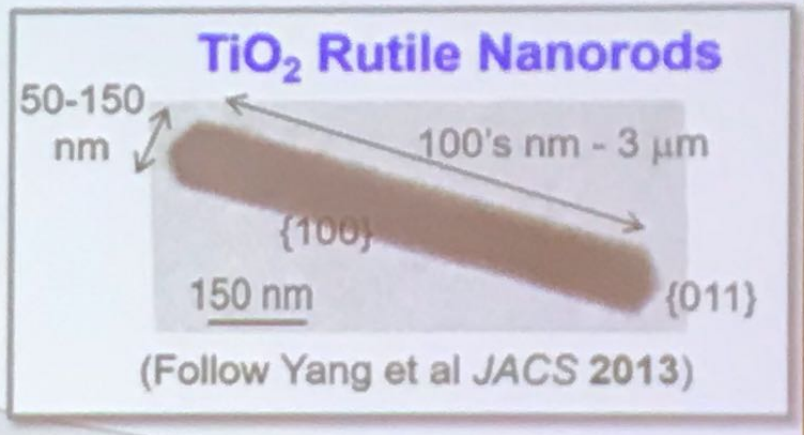
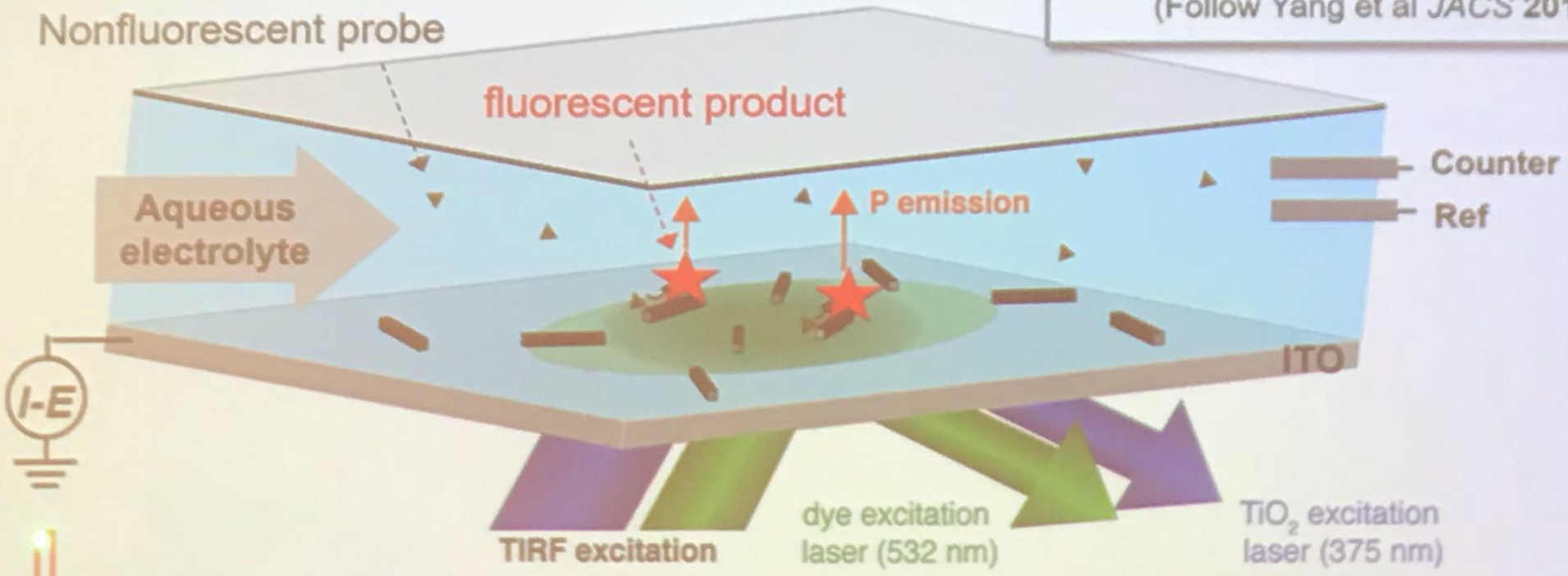
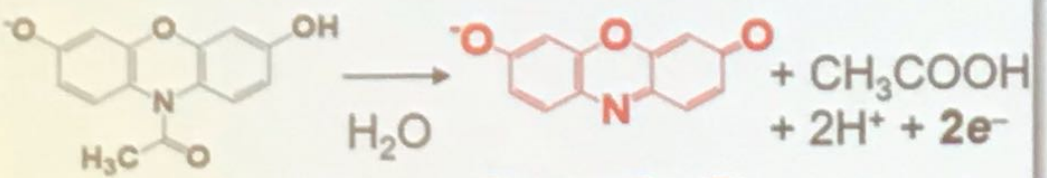




- Fixed *E* (then step) → steady state, anodic photocurrent
- Photocurrent dominated by H_2O oxidation (1M KCl, 100mM pH8 borate, degassed)

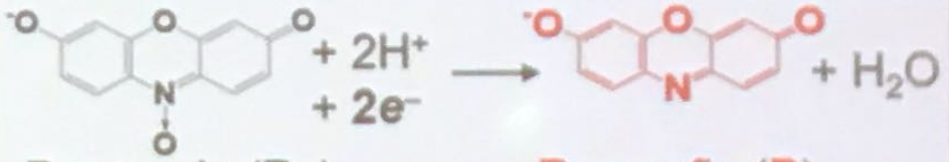
Electrochemistry of Carrier-Selective Probes

h^+ probe rxn

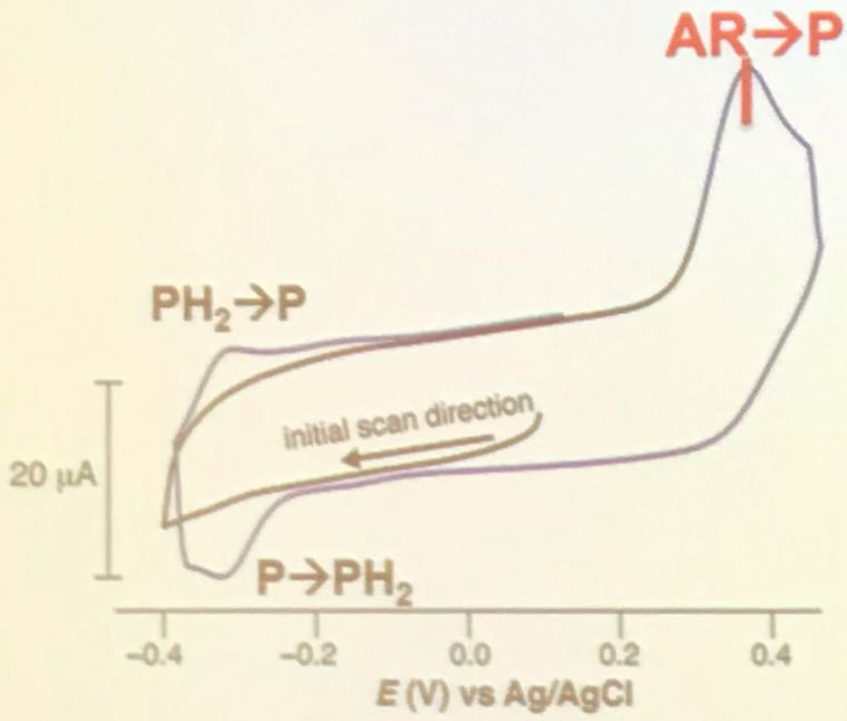


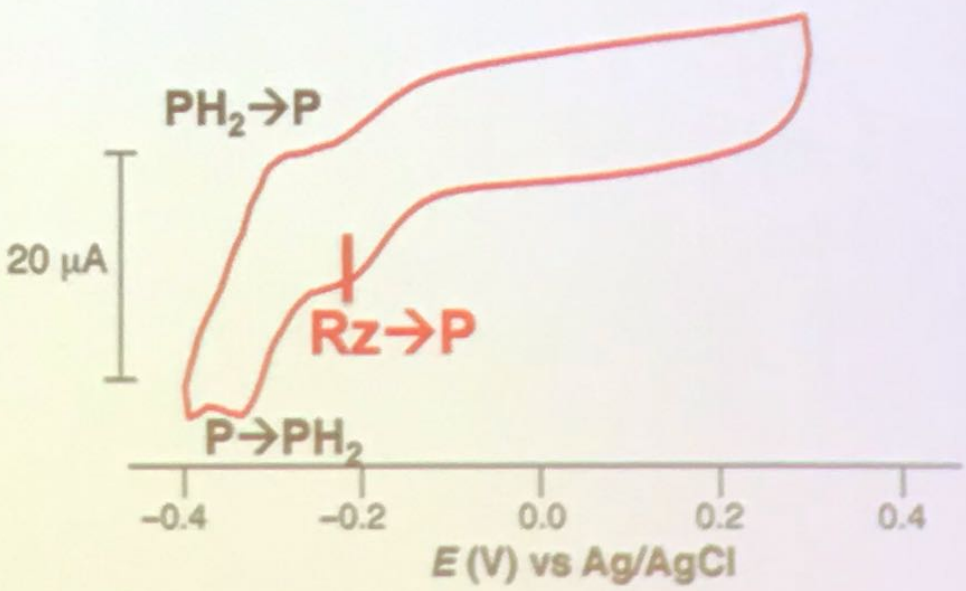
Amplex red (**AR**) Resorufin (**P**)

e^- probe rxn



Resazurin (**Rz**) Resorufin (**P**)





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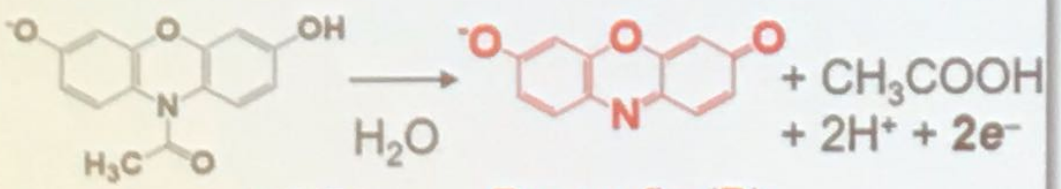

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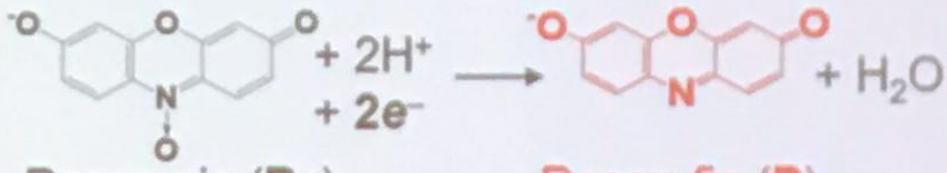

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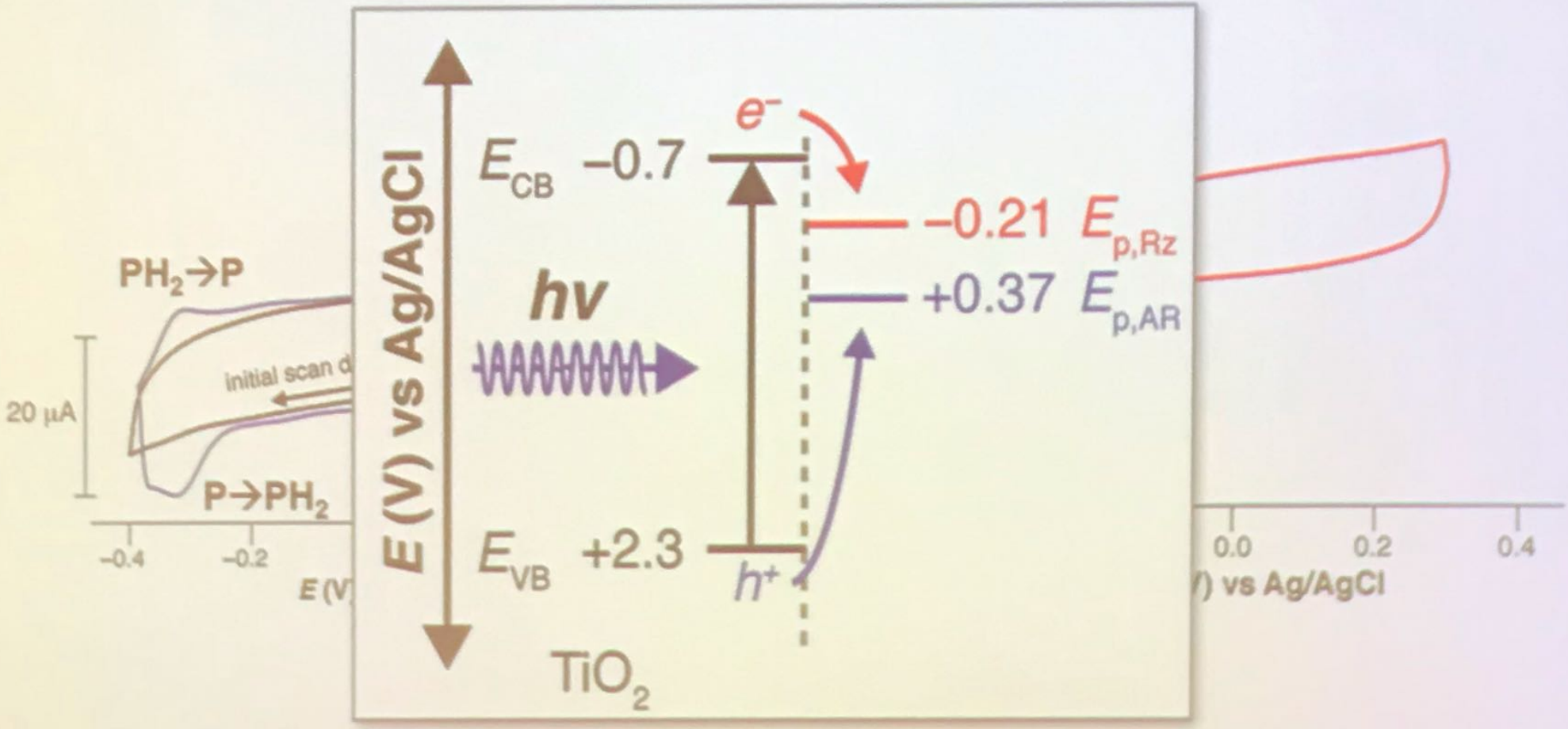
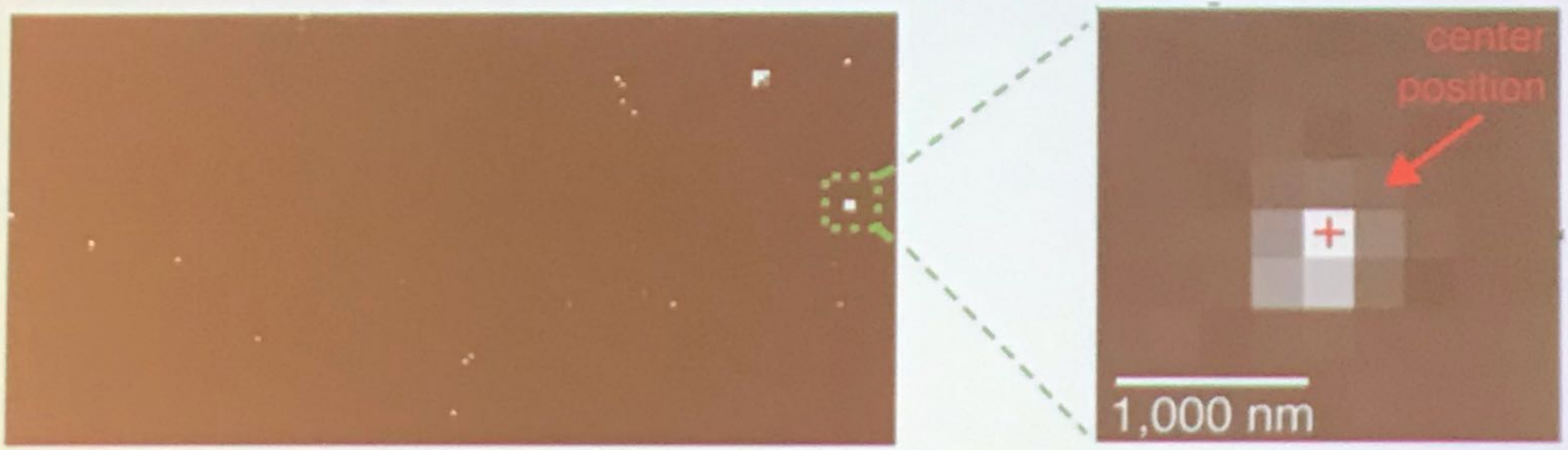


Super-resolution Reaction Mapping (e.g., h^+-induced)

Fluorescence image from a movie (15 ms/frame)



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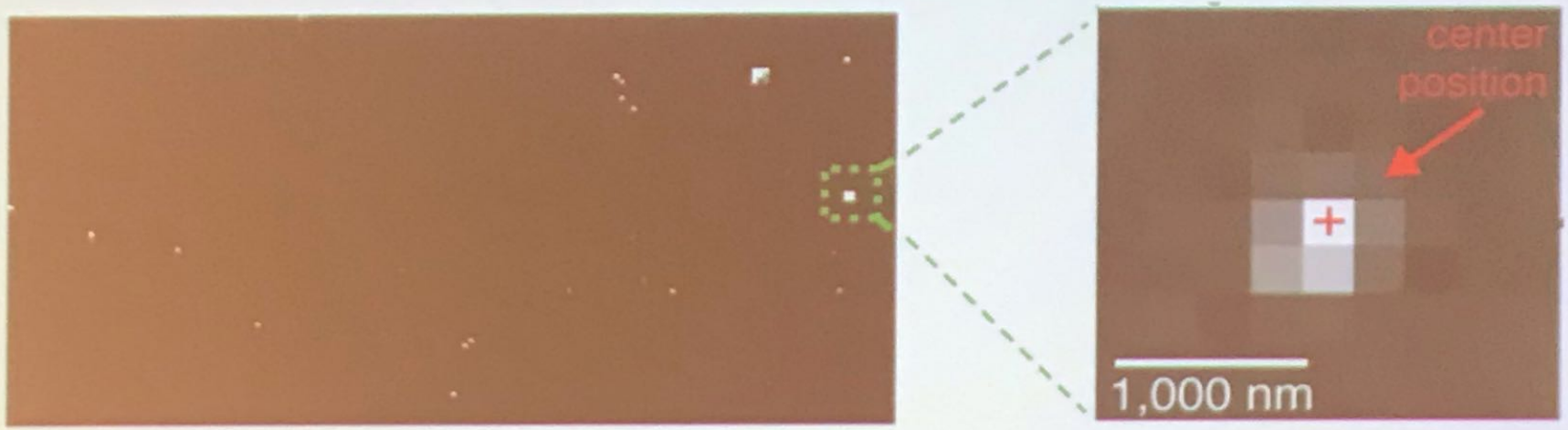

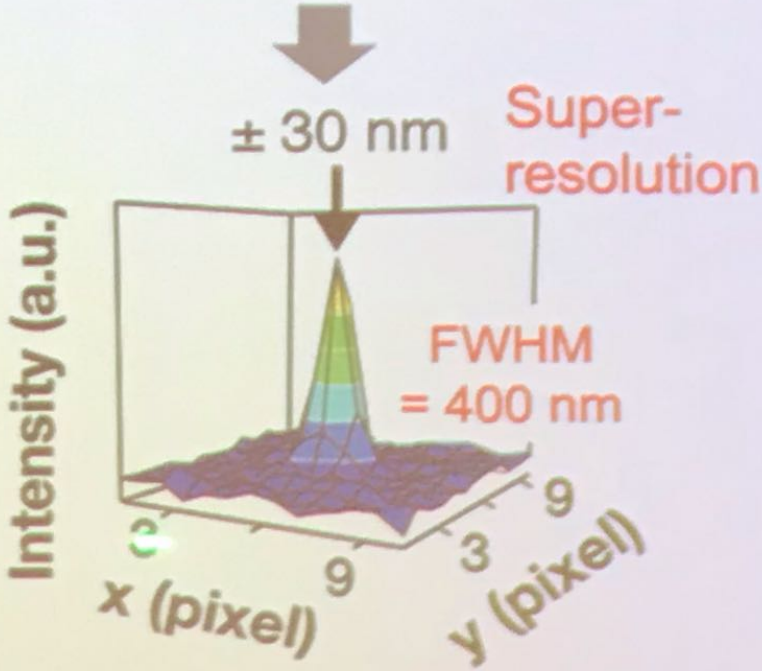

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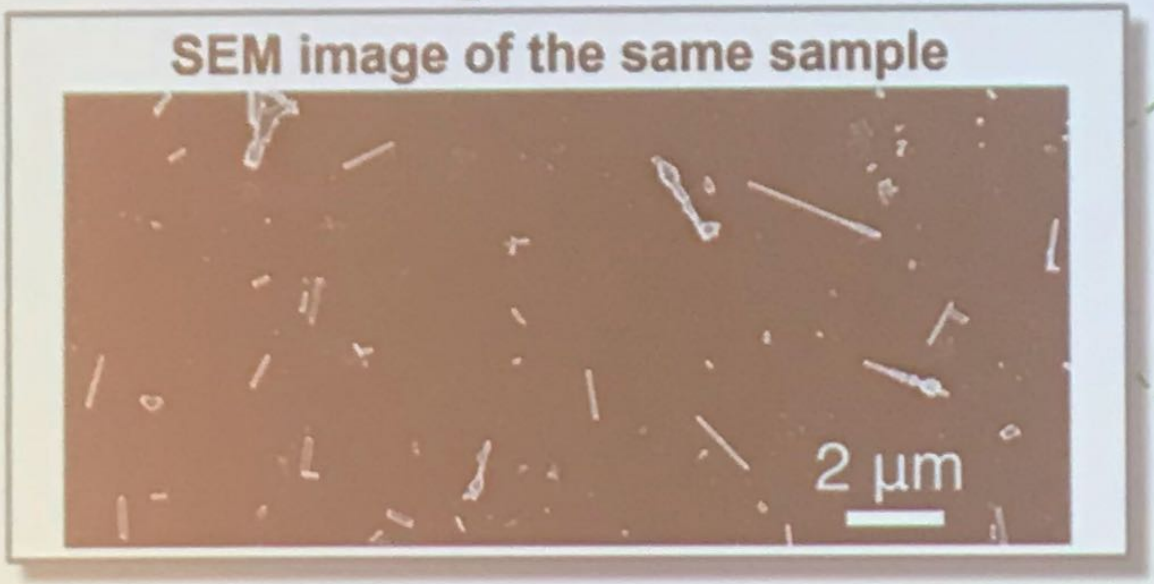
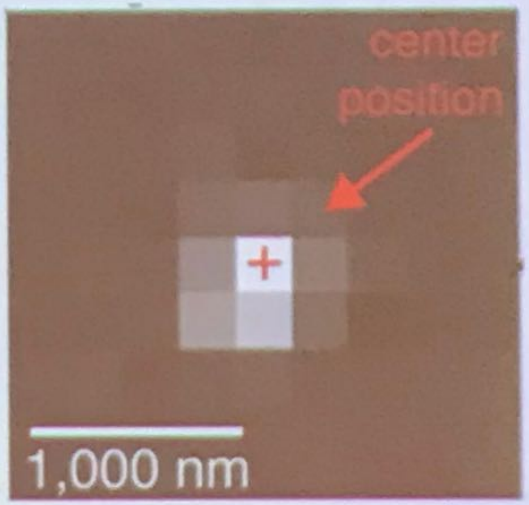
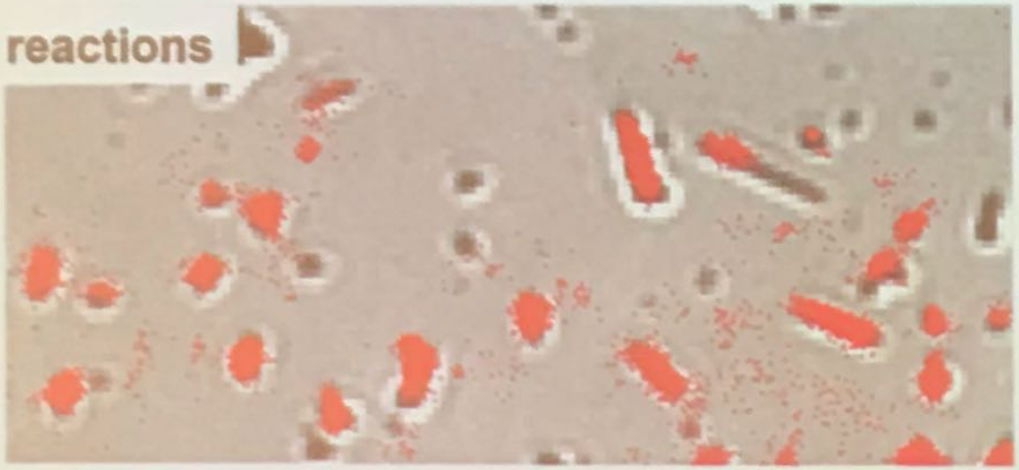
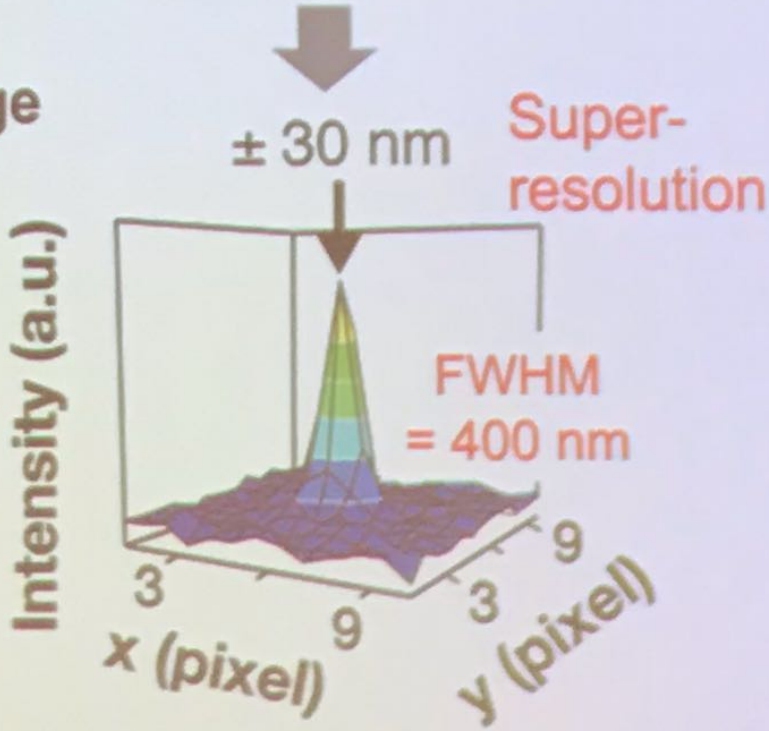




Overlay of 1000s' rxns on transmission image





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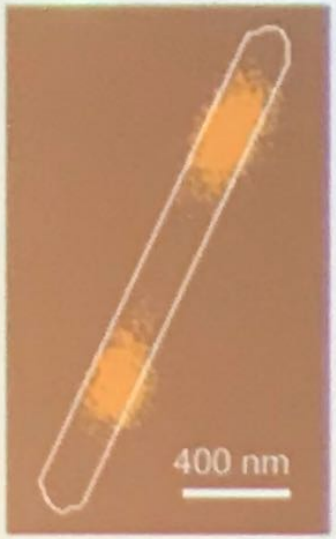
Super-resolution Single-nanorod h^+ & e^- Reaction Mapping

h^+ reactions ($E \geq -0.03$ V)



Scatter plot

Super-resolution Single-nanorod h^+ & e^- Reaction Mapping

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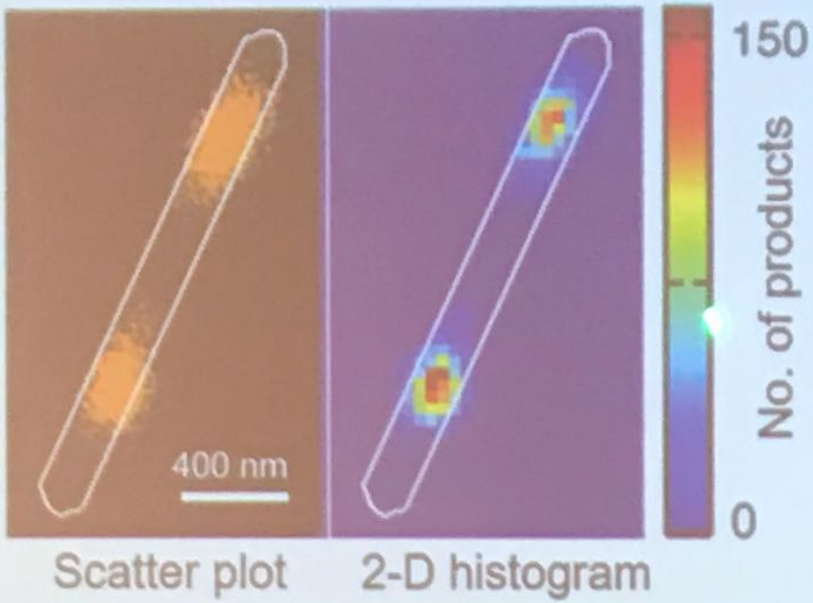

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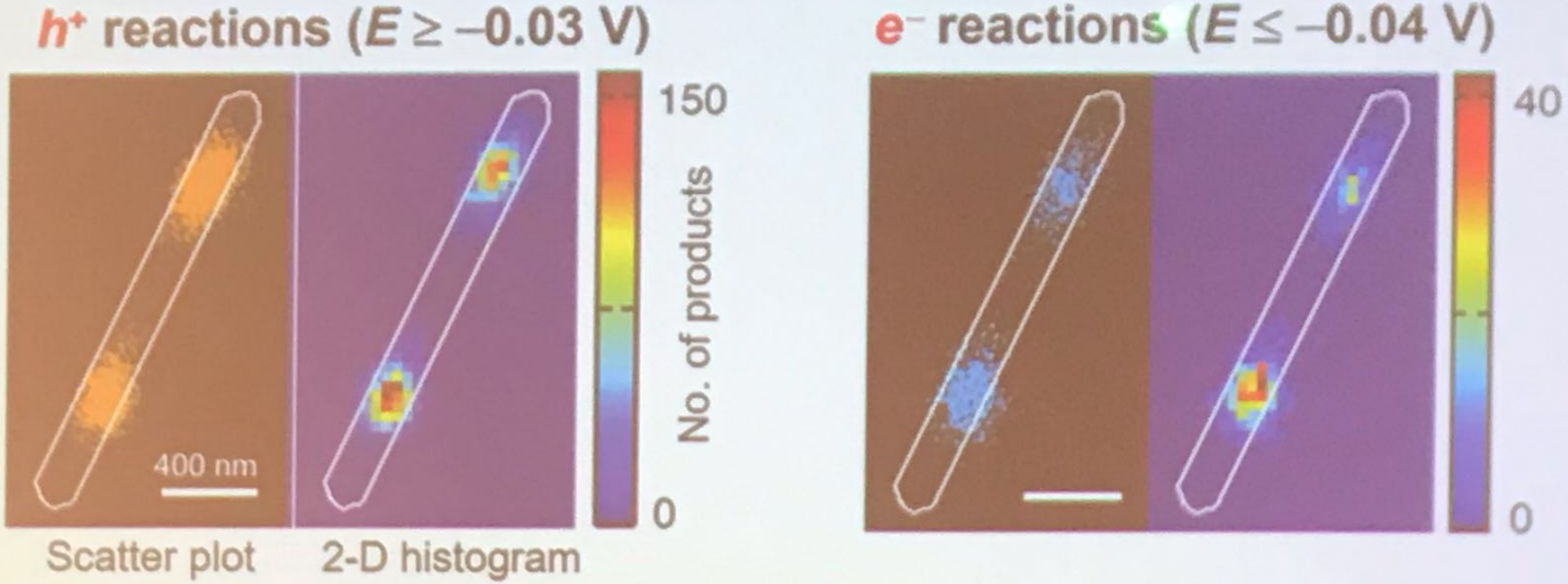

- Reactions non-uniform, w/ nanoscale hot spots! (→ impurity atoms or defects)

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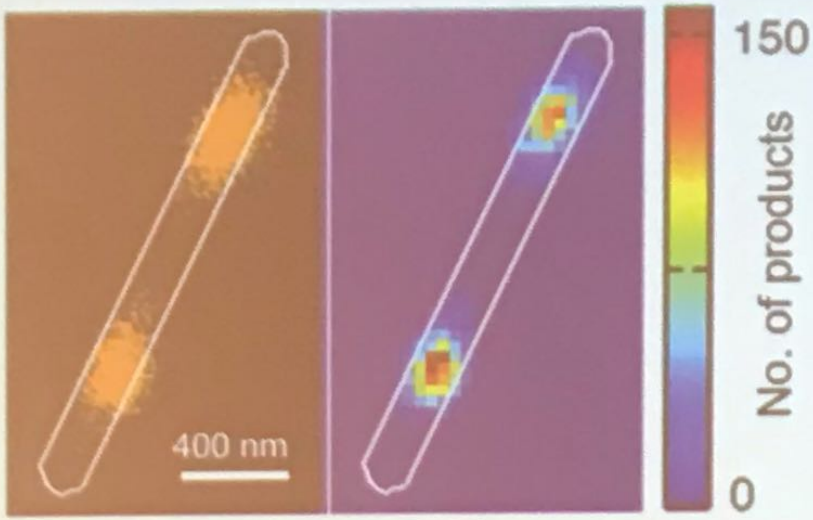
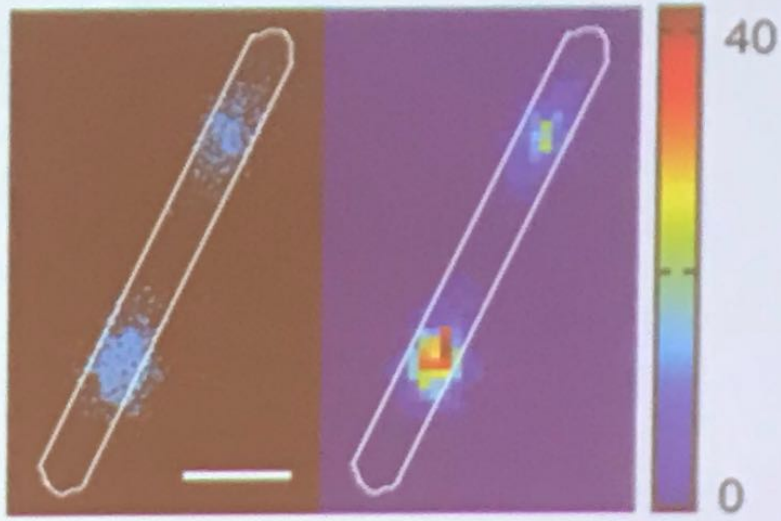
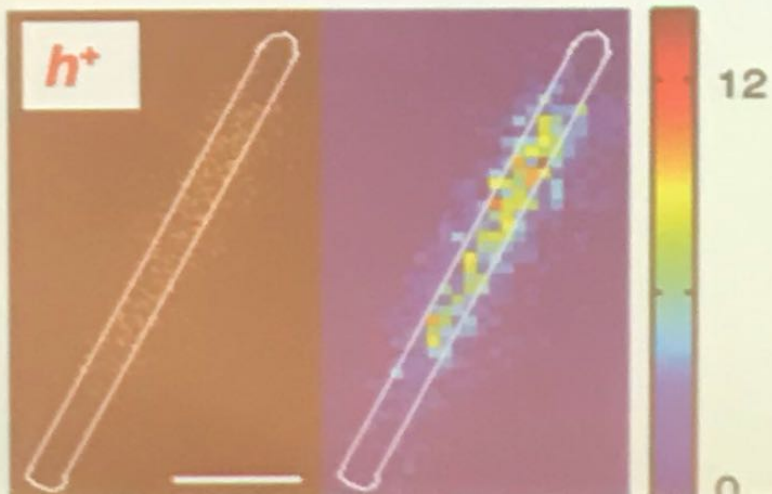


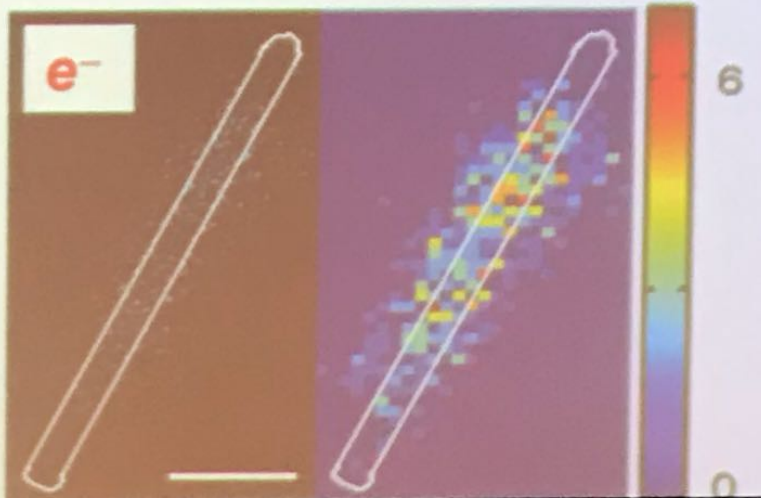
e^- reactions ($E \leq -0.04$ V)



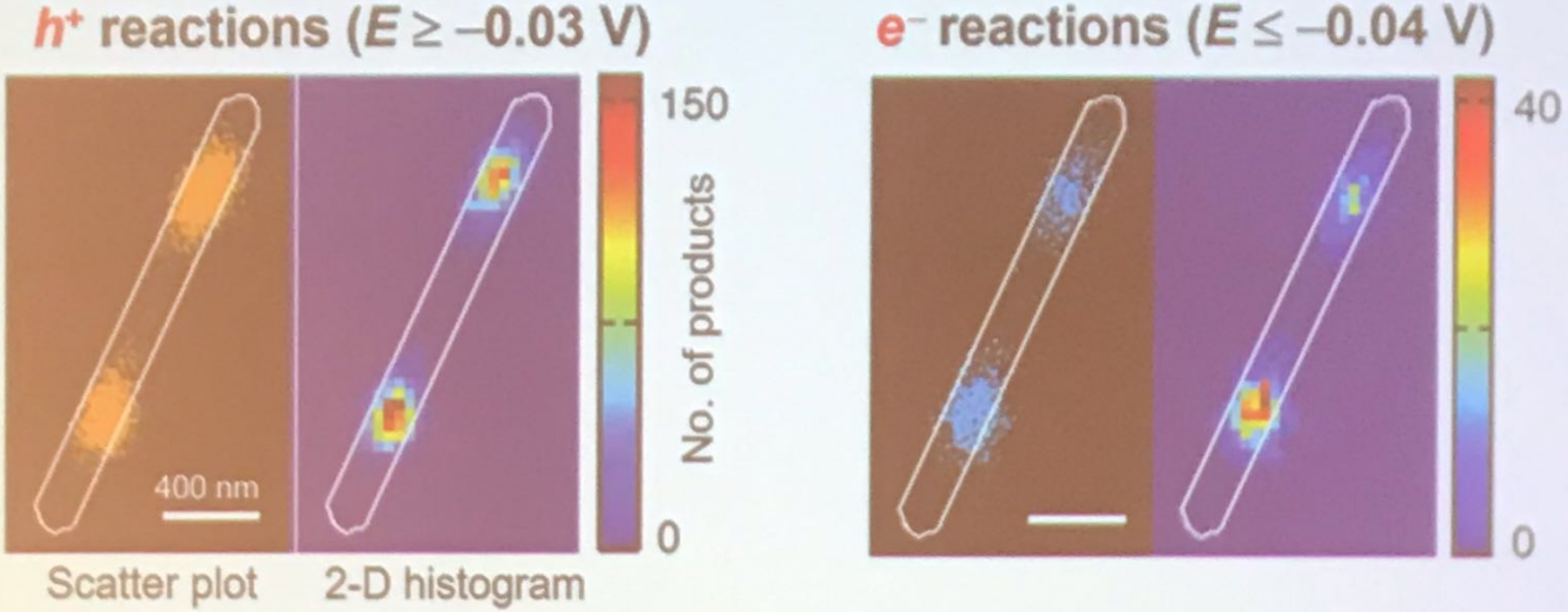
- Reactions non-uniform, w/ nanoscale hot spots! (→ impurity atoms or defects)

Another TiO_2 nanorod → non-uniform, but more delocalized





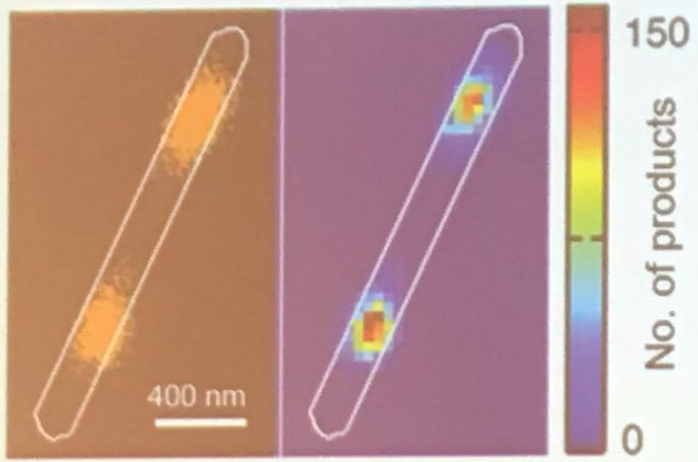
Super-resolution Single-nanorod h^+ & e^- Reaction Mapping



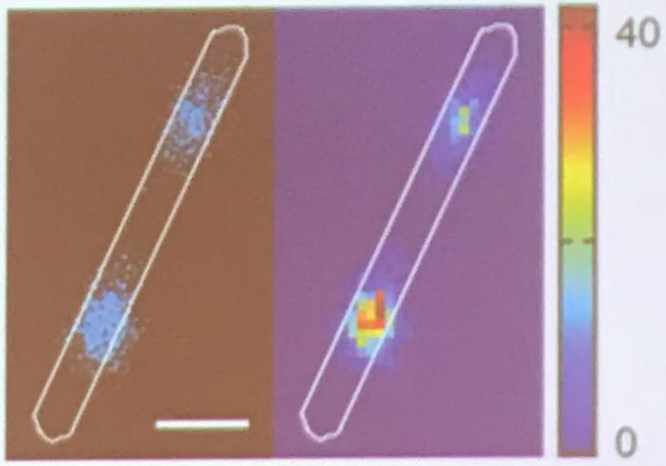
- h^+ & e^- reactions spatially correlated
  → Surprise!

Super-resolution Single-nanorod h^+ & e^- Reaction Mapping

h^+ reactions ($E \geq -0.03$ V)



e^- reactions ($E \leq -0.04$ V)



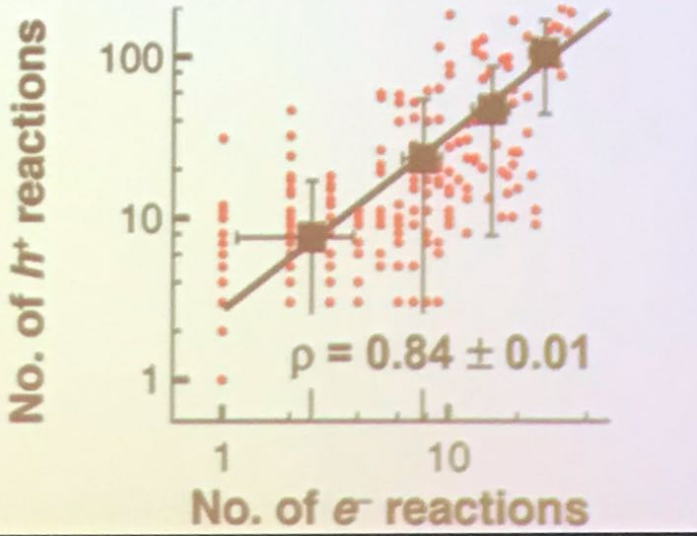
- h^+ & e^- reactions spatially correlated
  → Surprise!

⇒ h^+ (oxid) & e^- (rdn): **prefer** same sites

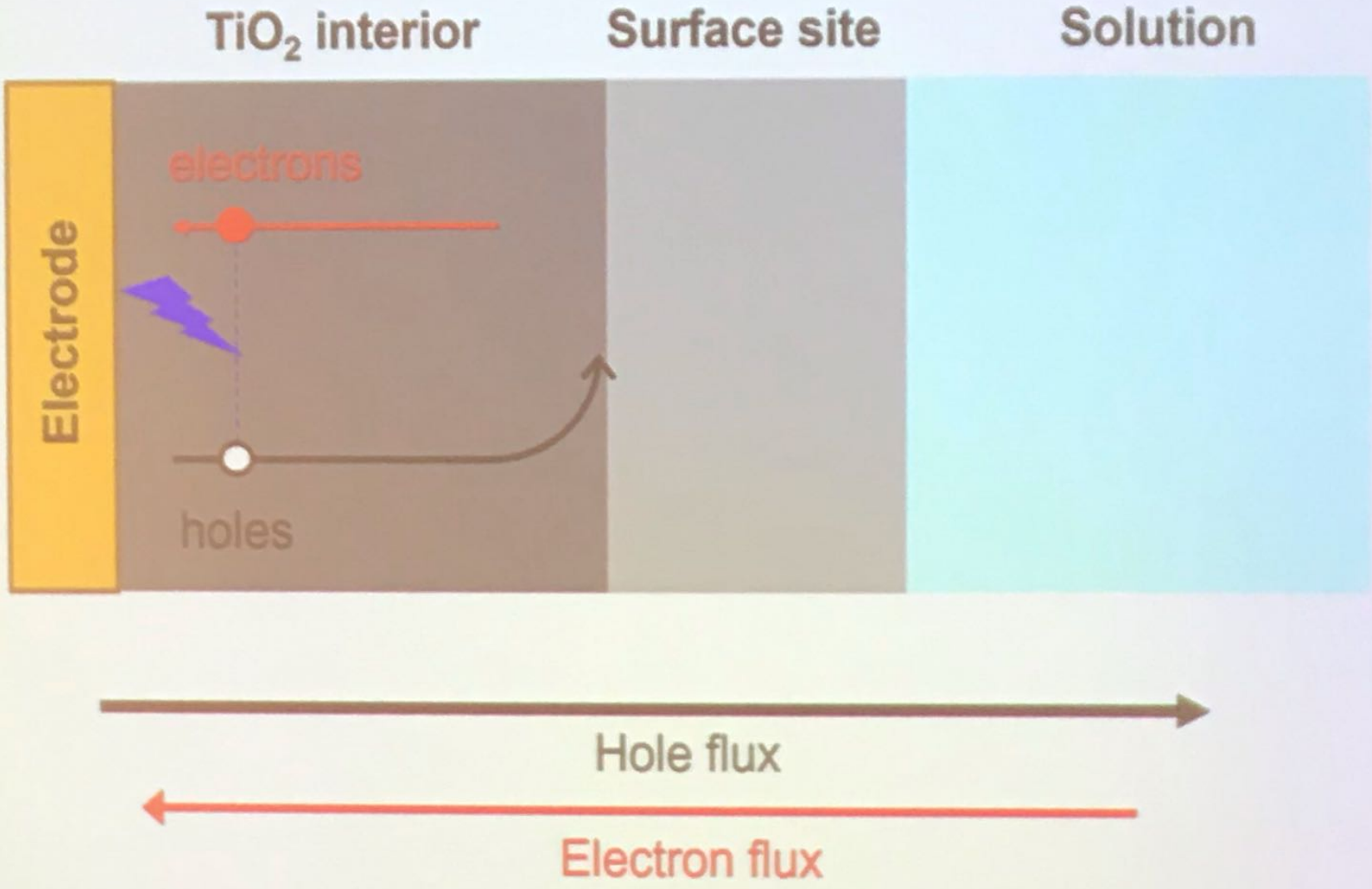
⇒ Active sites = **dual ox-red activity**
→ **recombination sites**

Why would they?

$h^+ \leftrightarrow e^-$ reaction correlation
All locations



Dual Ox-Red Activity for Efficient "Redox-cycling" for Water Oxidation



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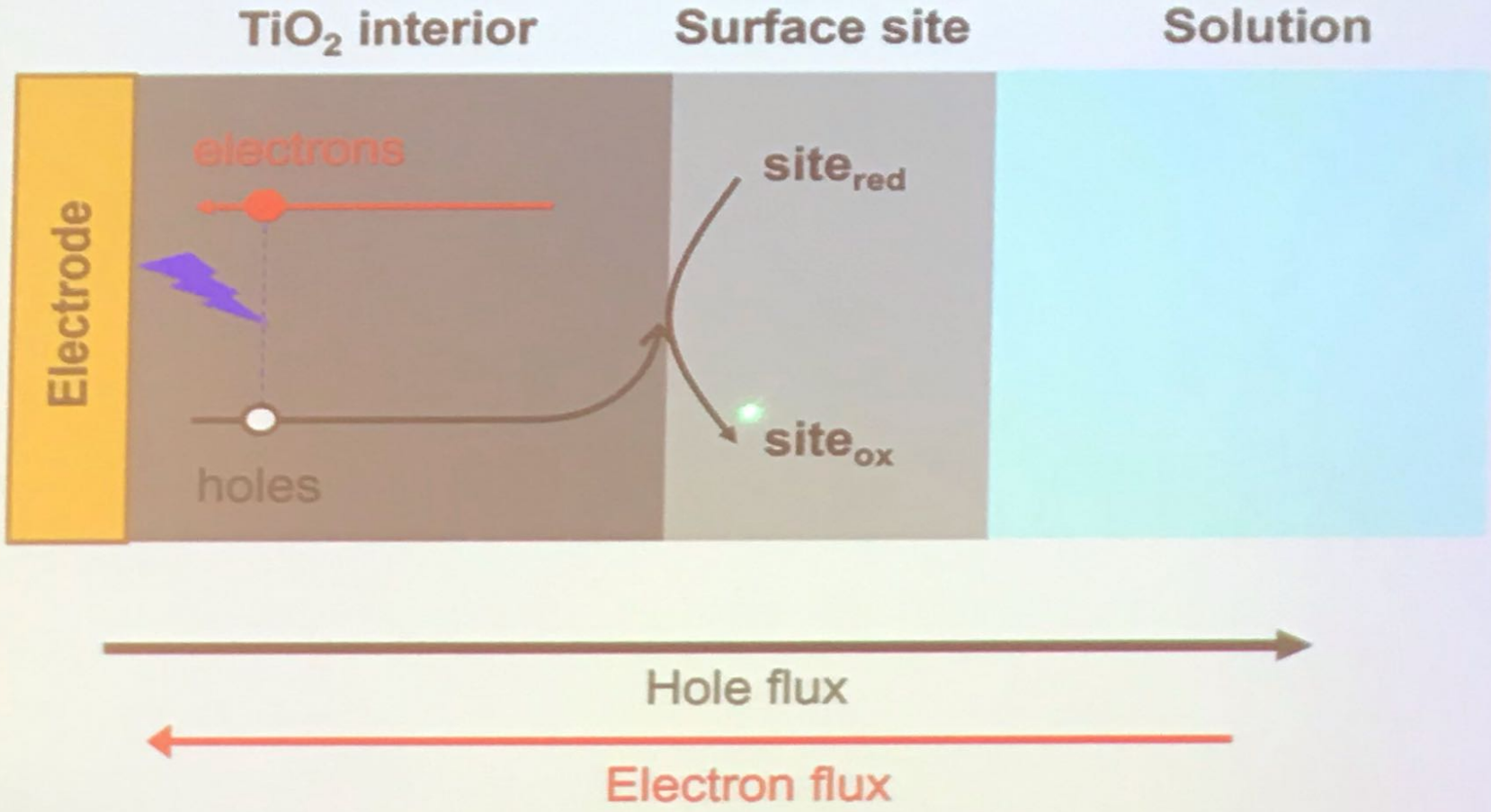

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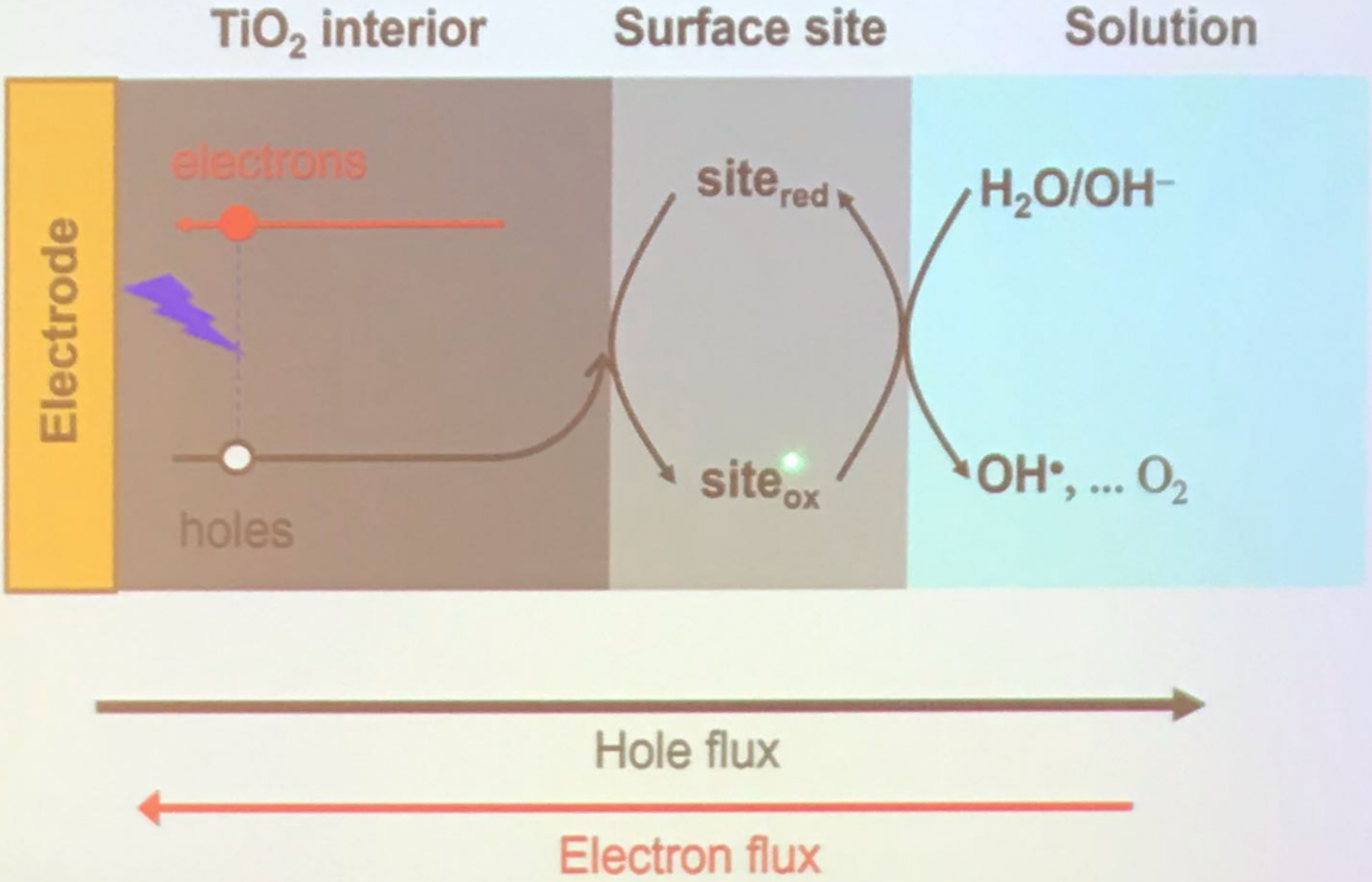

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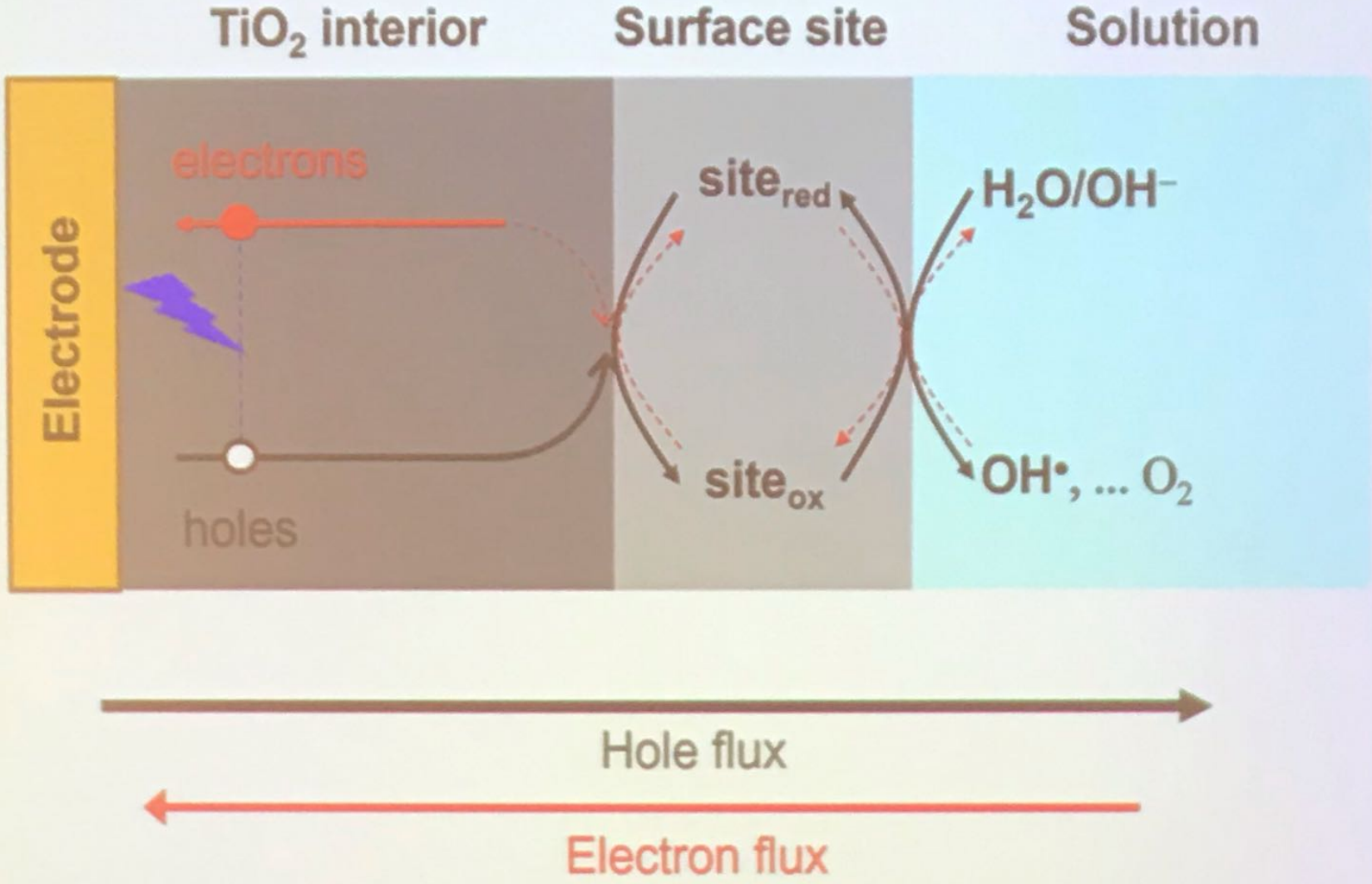


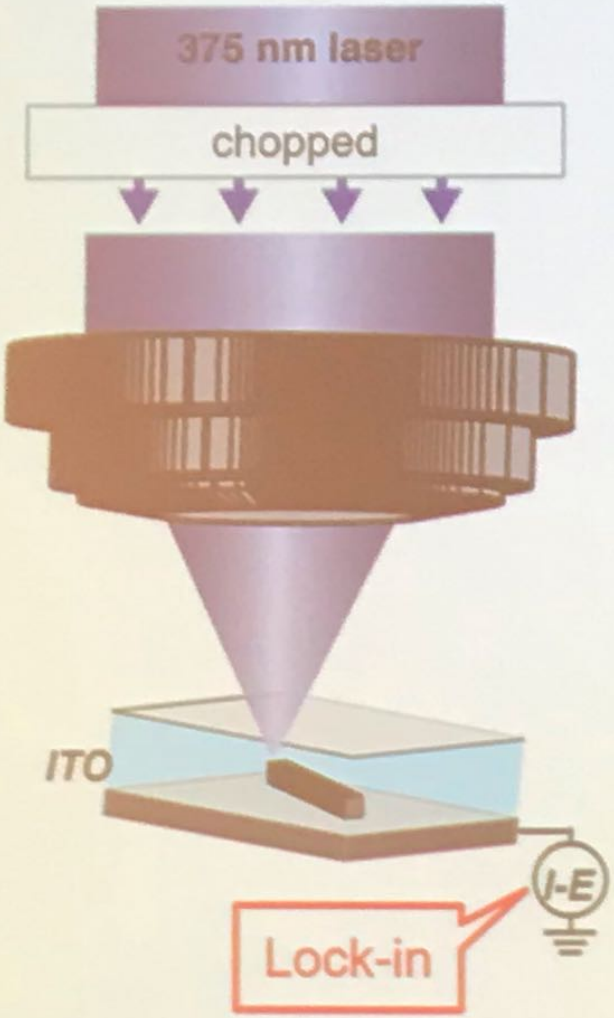
Sambur, Chen, Choudhary, Chen, Nissen, Thomas, Zou, P.C., *Nature* **2016**, *530*, 77.

Know:

1. Surface h^+ and e^- activity at nm resolution
2. They are spatially correlated

Connection to local water oxidation efficiency?

Sub-nanorod Photocurrent Measurements



- Photocurrent ∝ water oxidation kinetics
- Sub-nanorod measurements : diffraction limited
- No inter-particle charger transfer

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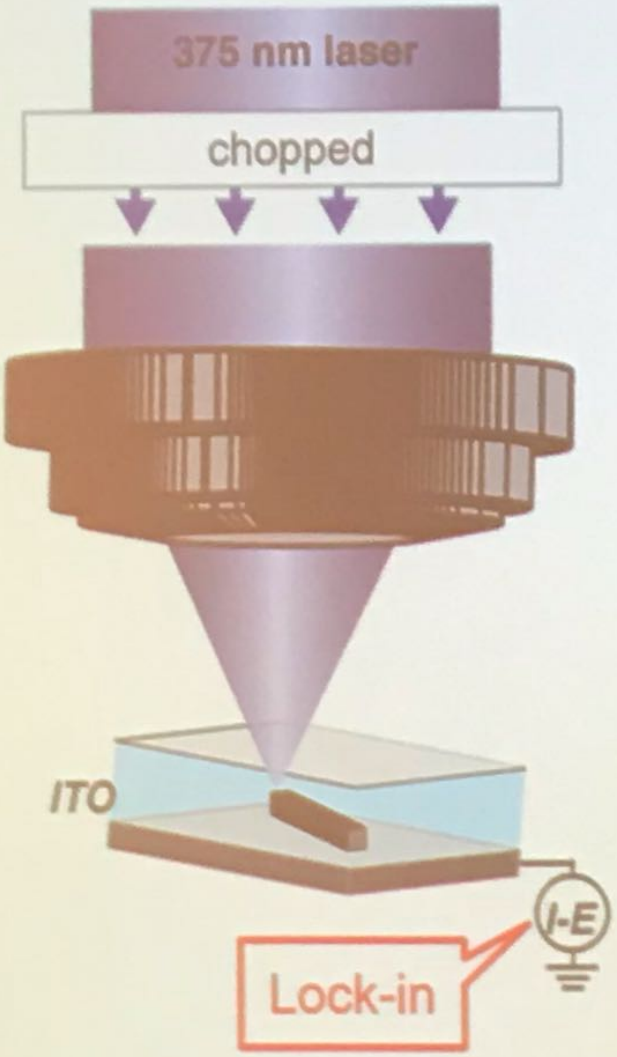

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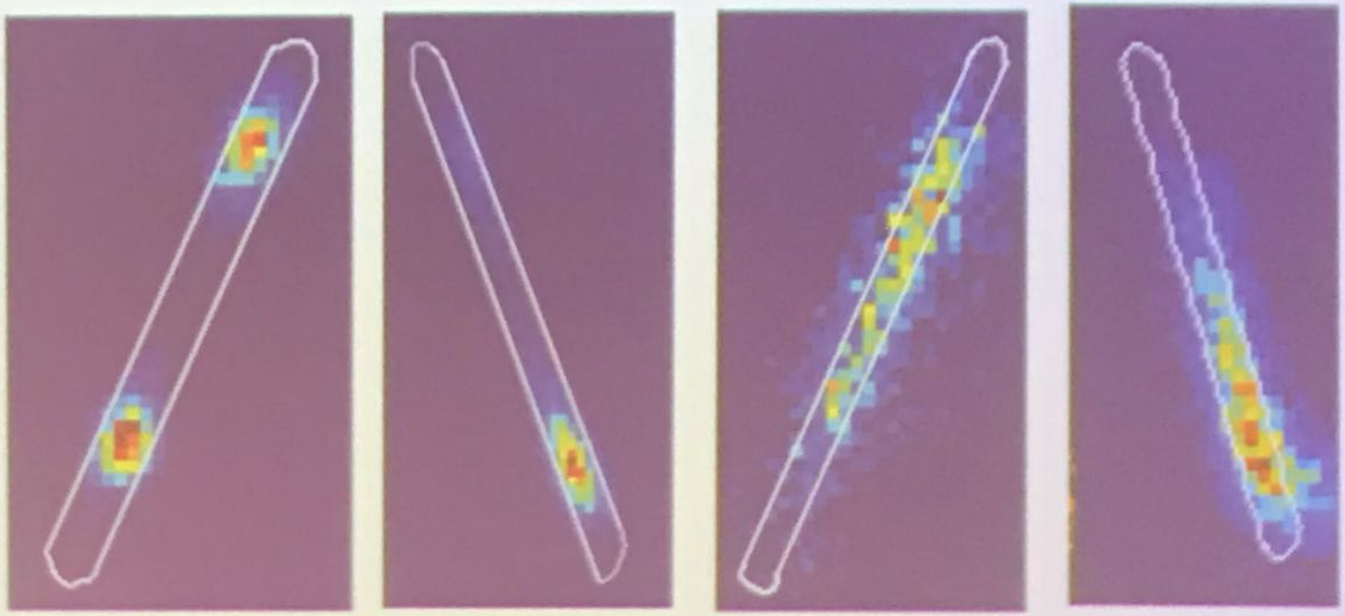
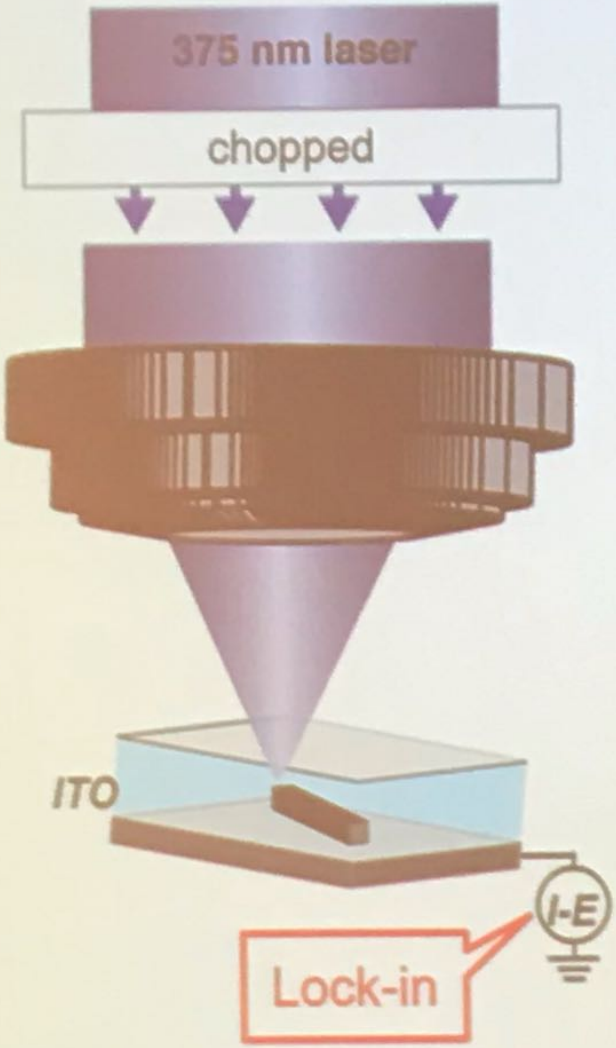
Use h^+ (e^-) reaction maps as guide



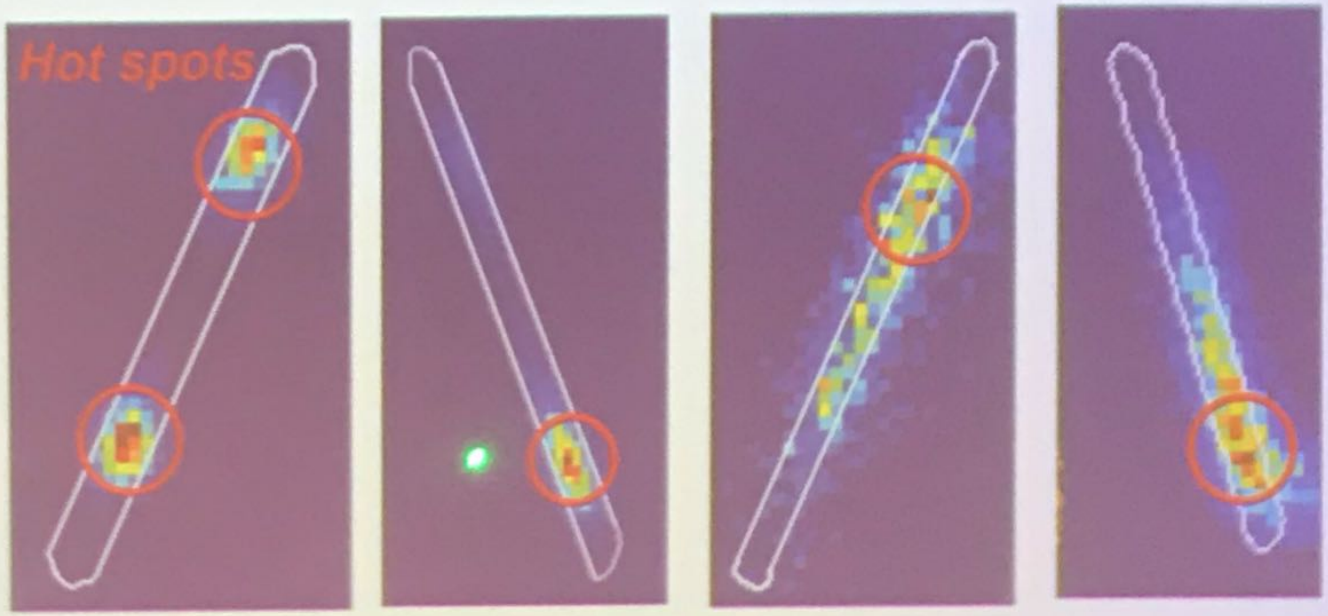
Sambur, Chen, Choudhary, Chen, Nissen, Thomas, Zou, P.C., *Nature* **2016**, *530*, 77.

Sub-nanorod Photocurrent Measurements



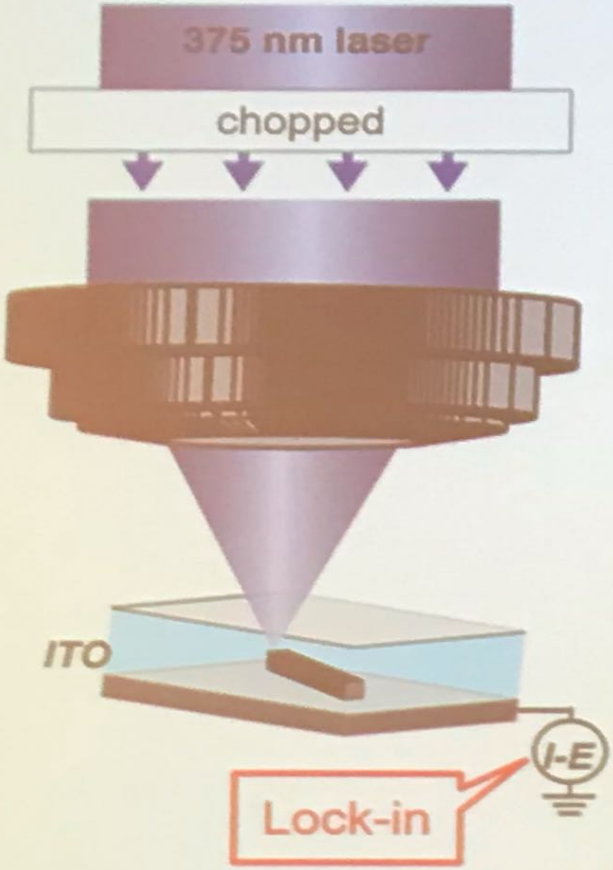
- Photocurrent ∝ water oxidation kinetics
- Sub-nanorod measurements : diffraction limited
- No inter-particle charger transfer

Use h^+ (e^-) reaction maps as guide



Sambur, Chen, Choudhary, Chen, Nissen, Thomas, Zou, P.C., *Nature* **2016**, *530*, 77.

Sub-nanorod Photocurrent Measurements



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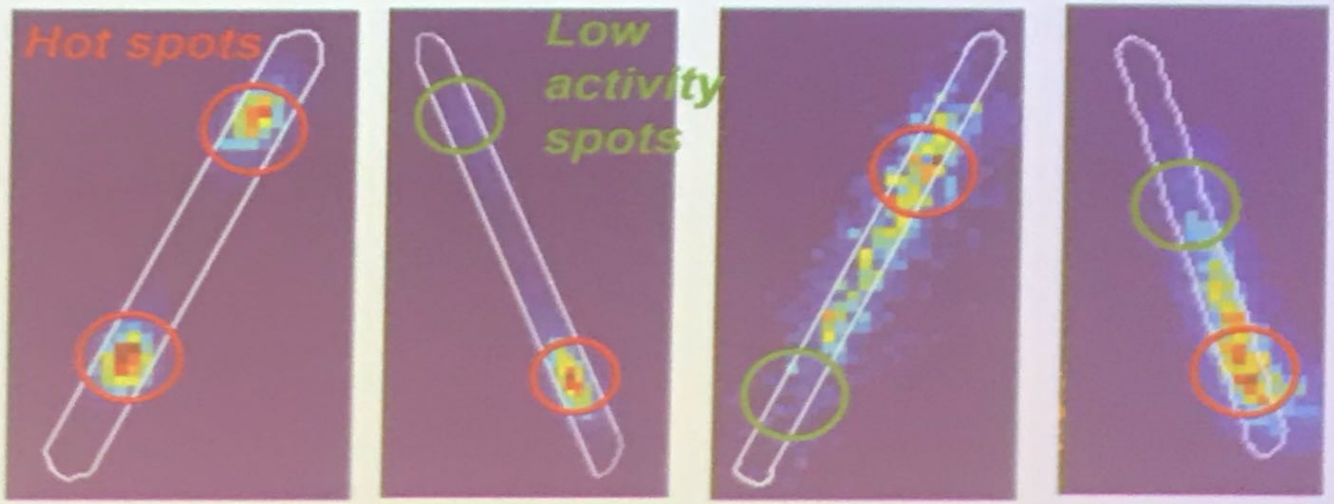

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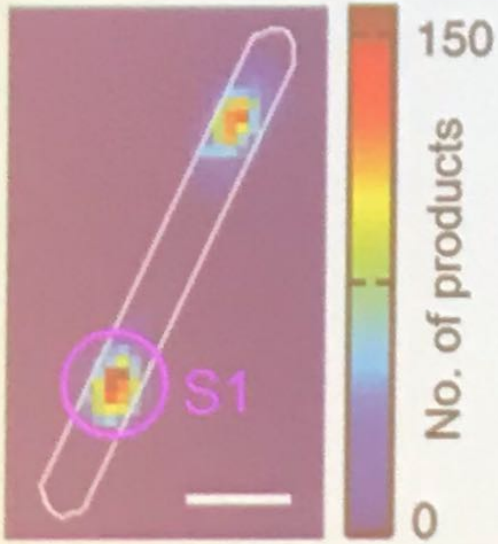
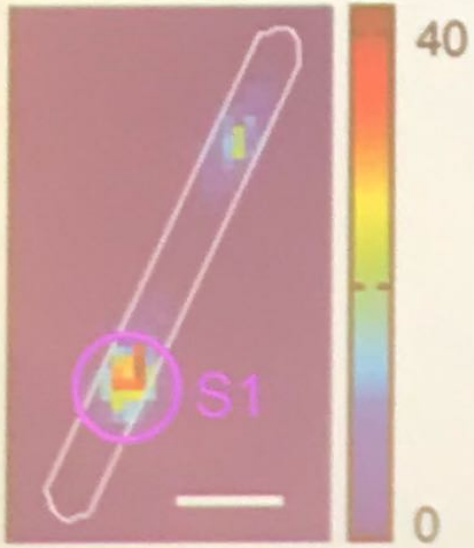
Sub-nanorod *i-E* Behaviors

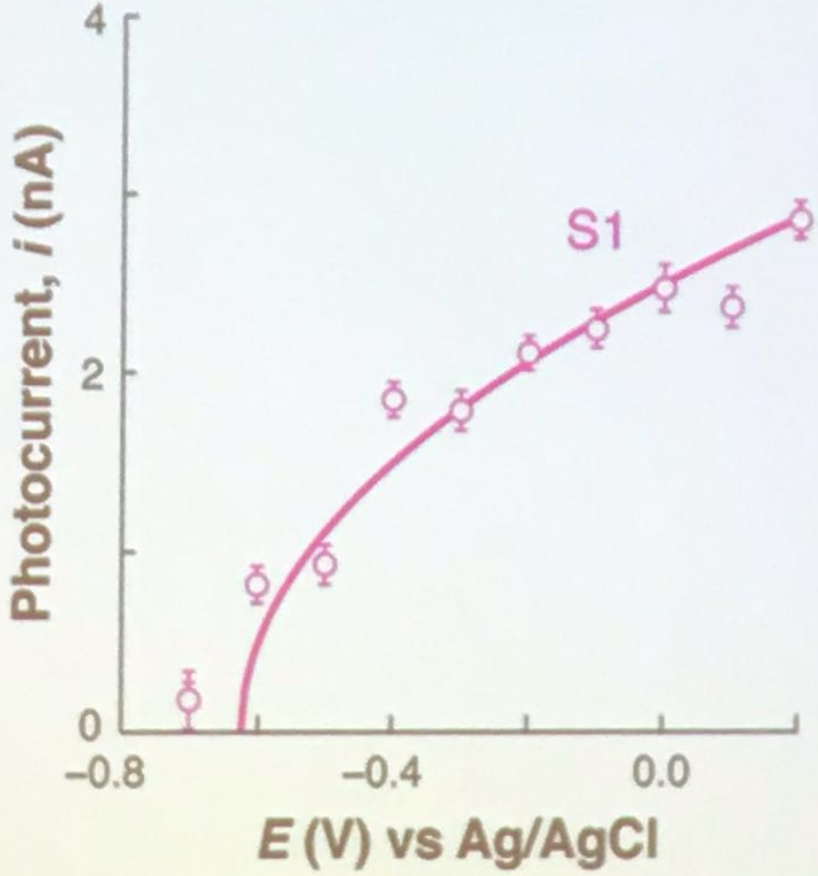
h^+ reactions



2-D histogram

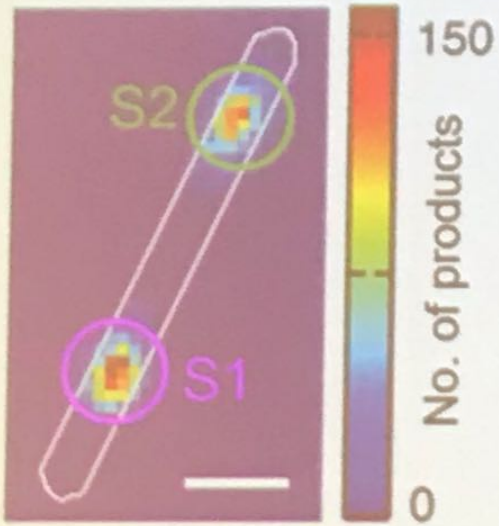
e^- reactions





Sub-nanorod *i-E* Behaviors

h^+ reactions



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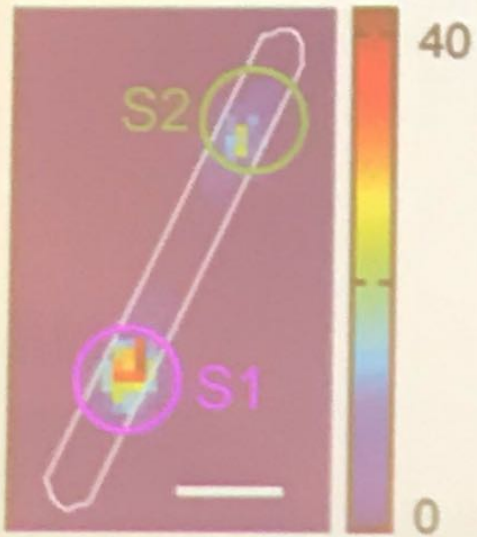

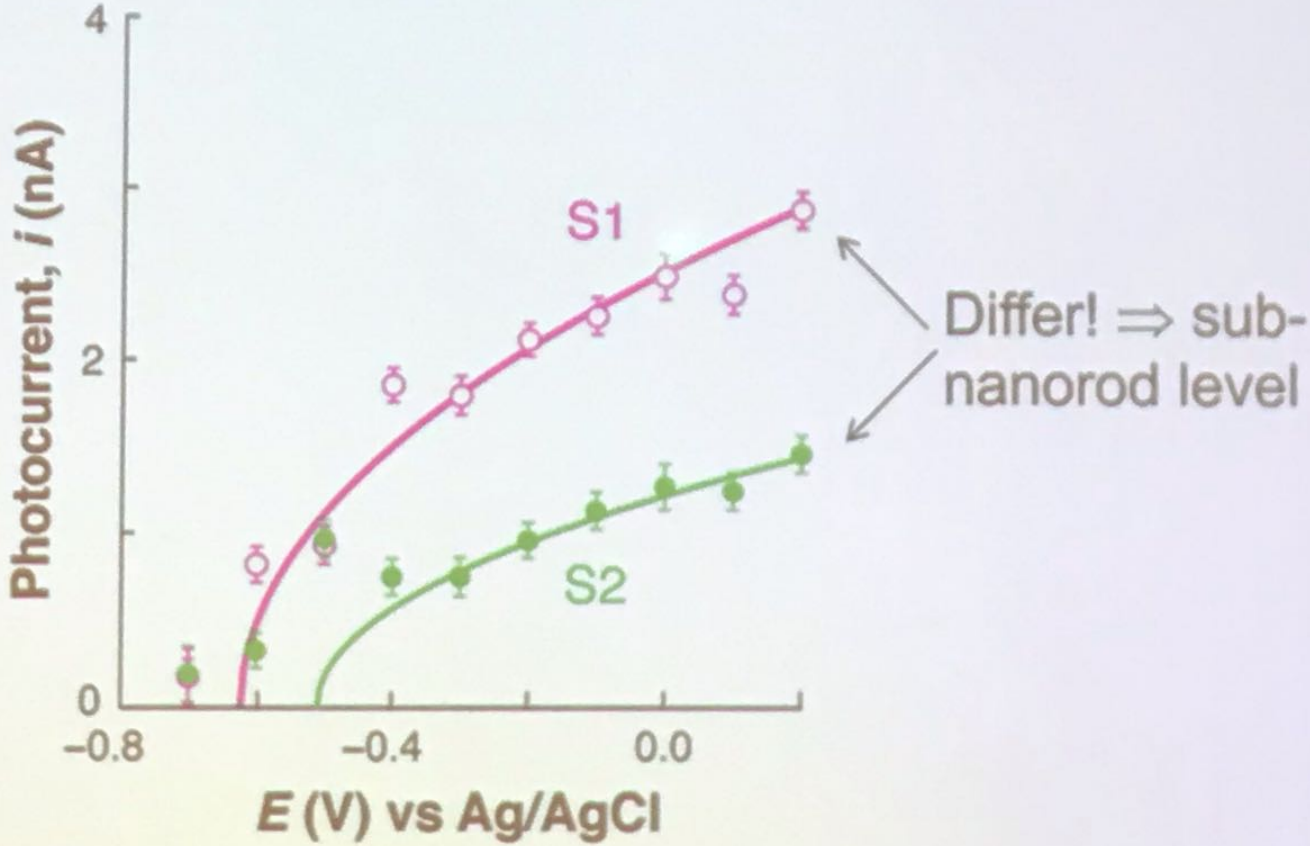

Sub-nanorod *i-E* Behaviors

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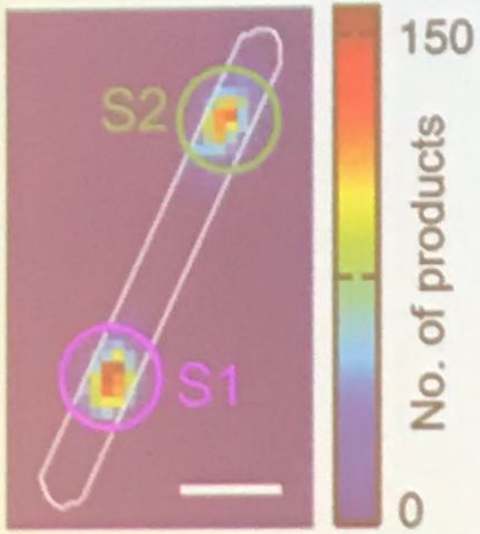

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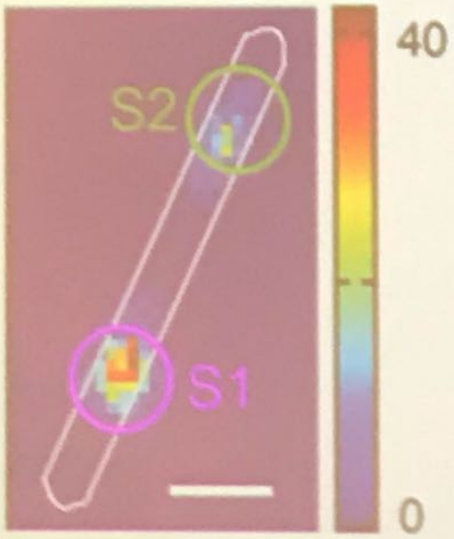


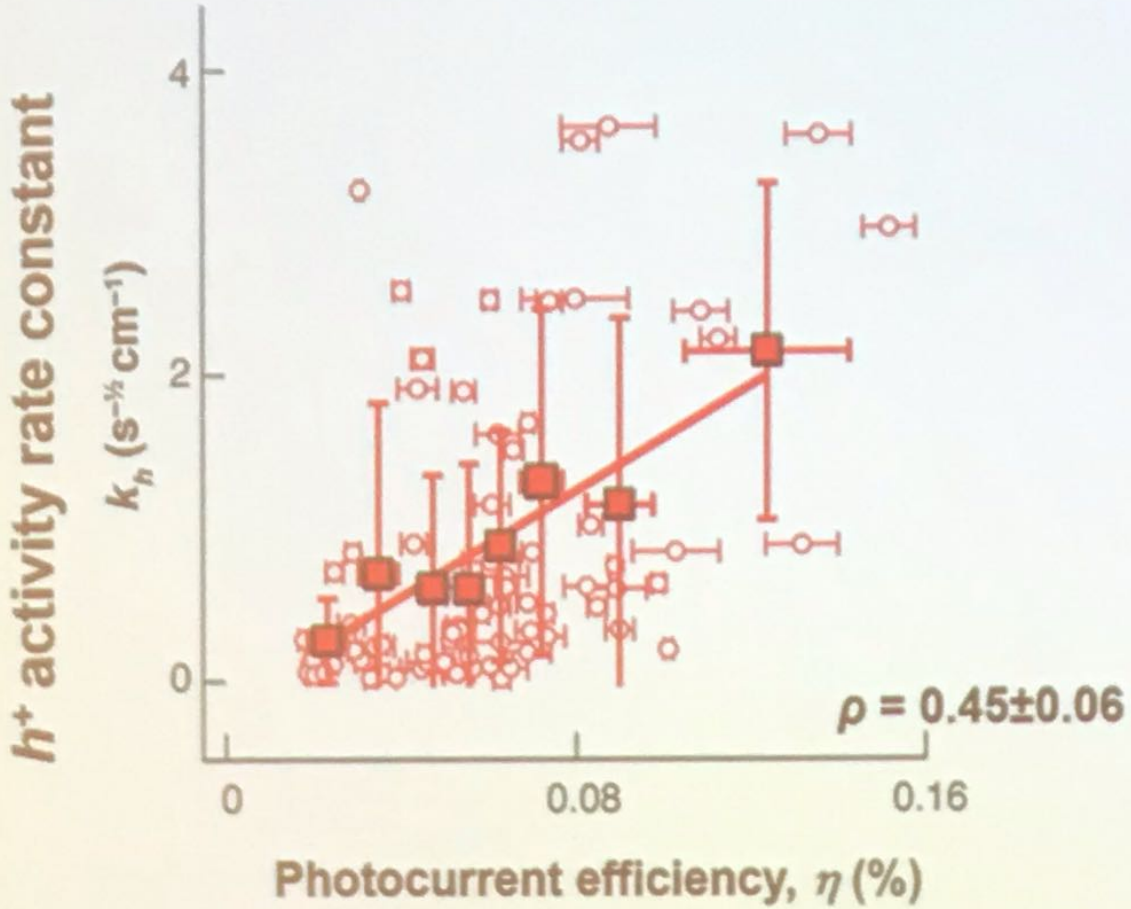
Gärtner-Butler model (*PR* 1955; *JAP* 1977)

$$i \propto \eta I_0 \sqrt{E - E_{on,GB}}$$

η : Absorbed photon in depletion layer to photocurrent efficiency

$E_{on,GB}$: Onset potential

Photocurrent Efficiency ⇔ Surface h^+ & e^- Activity



- Higher h^+ (& e^-) activity = larger photocurrent
- (Note k_h and k_e correlated)

⇒ Surface activity (h^+ & e^-) = *indicator* & perhaps *determinant* of water oxidation efficiency

Sambur, Chen, Choudhary, Chen, Nissen, Thomas, Zou, P.C., *Nature* **2016**, *530*, 77.

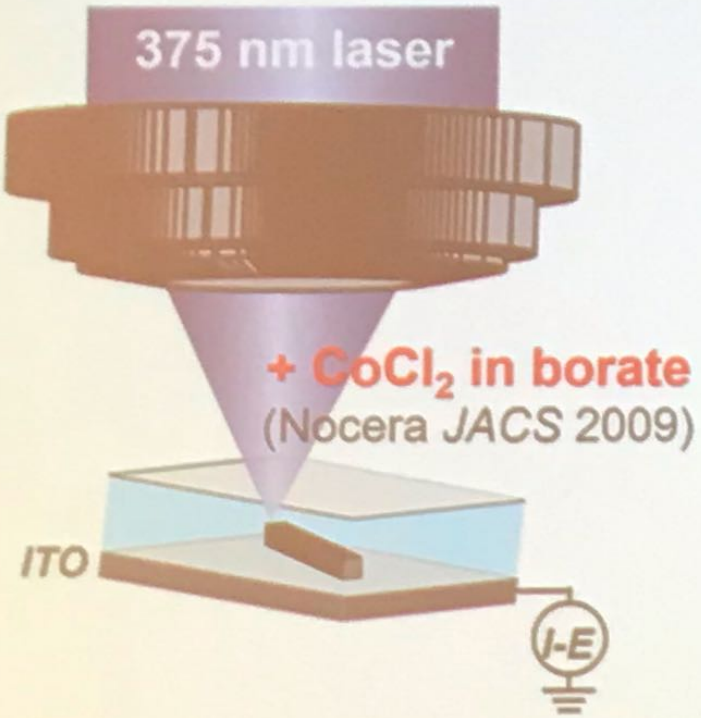
Know:

Surface h^+ & e^- activity ⇔ photocurrent of water oxidation

1. Effects of OECs on *i* and E_{on}?

2. Where best?

Spatially Controlled Photoelectrodeposition of OEC (CoB_i)



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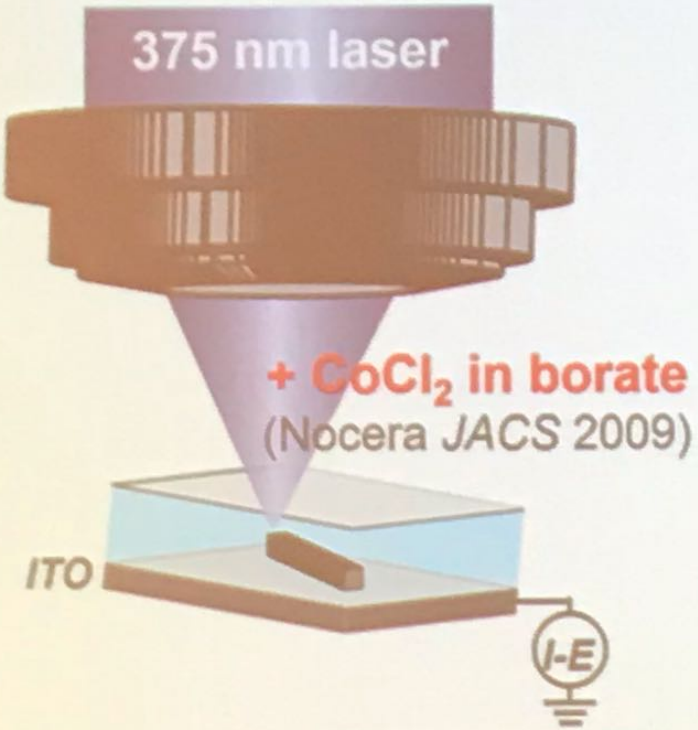
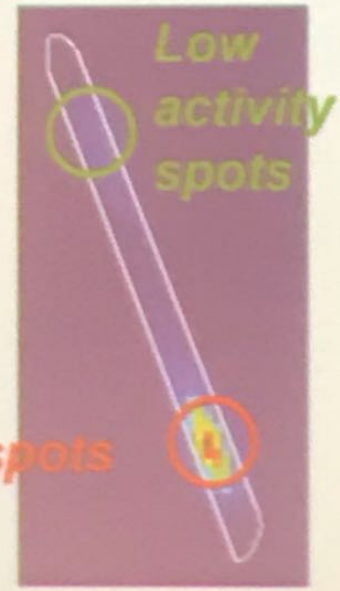


→ Based on h^+/e^- reaction maps (where better?)



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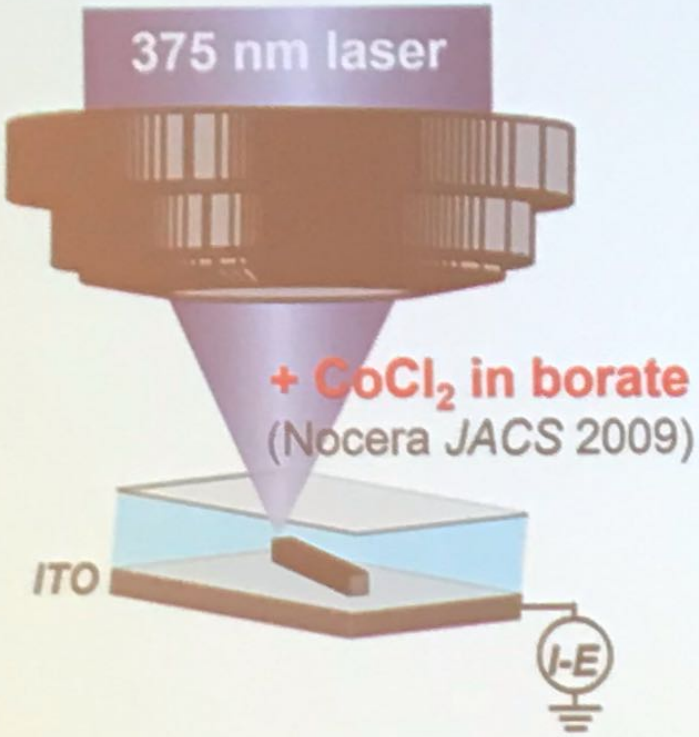

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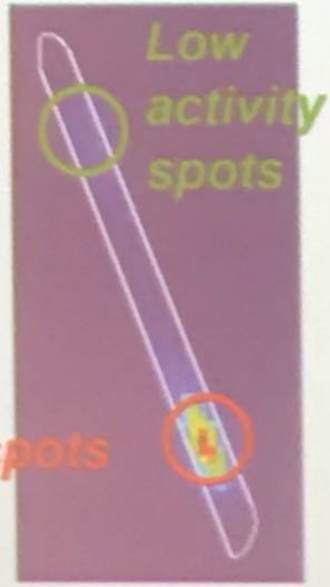

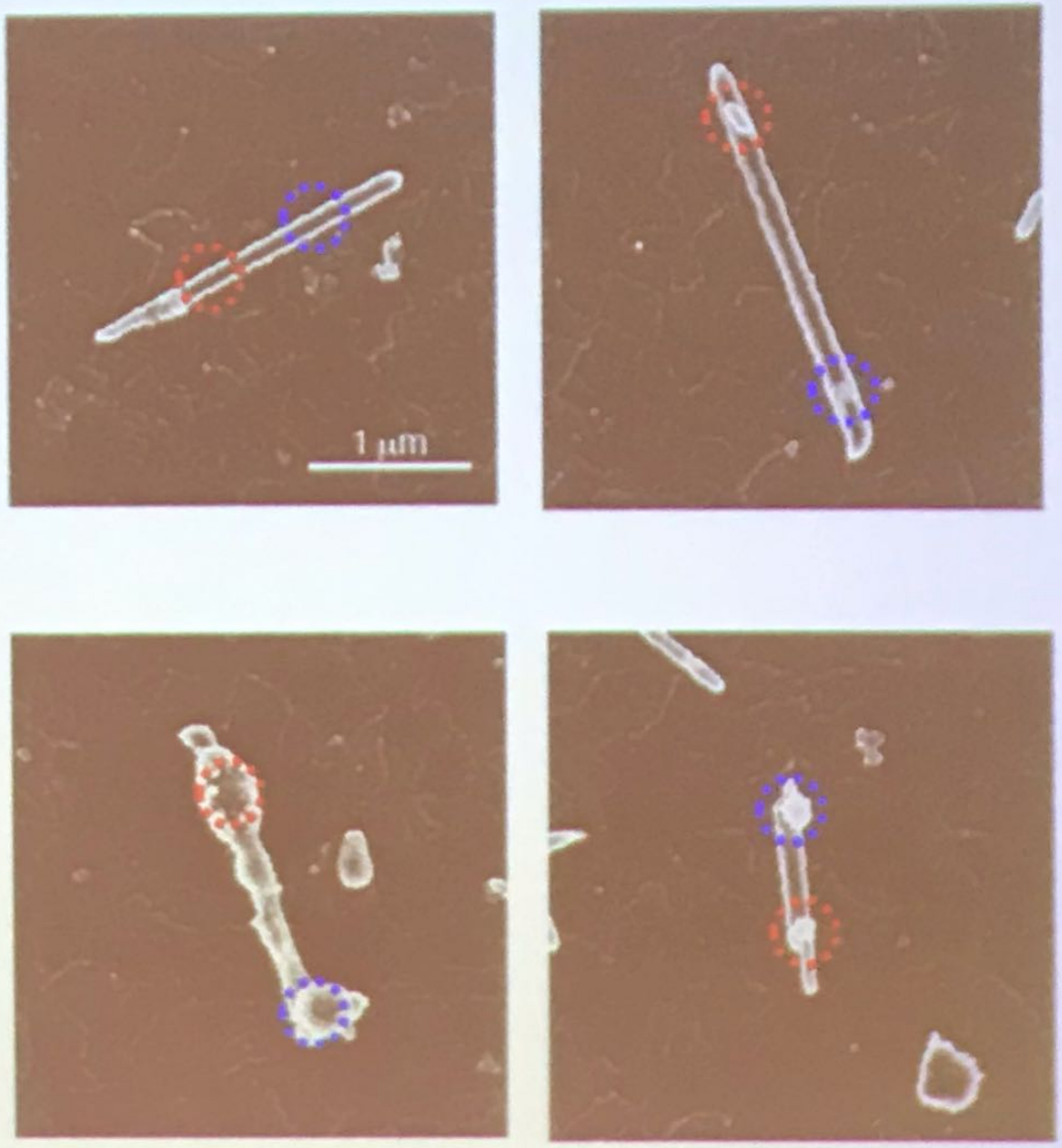

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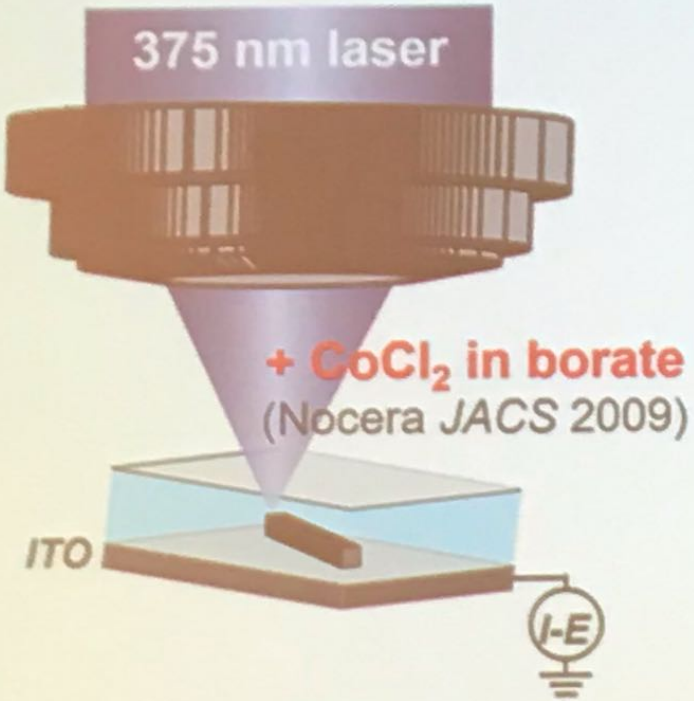

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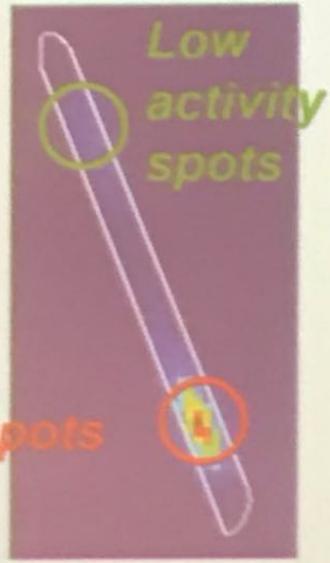
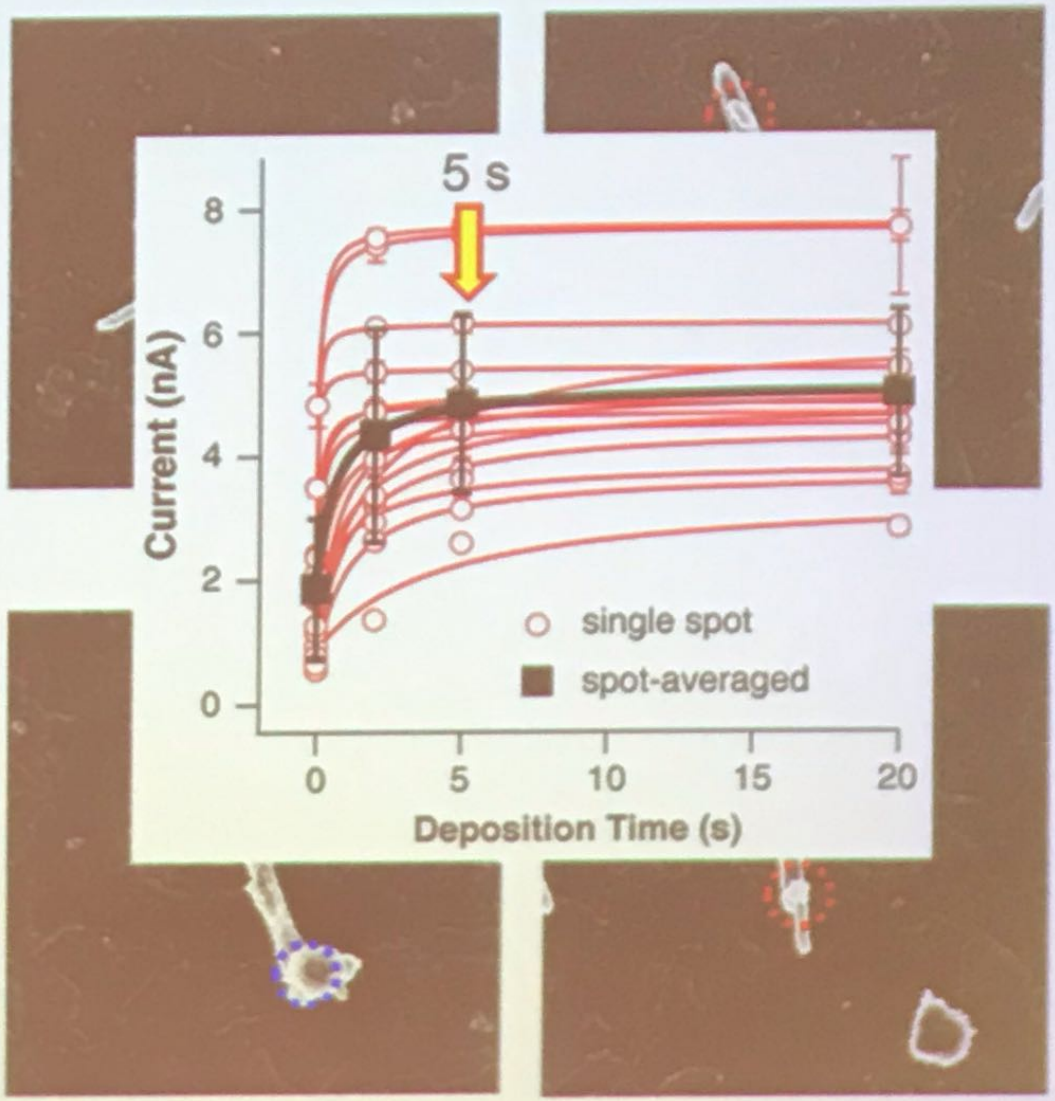
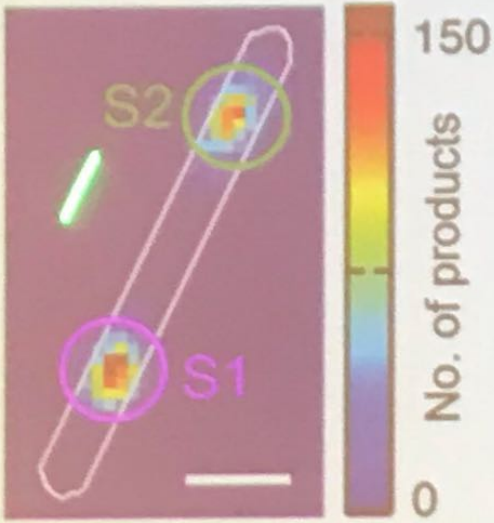




⇒ Catalyst amount saturates photocurrent of water oxidation

OEC Improves Photocurrent & Onset Potential

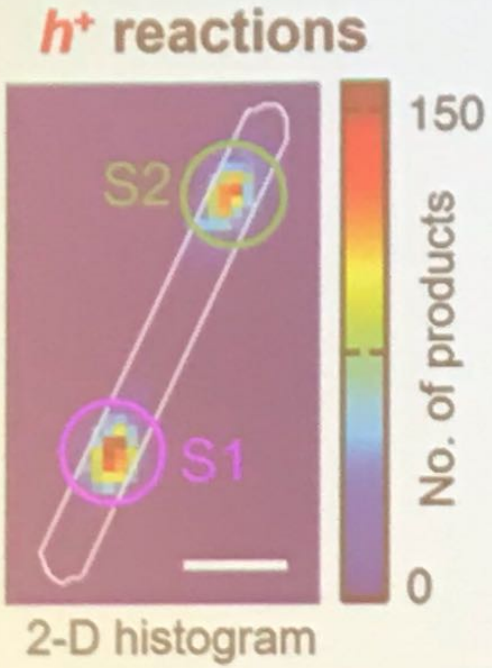
h^+ reactions

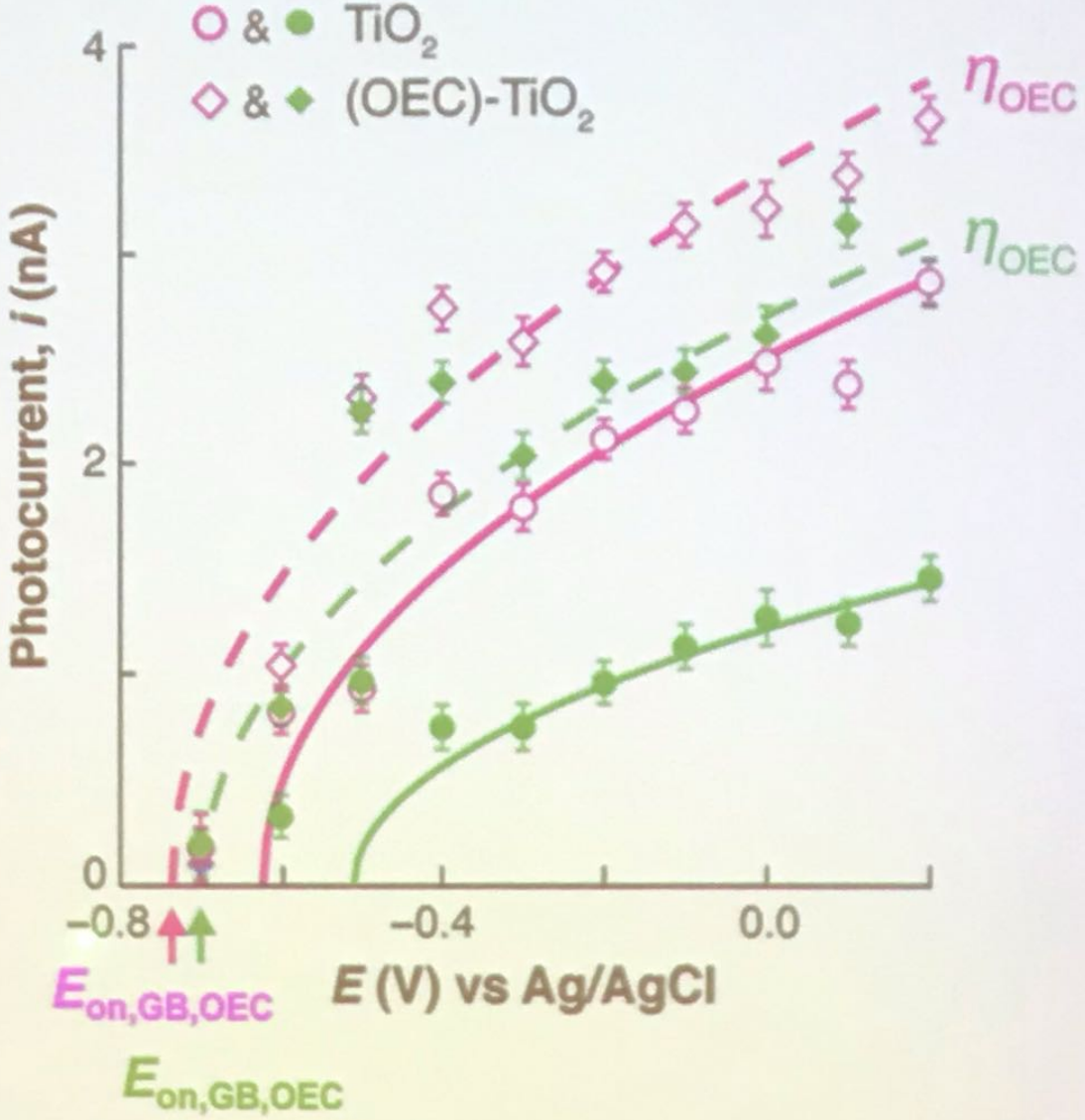


2-D histogram

SEM

OEC Improves Photocurrent & Onset Potential





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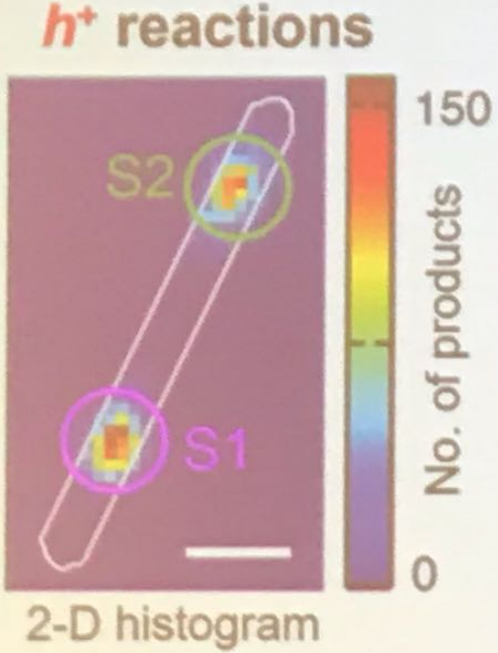
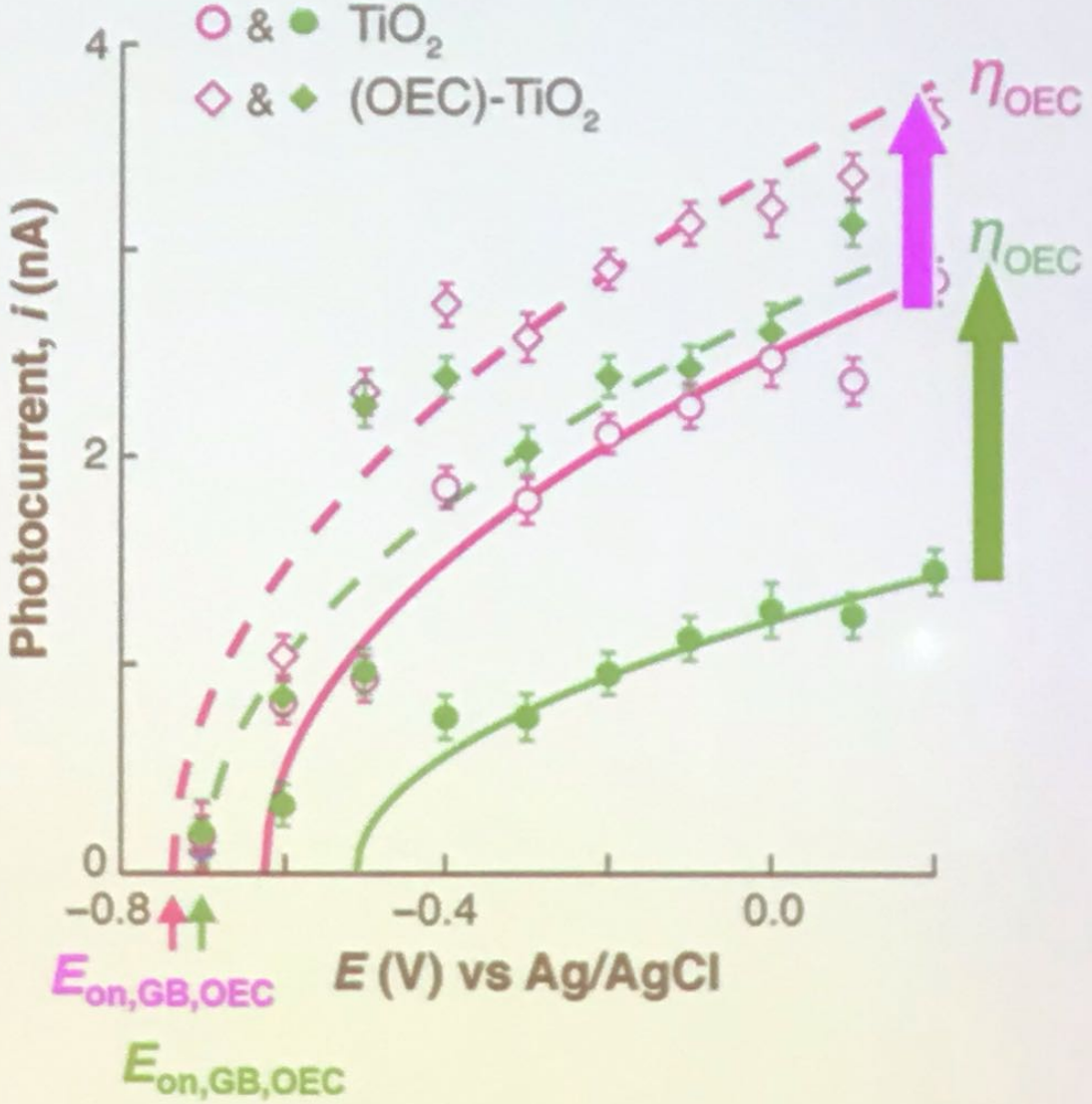
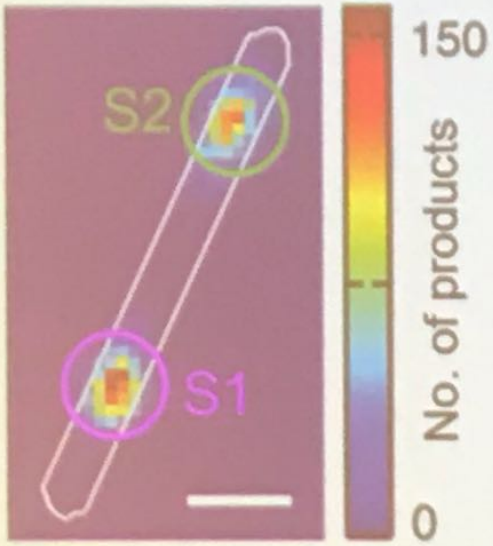




After OEC
- Photocurrent efficiency η, ↑
- Onset potential $E_{on,GB}$, ↓

OEC Improves Photocurrent & Onset Potential

h^+ reactions



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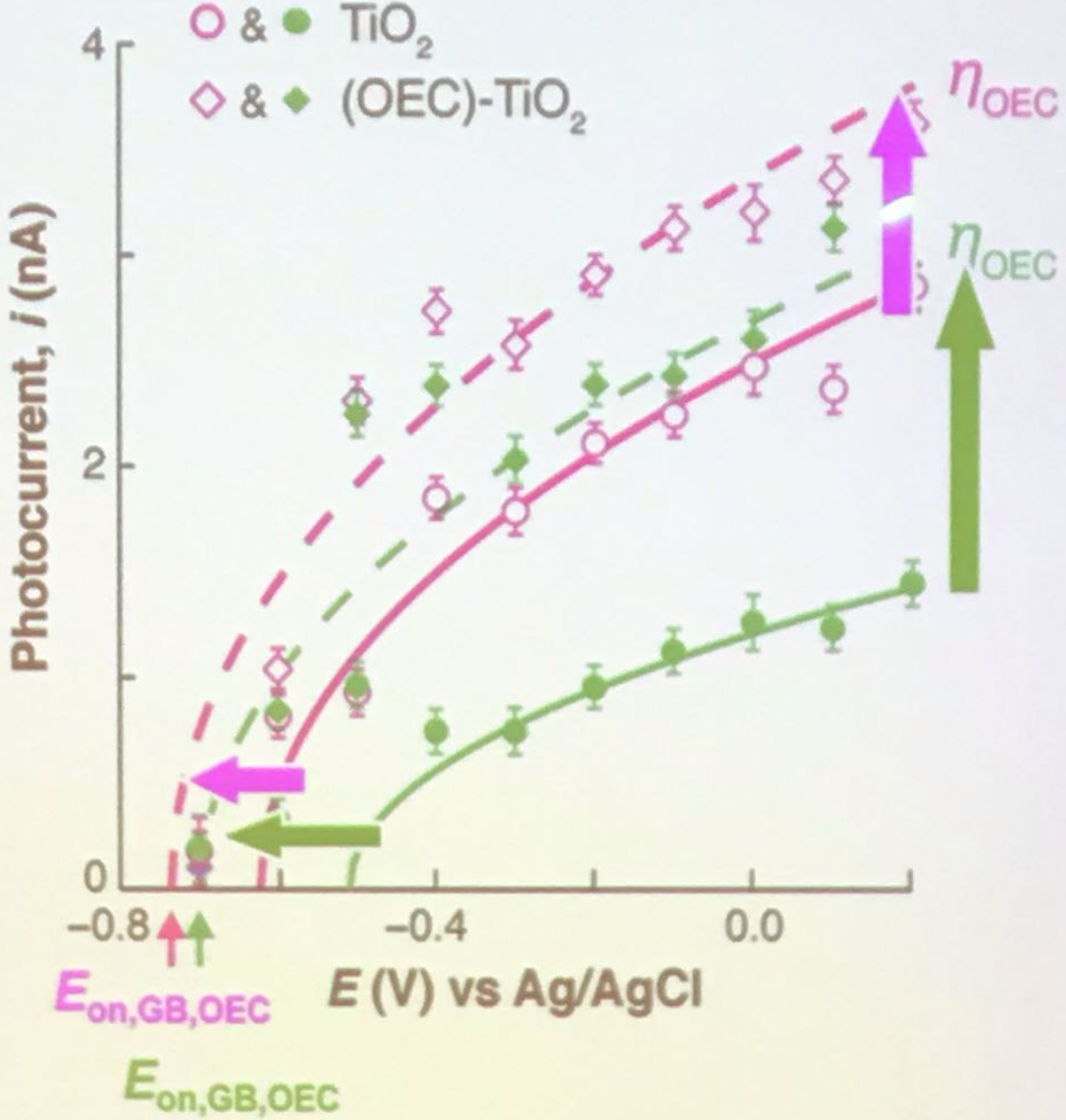

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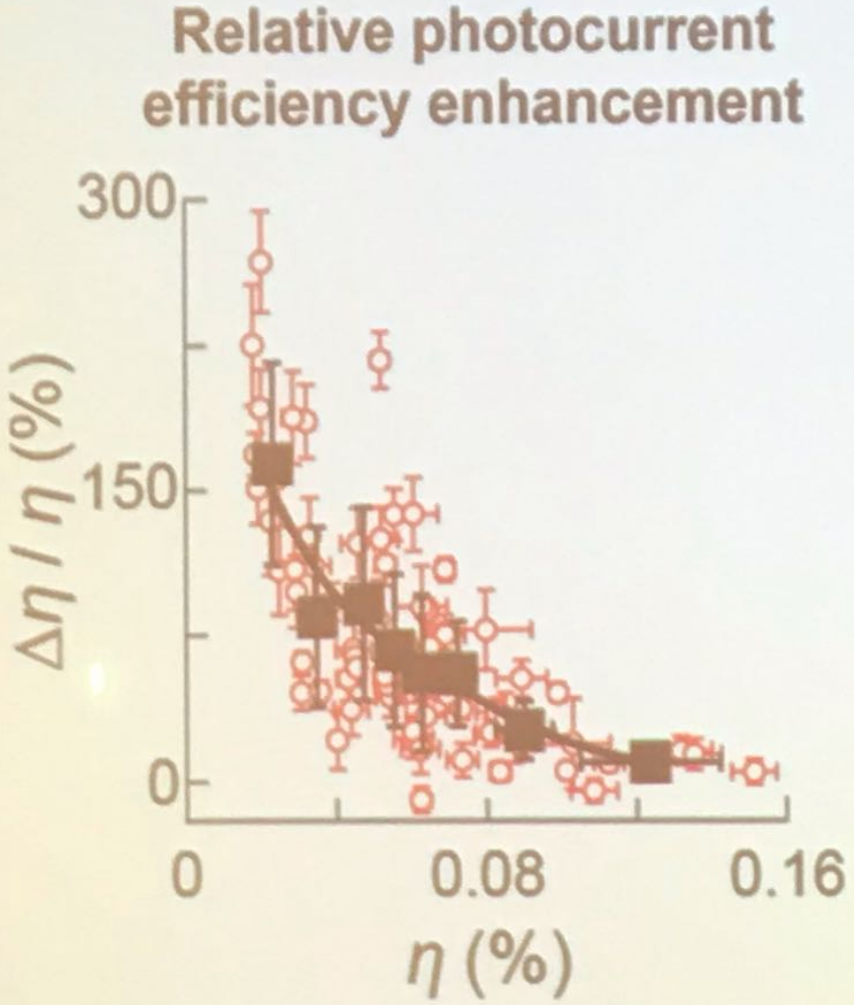
Optimal Sites for Catalysts



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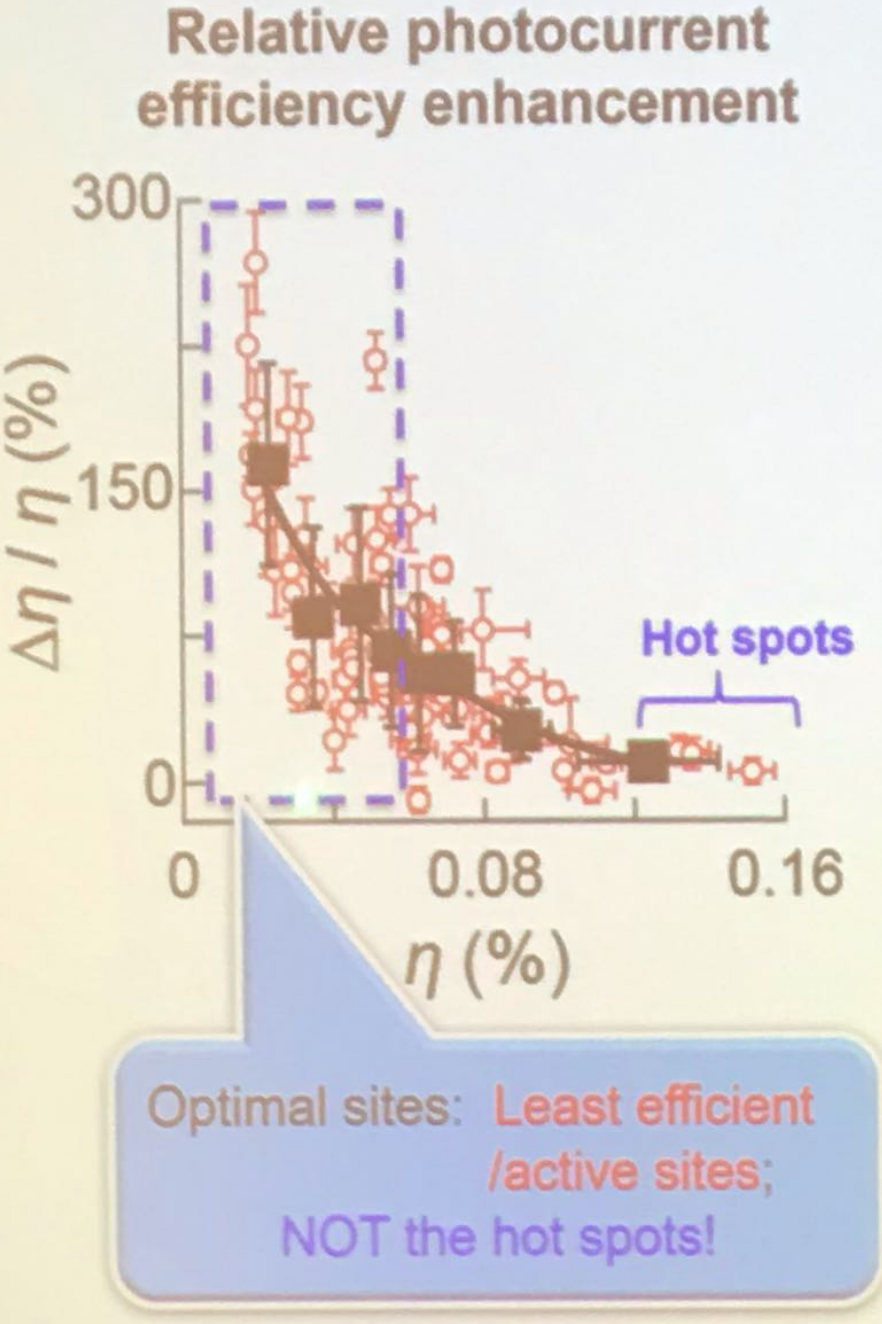
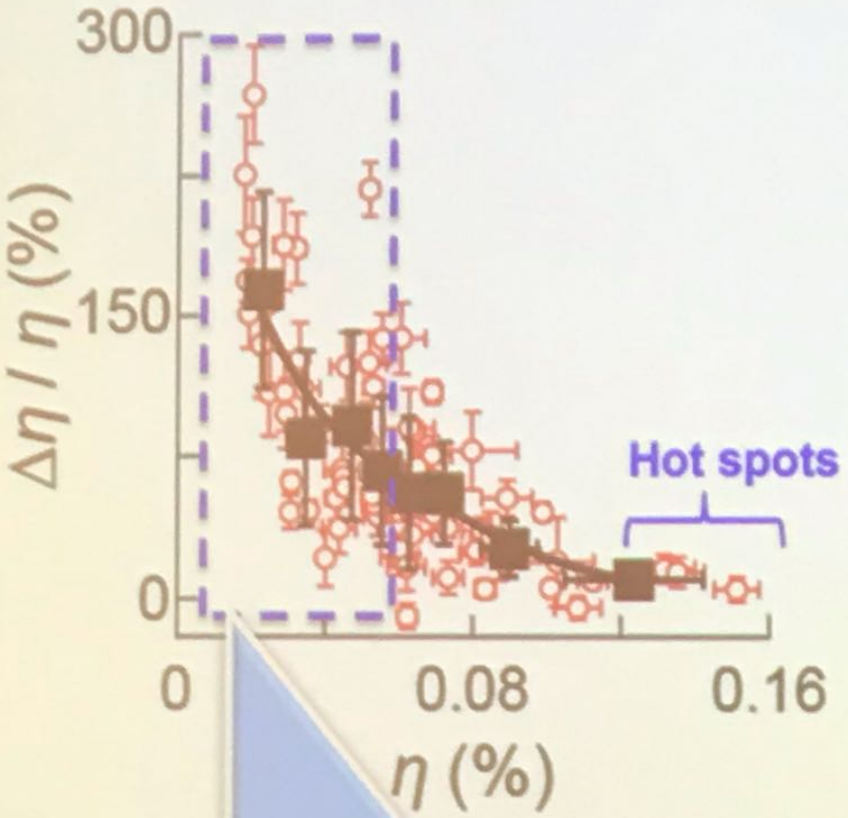
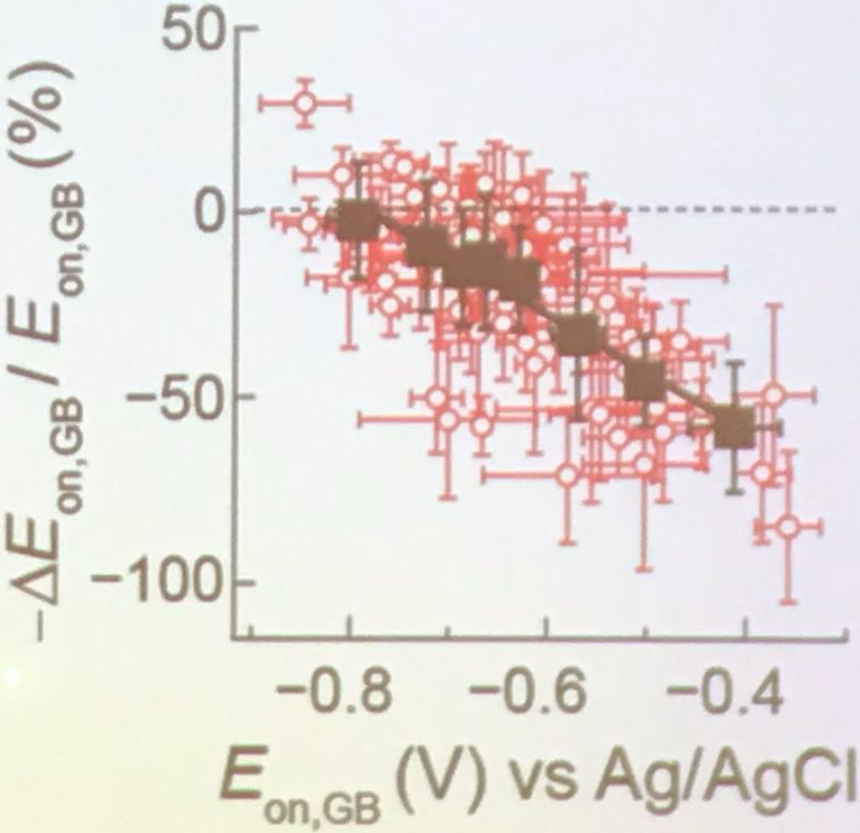


Optimal Sites for Catalysts

Relative photocurrent efficiency enhancement



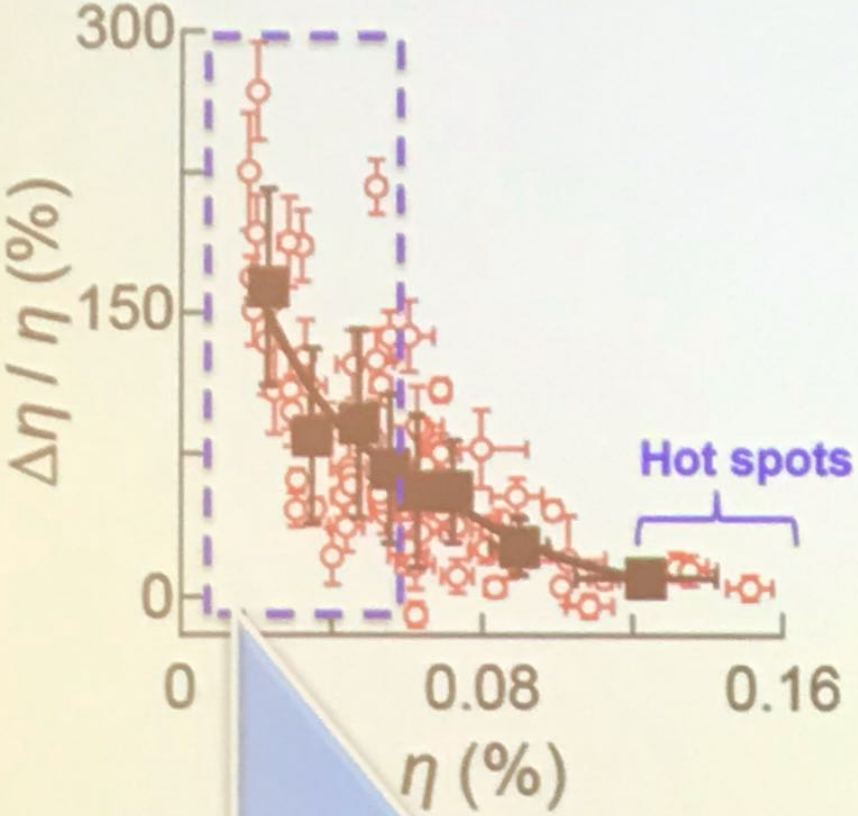
Relative onset potential reduction



Optimal sites: Least efficient /active sites;
NOT the hot spots!

Optimal Sites for Catalysts

Relative photocurrent efficiency enhancement



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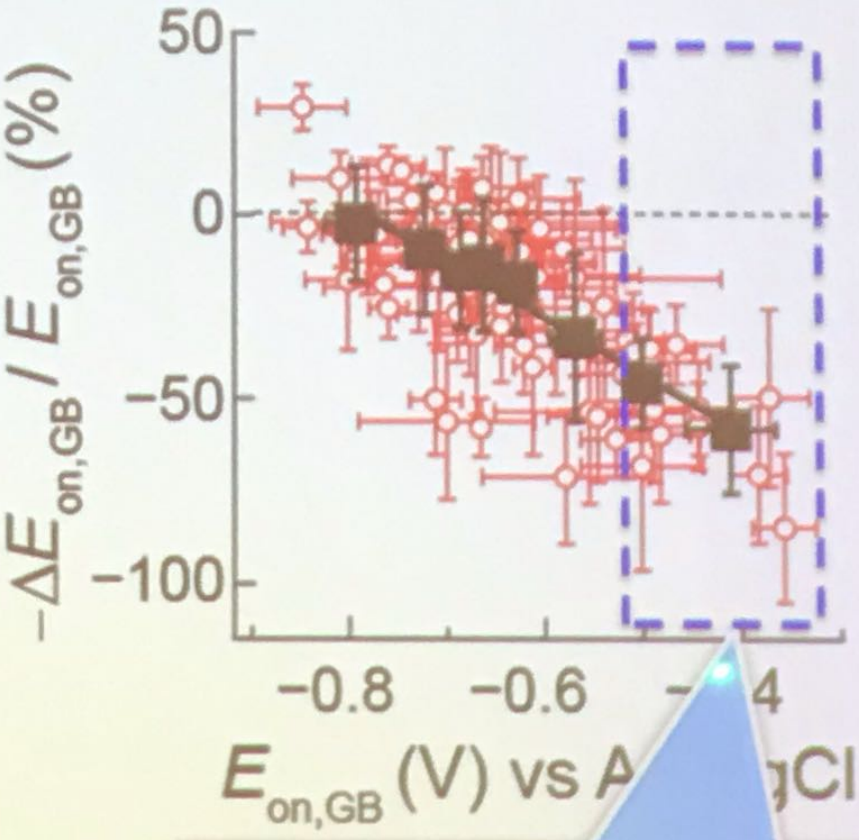
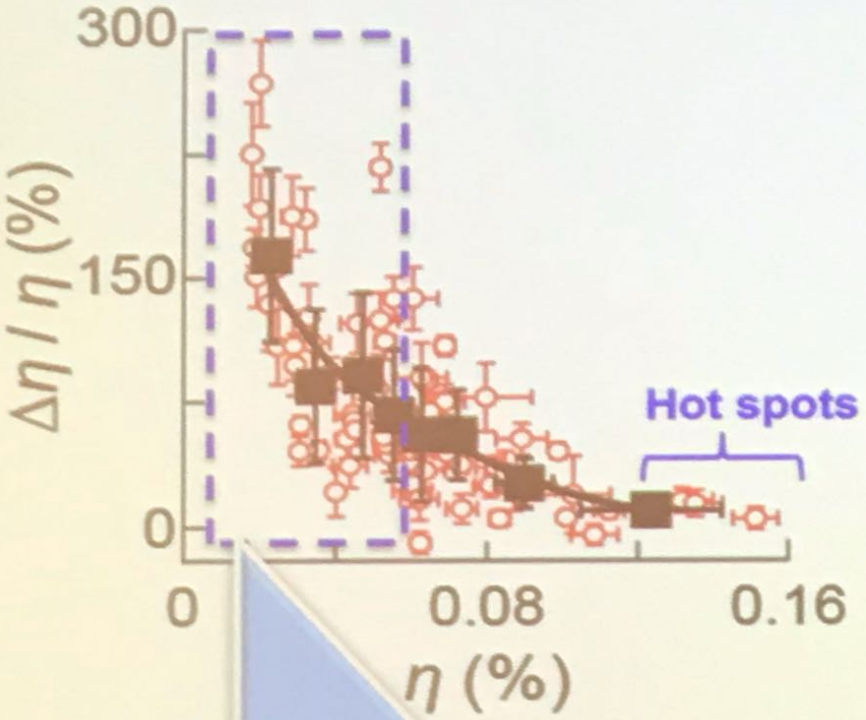


Optimal sites: Most positive onset potential sites

Optimal Sites for Catalysts

Relative photocurrent efficiency enhancement



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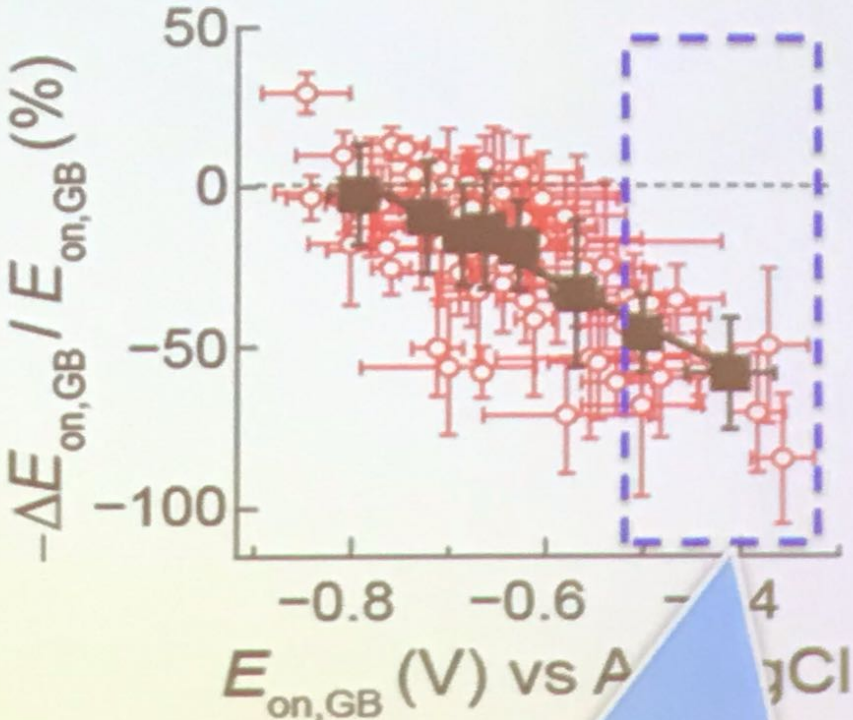


Optimal sites: Least efficient /active sites; NOT the hot spots!

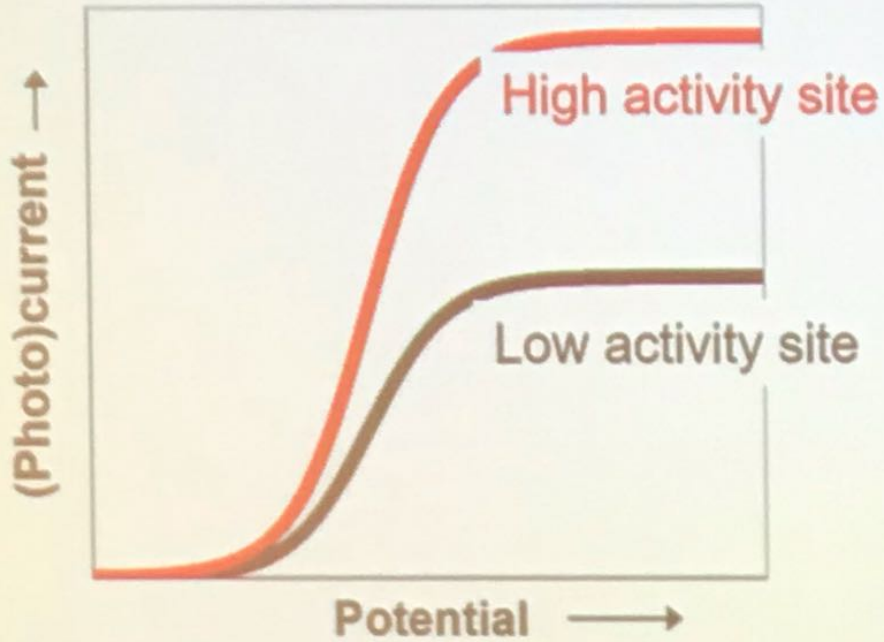
≠

Optimal sites: Most positive onset potential sites

⇒ **Opposite to what's obtainable conventionally!**

Challenges for Engineering Photoanodes with Catalysts via (Photo)(electro)deposition

Sites differ in activity



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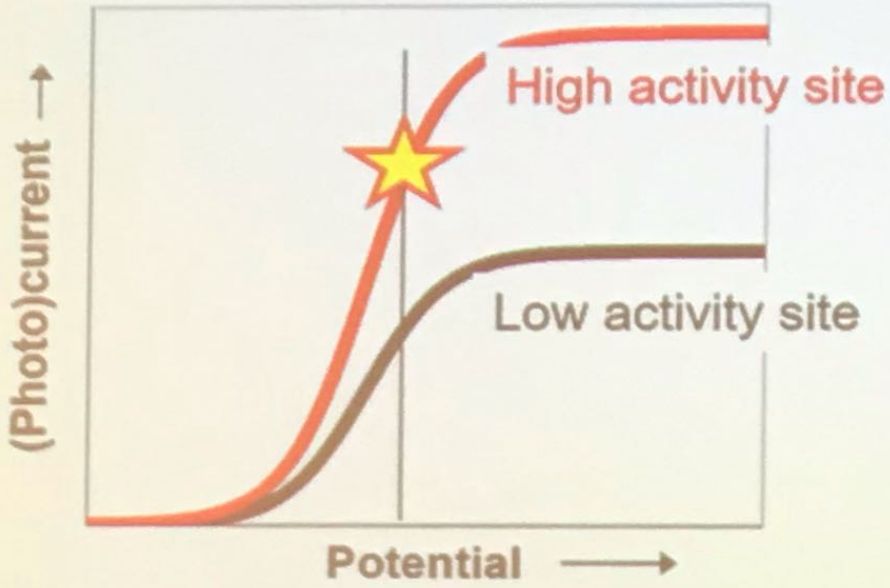

- High activity sites get more catalysts

Challenges for Engineering Photoanodes with Catalysts via (Photo)(electro)deposition

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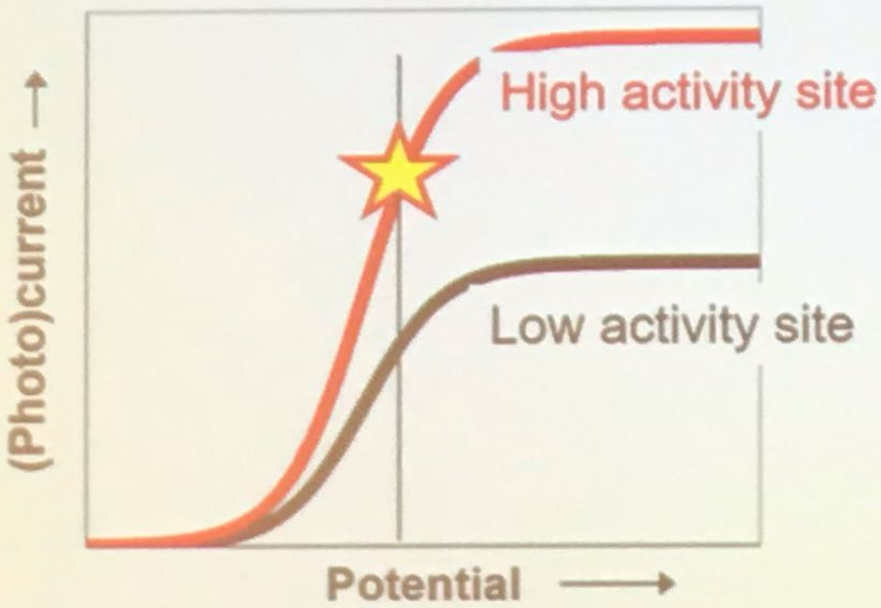
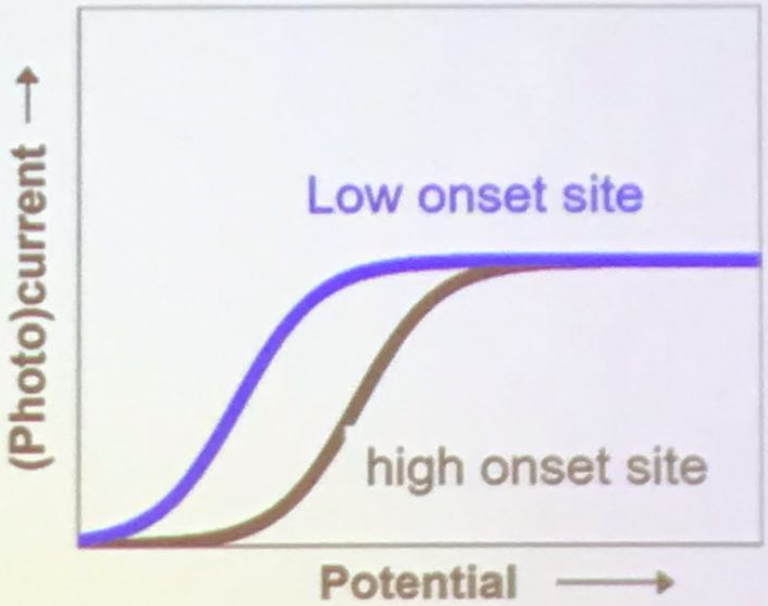


Sites differ in onset potential



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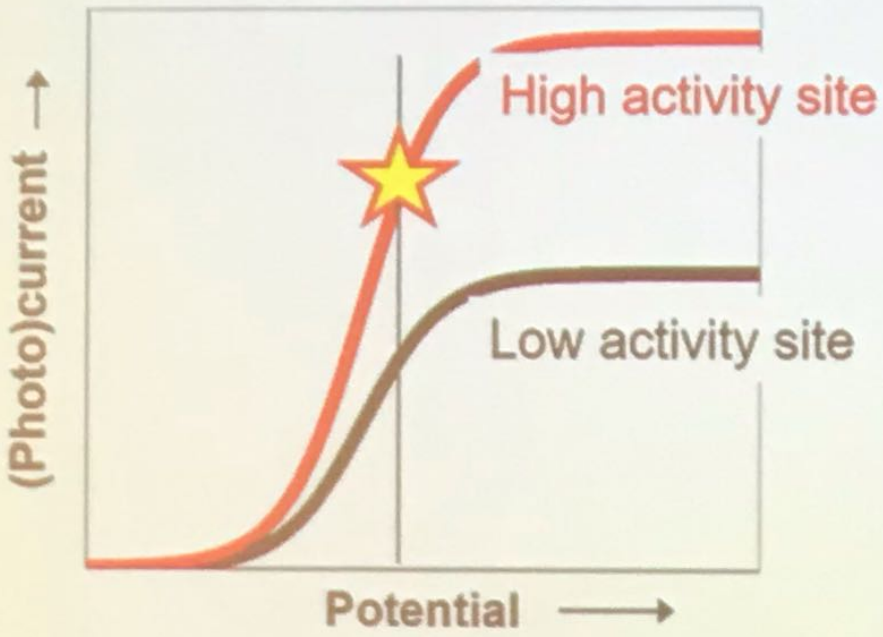

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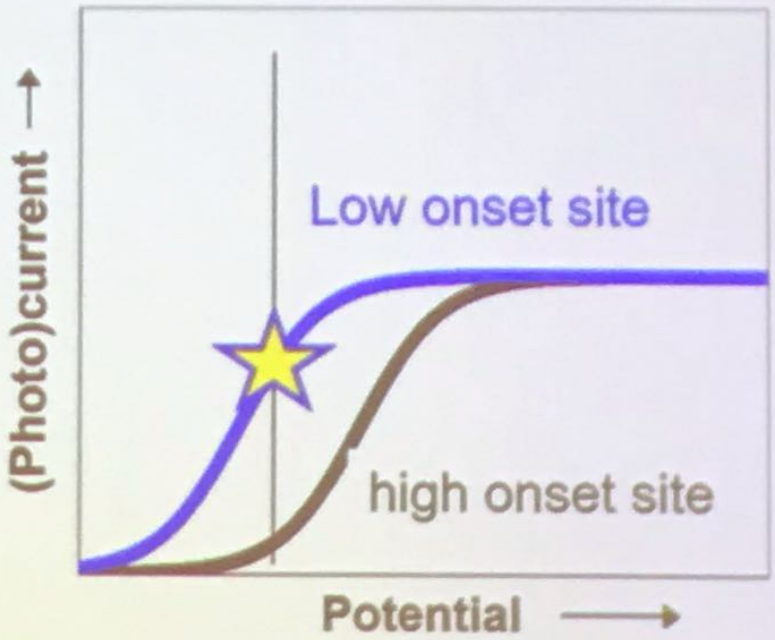
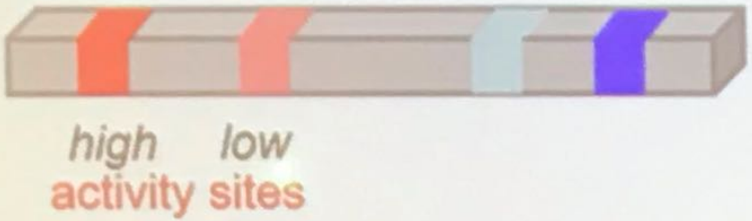


- Low onset potential sites get catalysts first

⇒ Both results are UN-desirable, opposite to the optimal sites
⇒ But how to overcome?

Function-based Strategy for Optimal Catalyst Deposition

Function-based Strategy for Optimal Catalyst Deposition

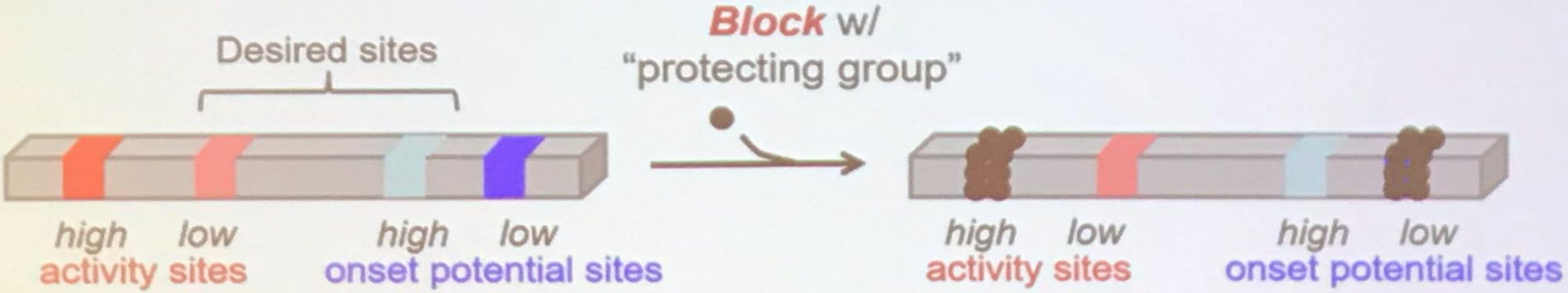


Function-based Strategy for Optimal Catalyst Deposition

high *low* *high* *low*

activity sites onset potential sites

Function-based Strategy for Optimal Catalyst Deposition



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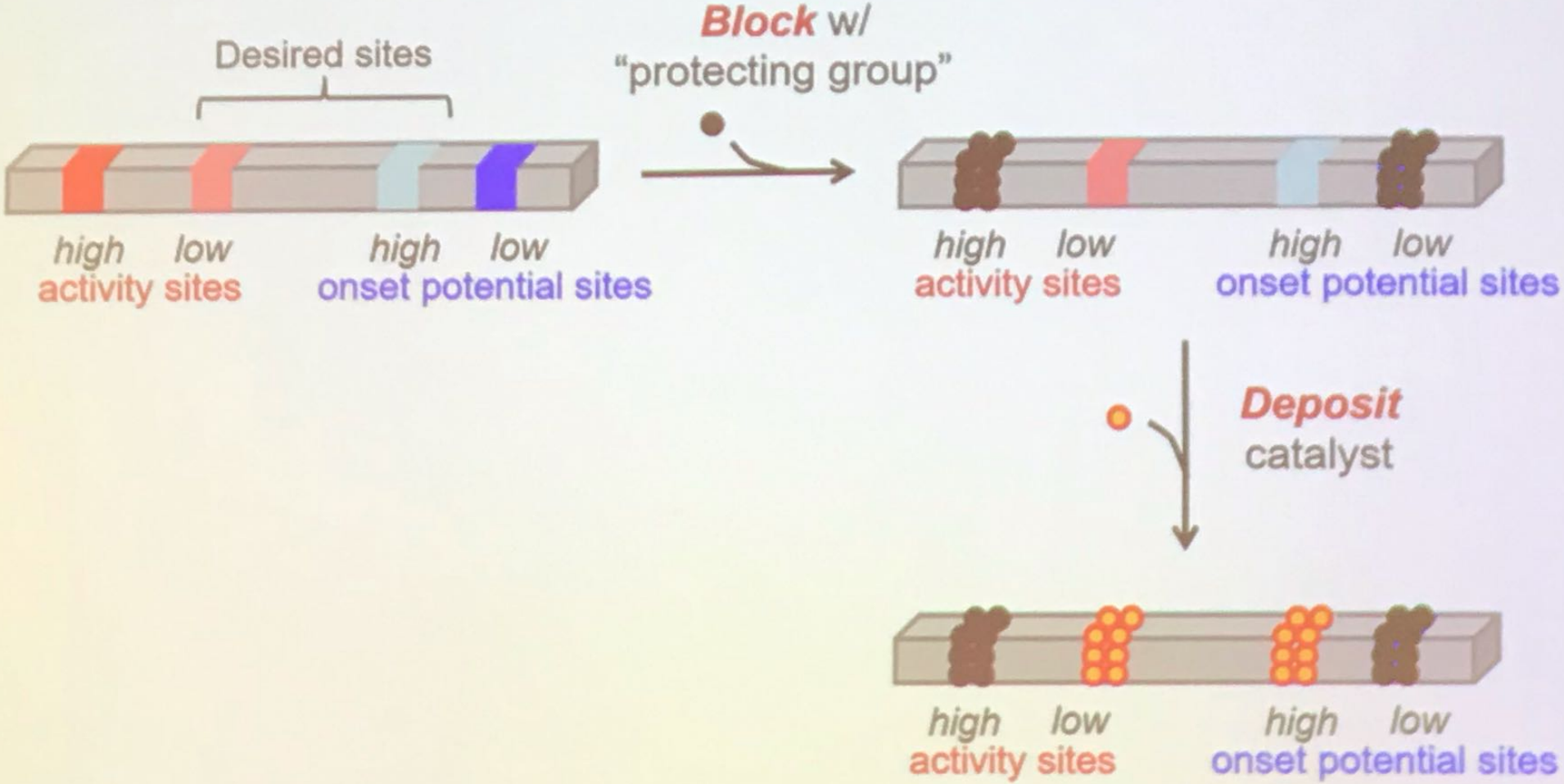

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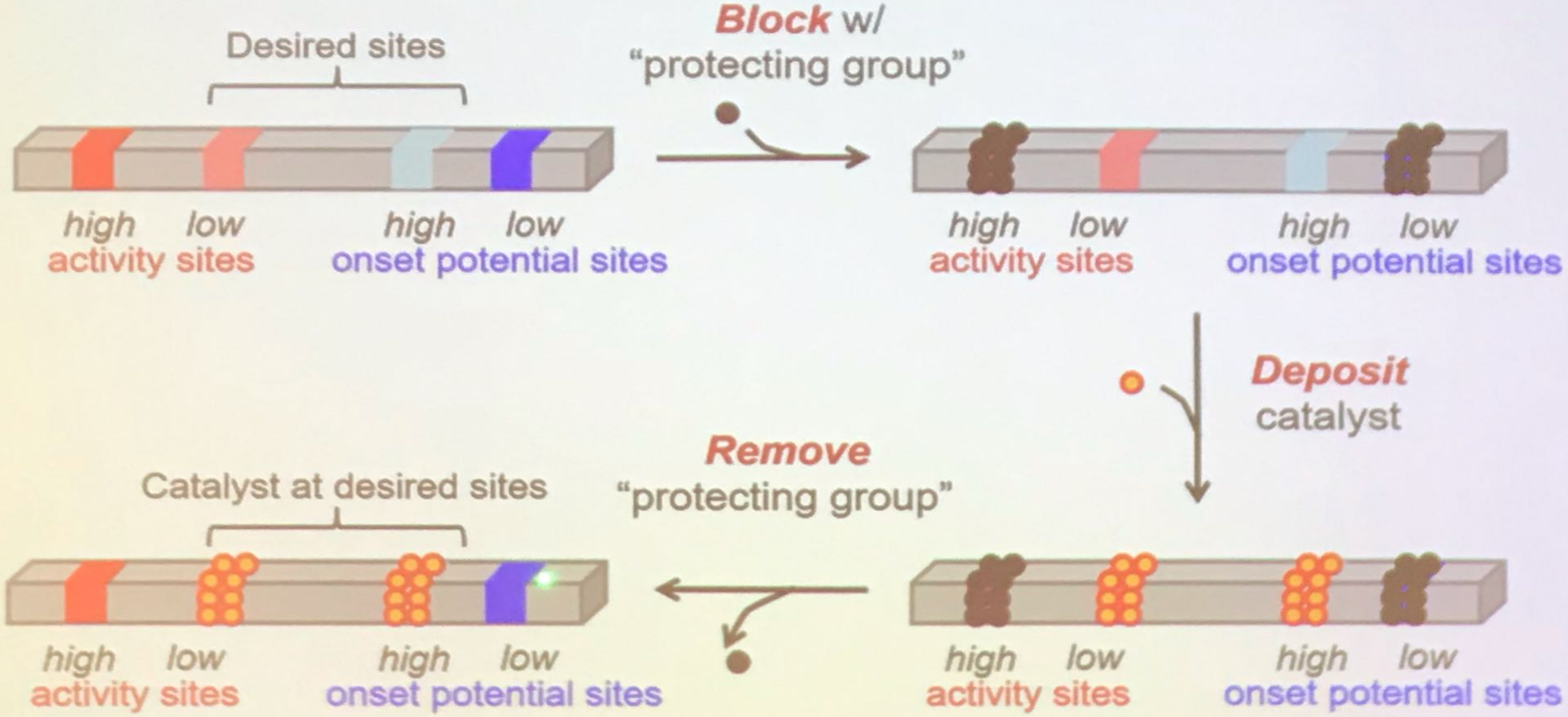

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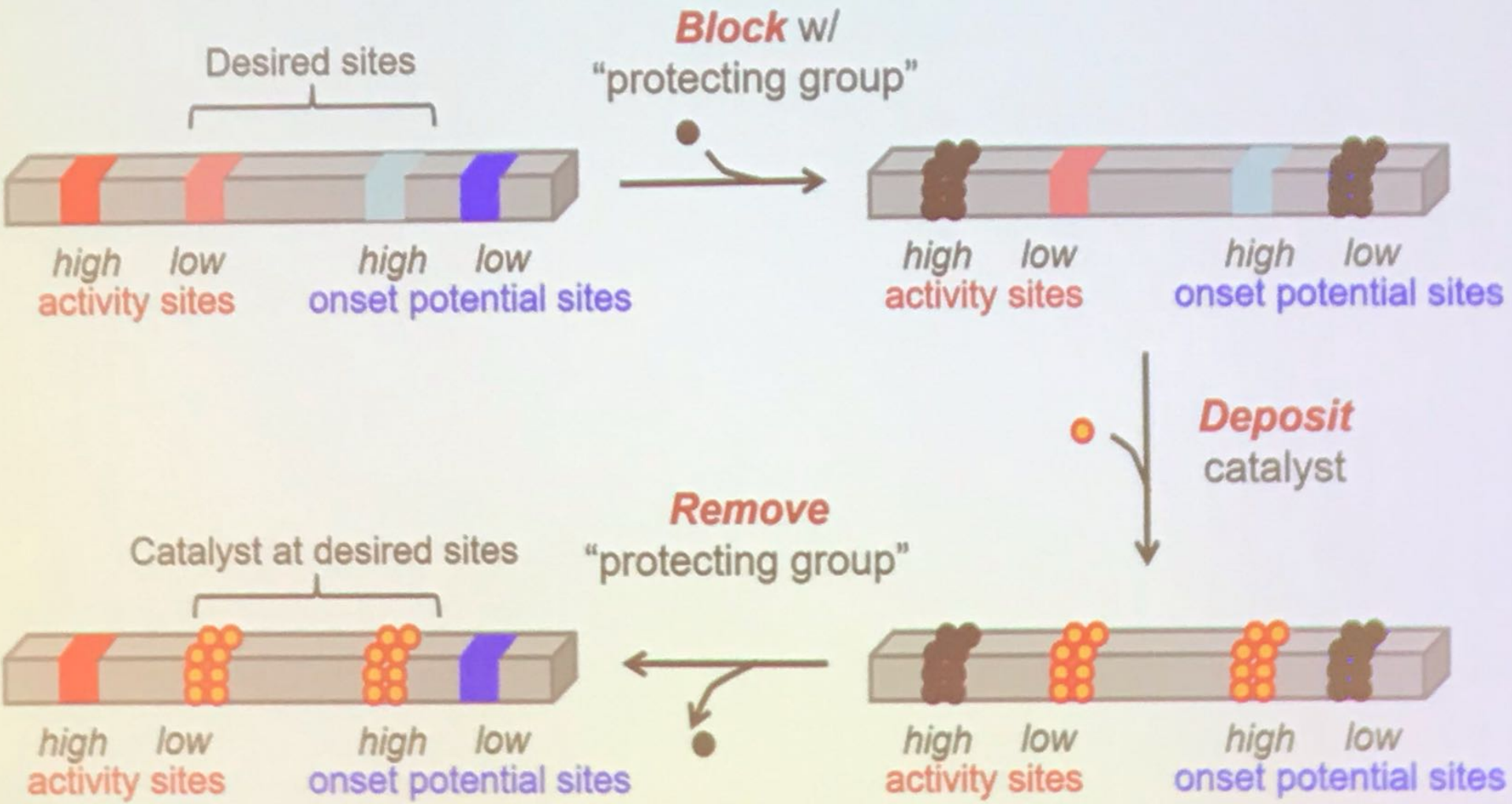
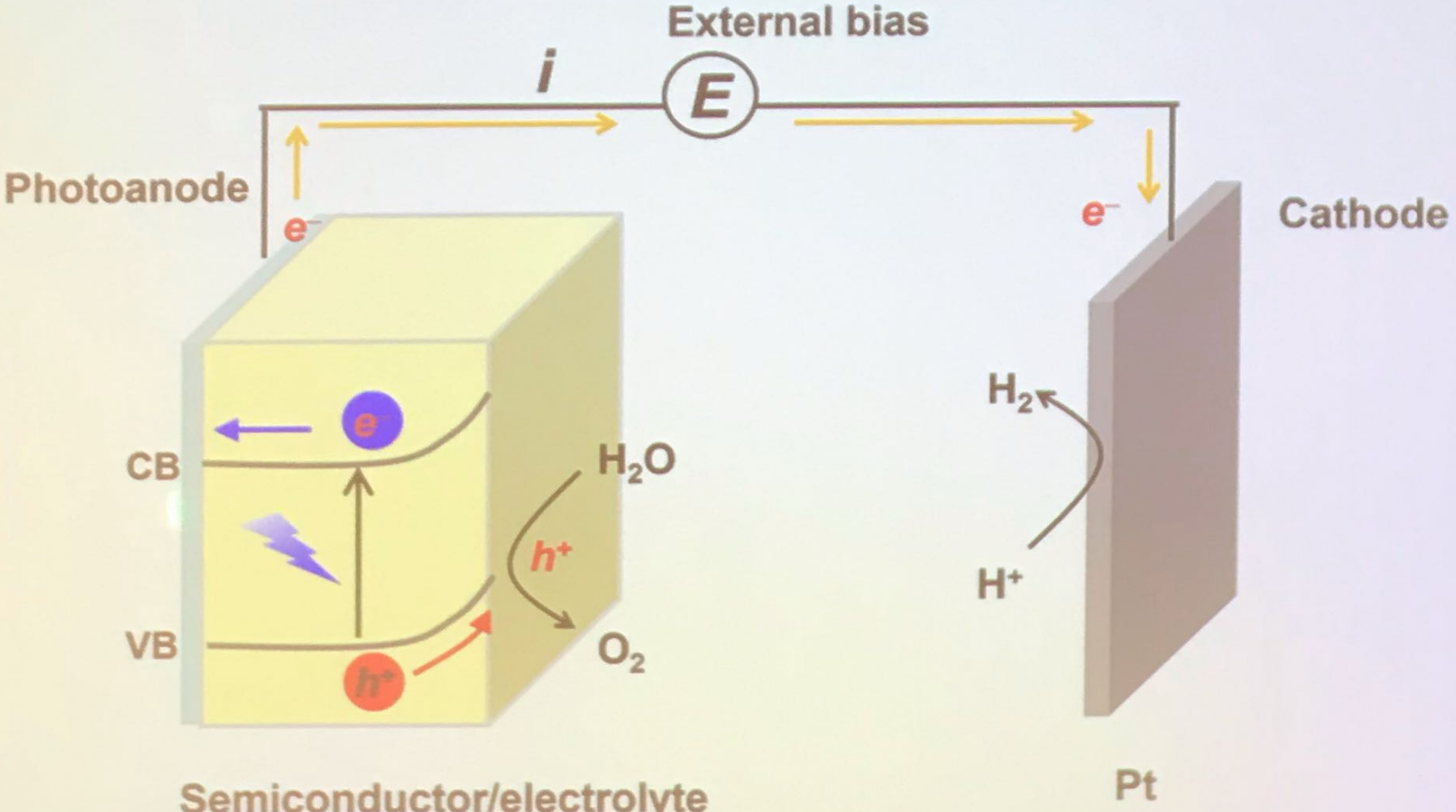


Broad relevance:

- Principles may vary depending on systems
- But, approaches are general

Photoelectrodes: Particle Interfaces?



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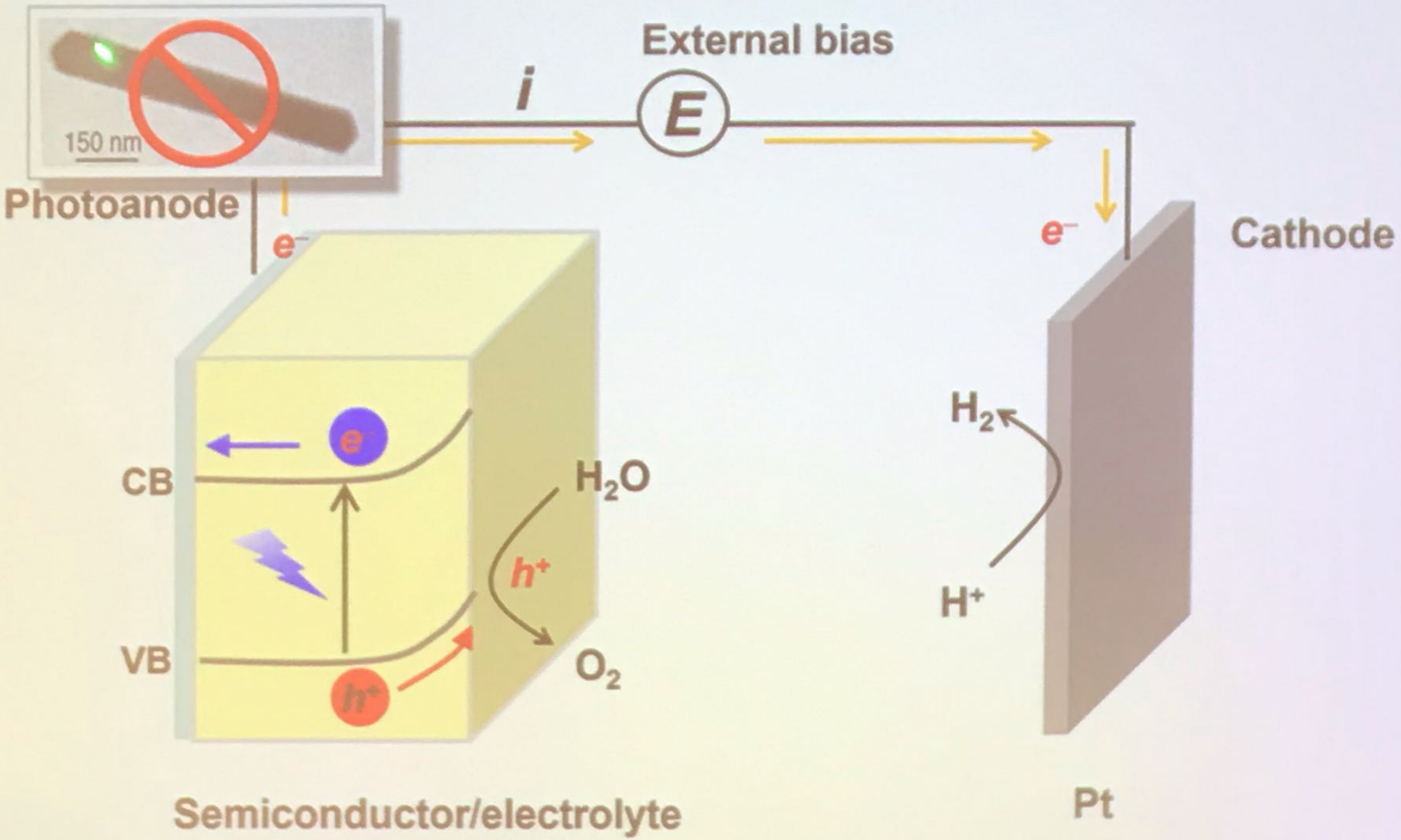

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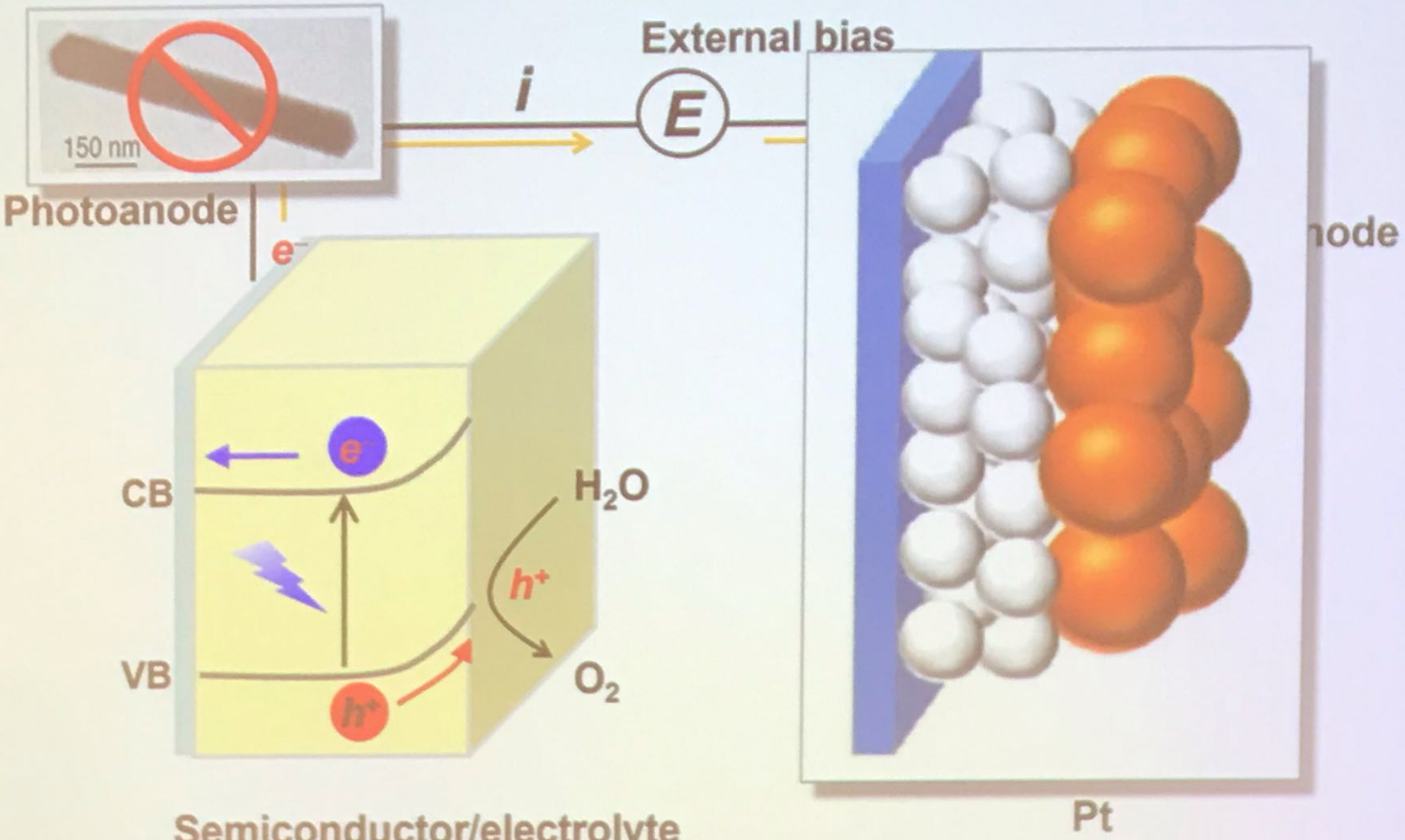

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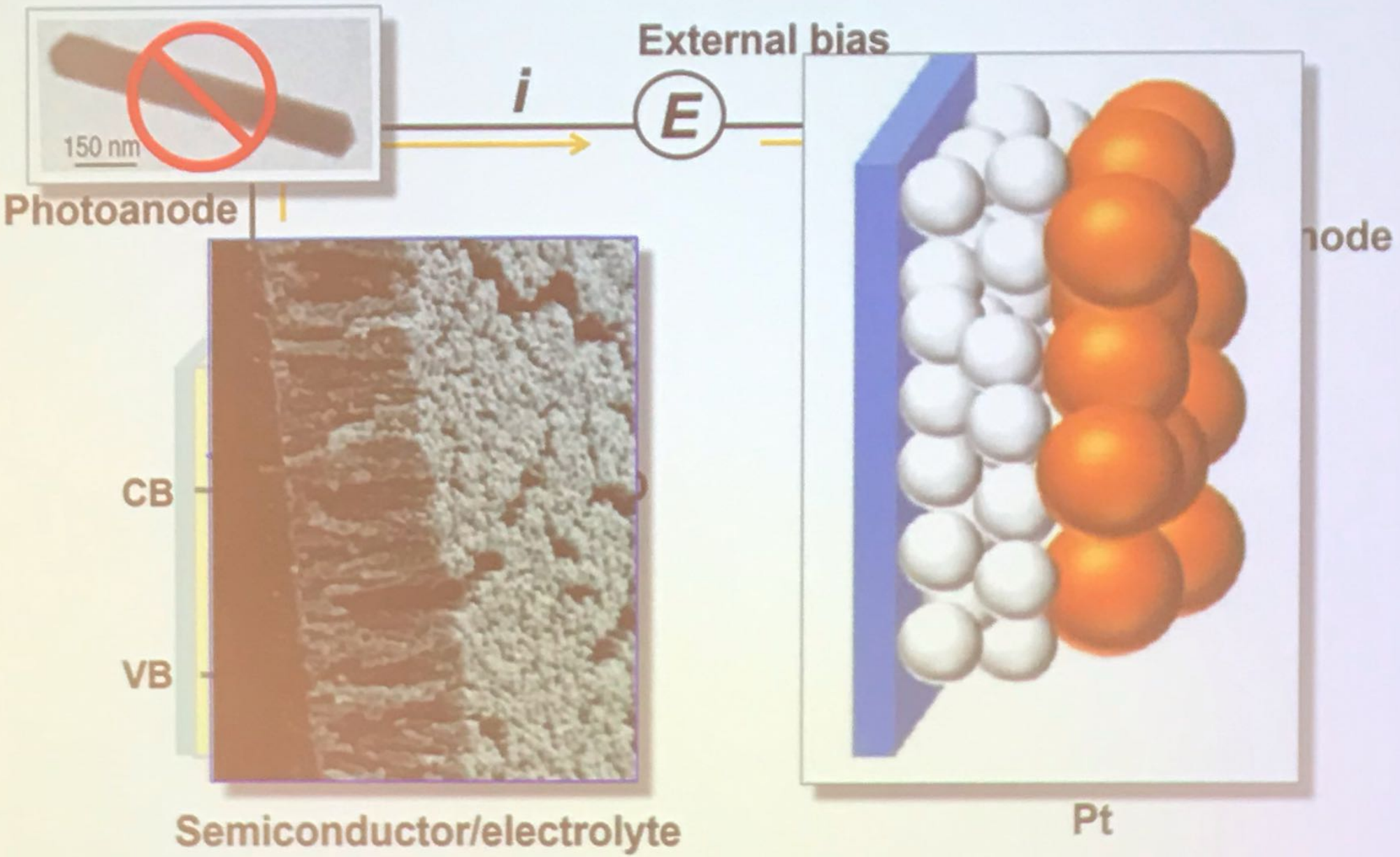
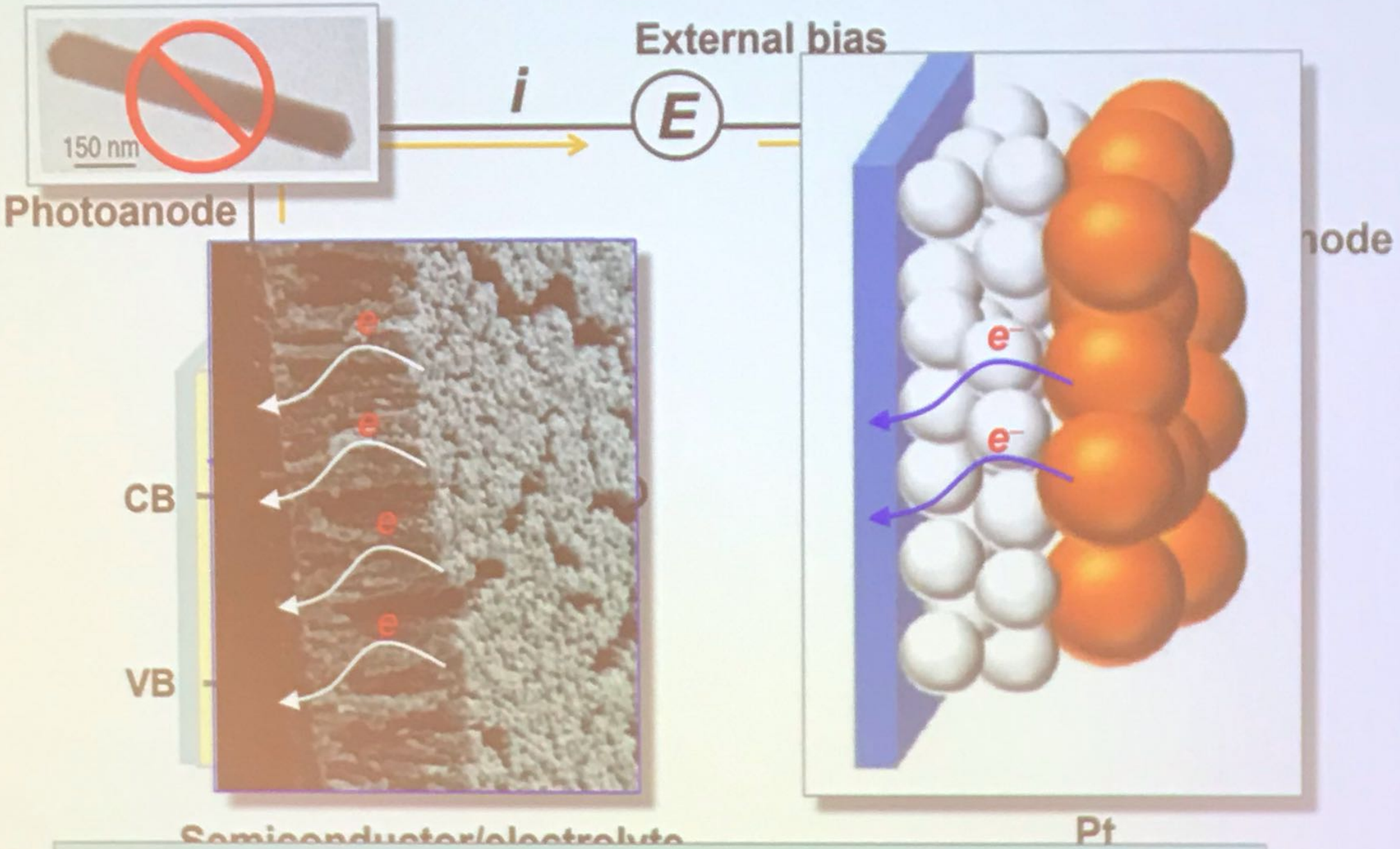


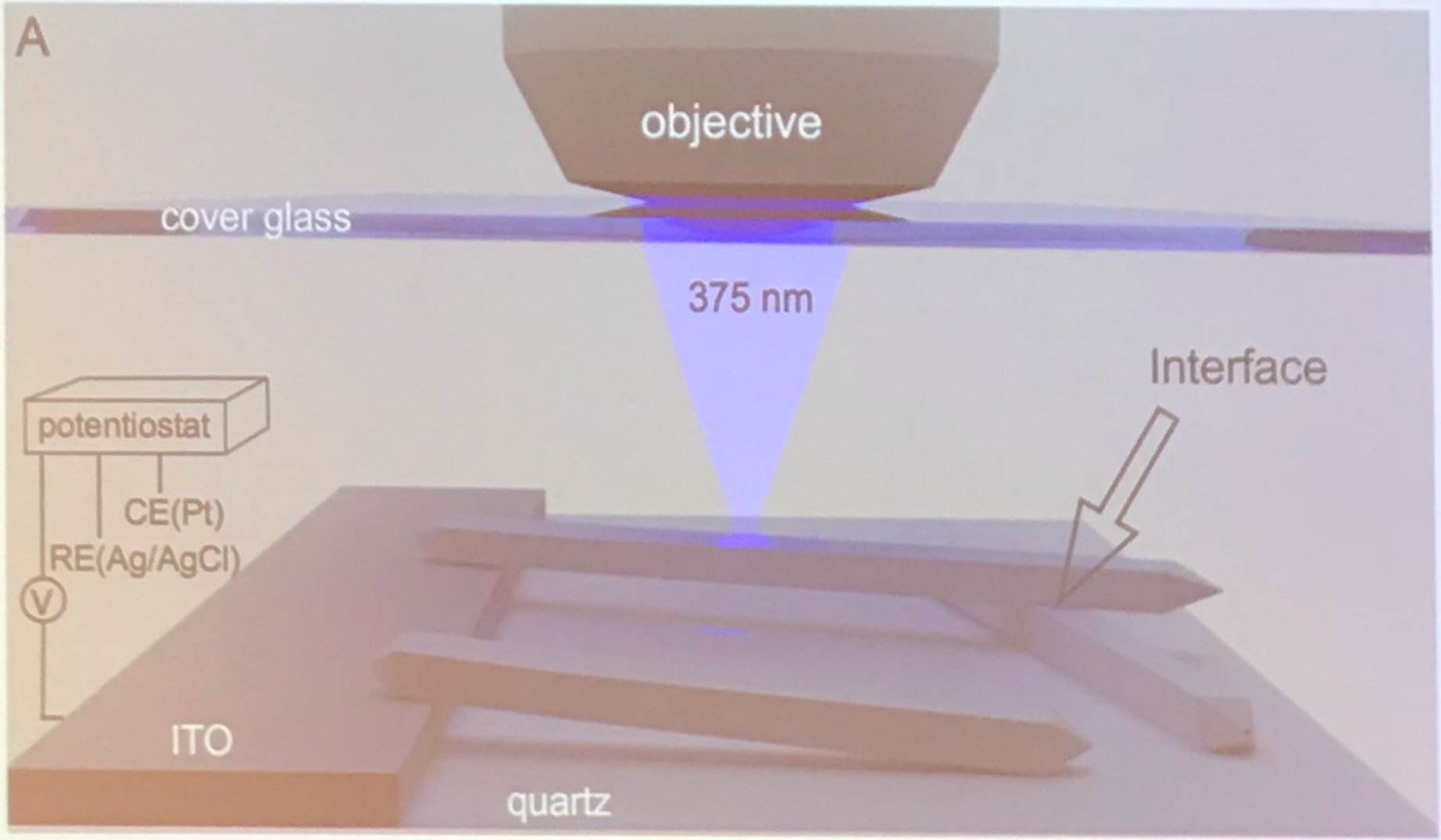
Photoelectrodes: Particle Interfaces?



Particle-particle interfaces ⇒ Loss of current, but how much?

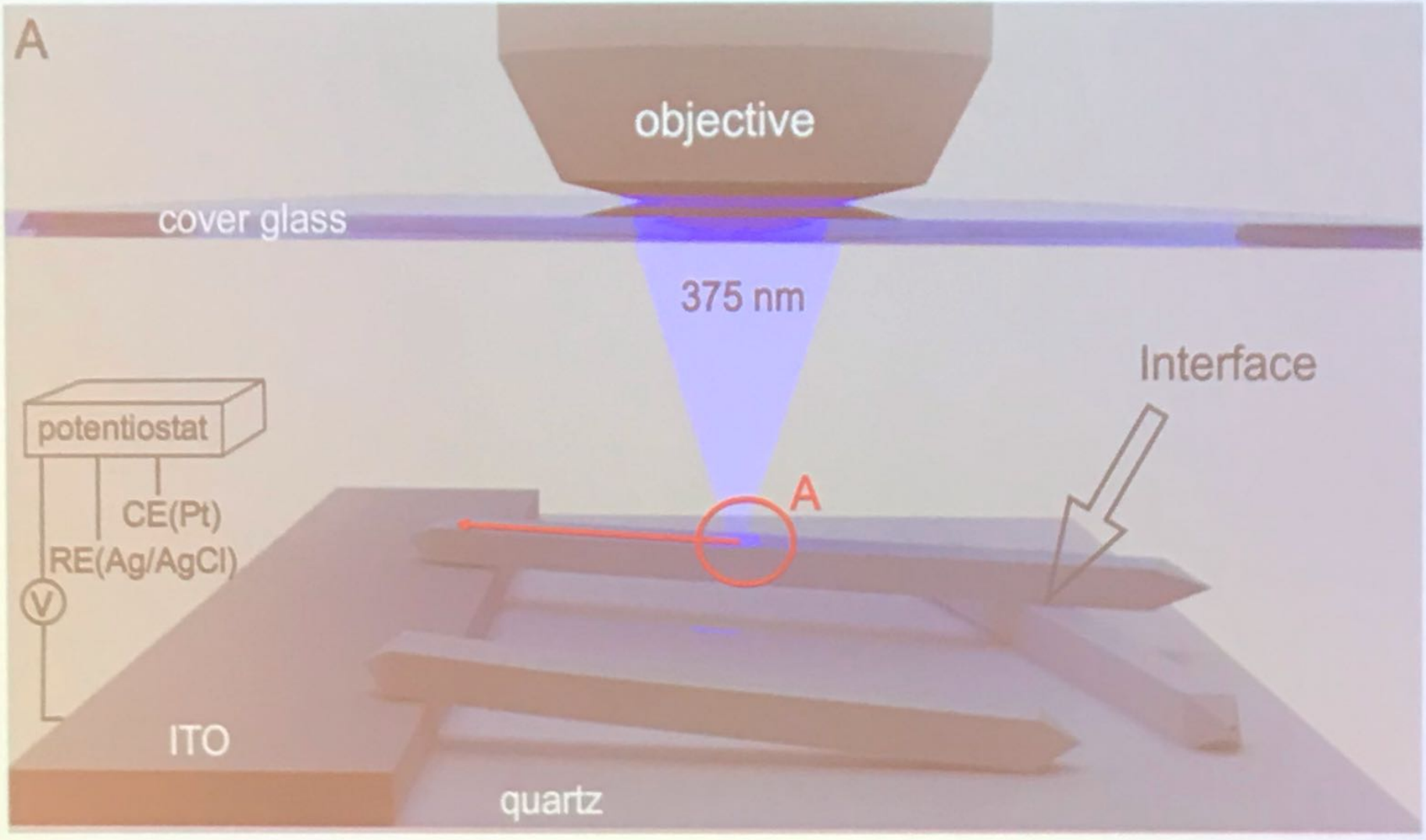
⇒ A single interface?

Single Interface Measurements on Crossed Structures



M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

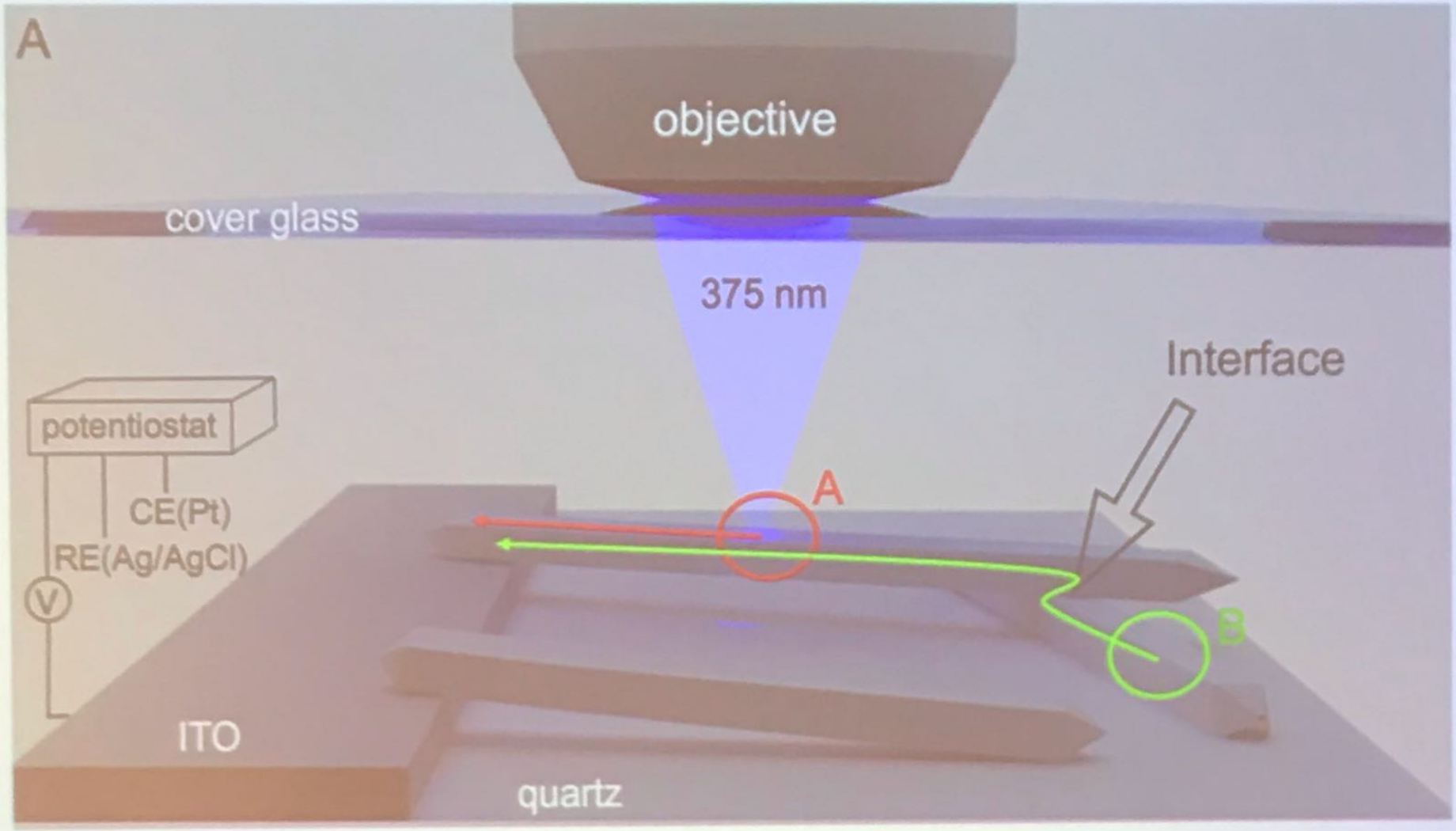
Single Interface Measurements on Crossed Structures



Type-A: current does not go through interface

M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

Single Interface Measurements on Crossed Structures



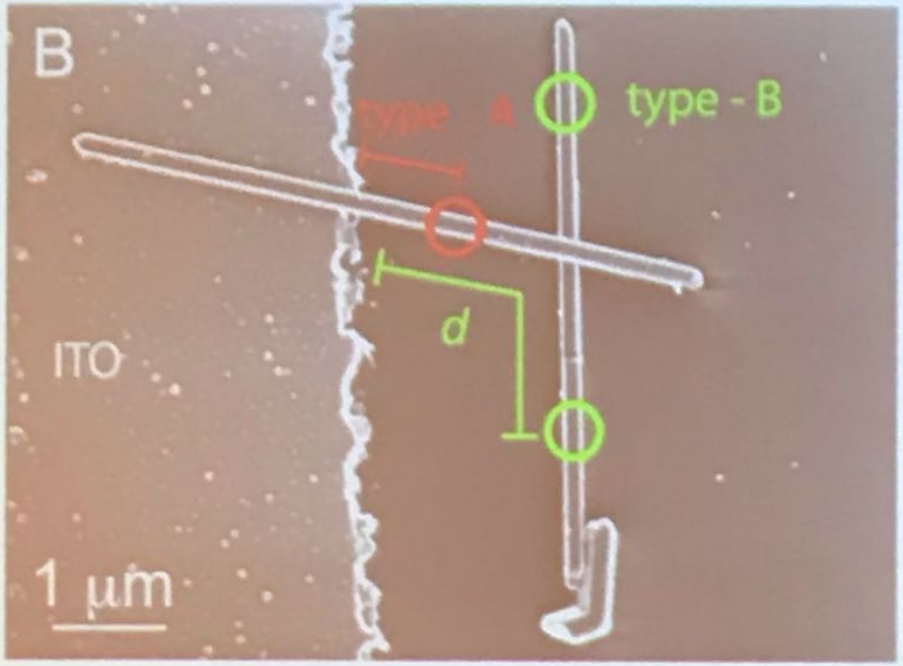
Type-A: current does not go through interface

Type-B: current passes a single interface

M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

TiO_2 nanorods: cross structures vs. isolated ones

SEM



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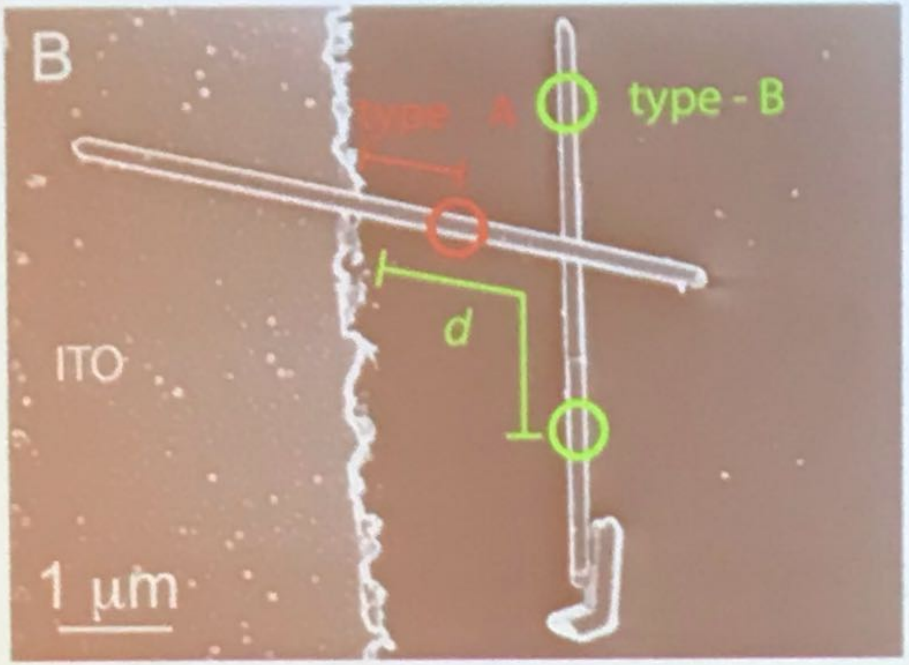
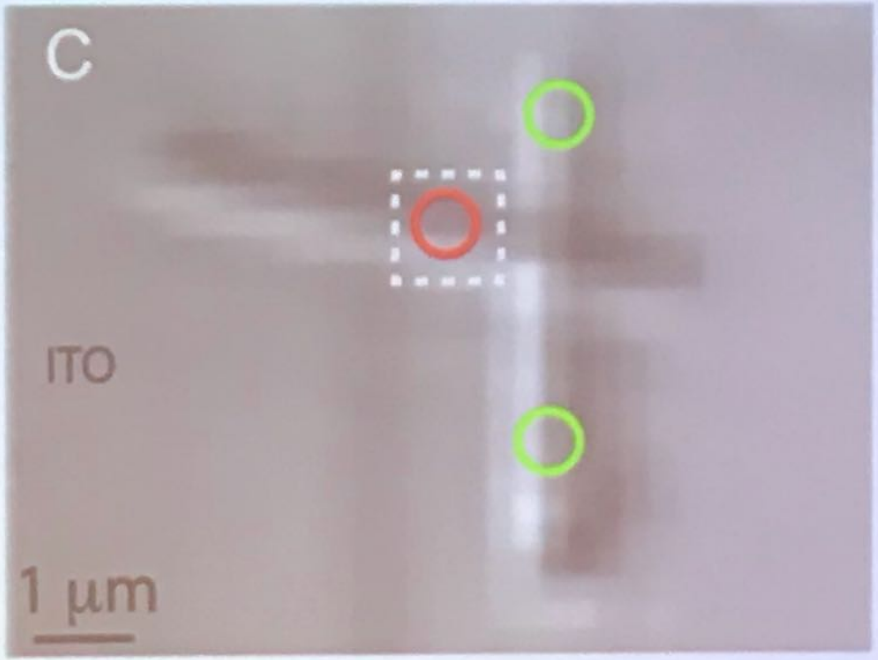


Optical transmission



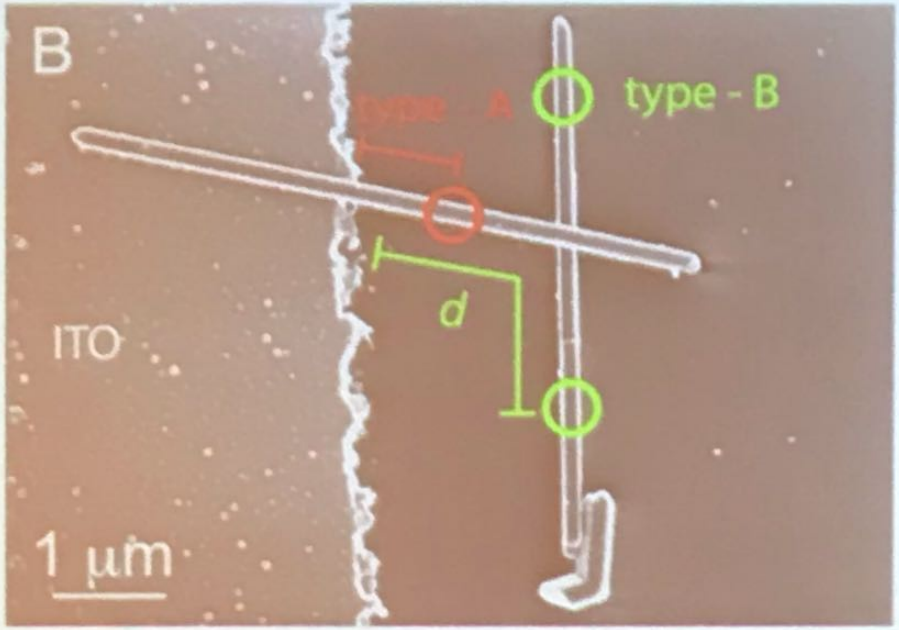
Interfaces formed under conditions directly relevant to film electrodes!

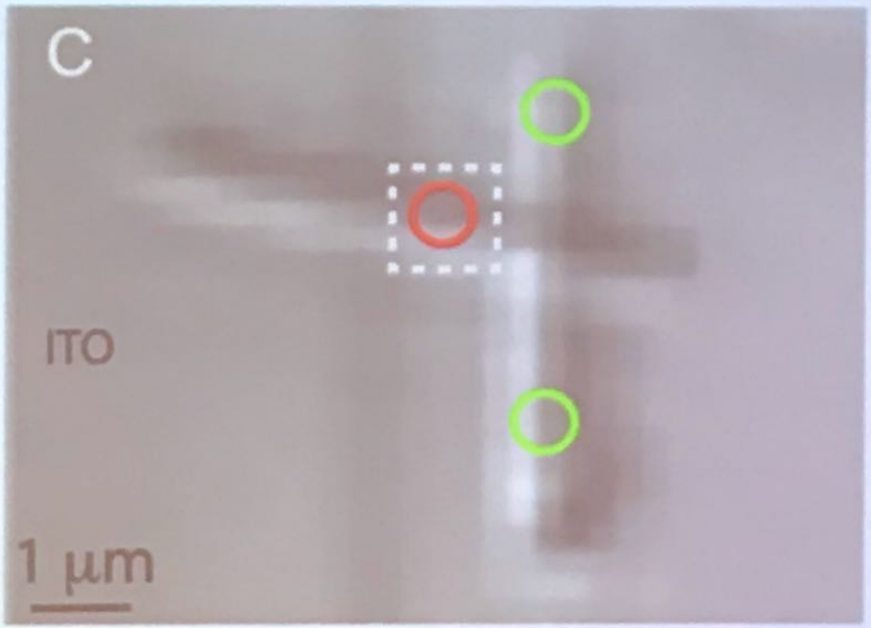
M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

TiO_2 nanorods: cross structures vs. isolated ones

SEM

Optical transmission





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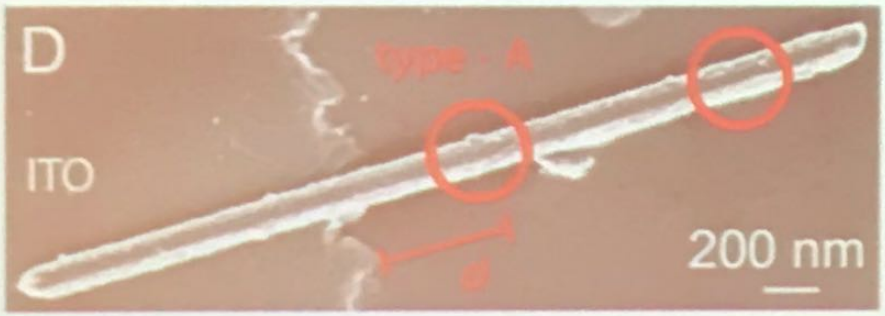
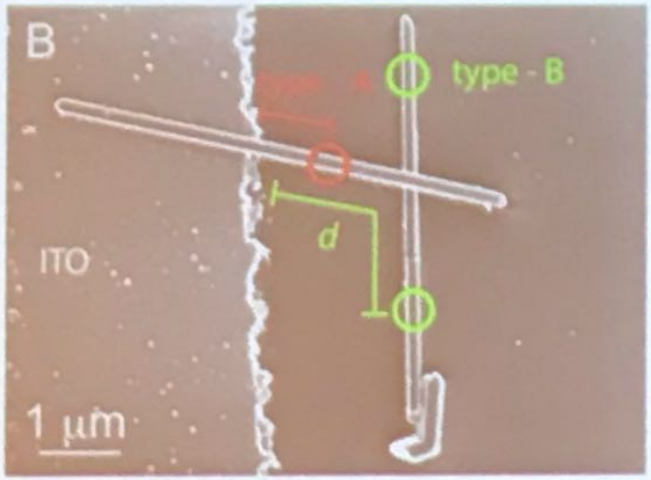


M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

Spot-averaged i_{ss} vs. E dependence

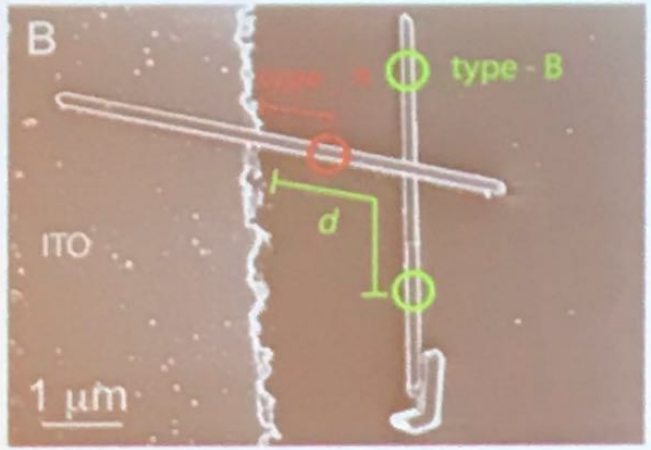


Solution: 0.1 M pH 8.3 borate, 1 M Na_2SO_4

0.6 M Na_2SO_3 (hole scavenger) → current enhancement

M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

Spot-averaged i_{ss} vs. E dependence



Δ = 2.1 nA

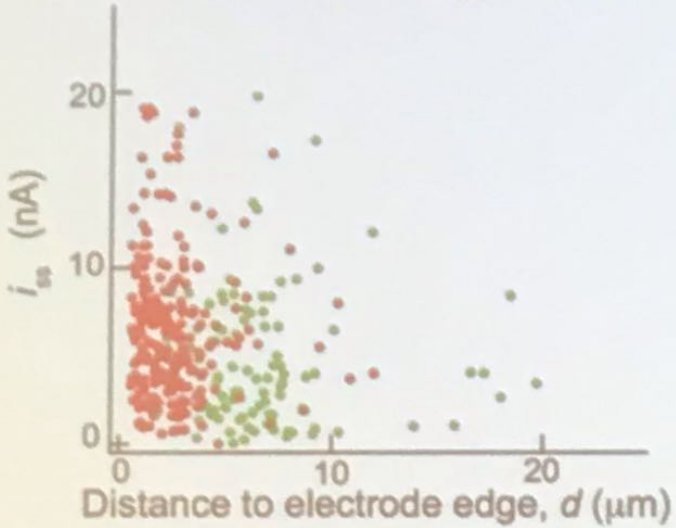
- Loss from a single interface!?
- Distance to electrode?

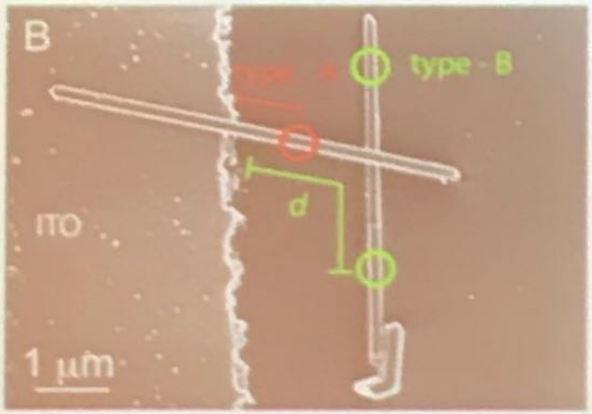
Solution: 0.1 M pH 8.3 borate, 1 M Na_2SO_4
0.6 M Na_2SO_3 (hole scavenger) → current enhancement

M. Hesari, J. B. Sambur, W. Jung, X. Mao, P.C. *Nano Lett.* **2019**, *19*, 958-962.

Current Loss from a Single Interface ⇒ Bench Mark

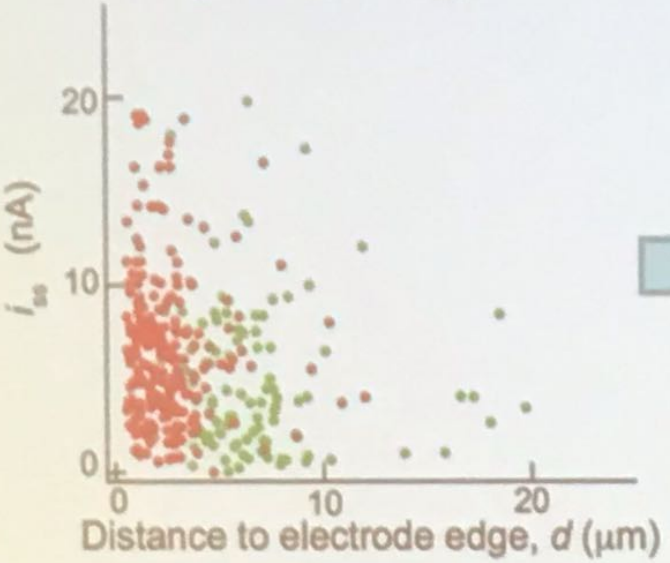
Single spot i_{ss} vs. d



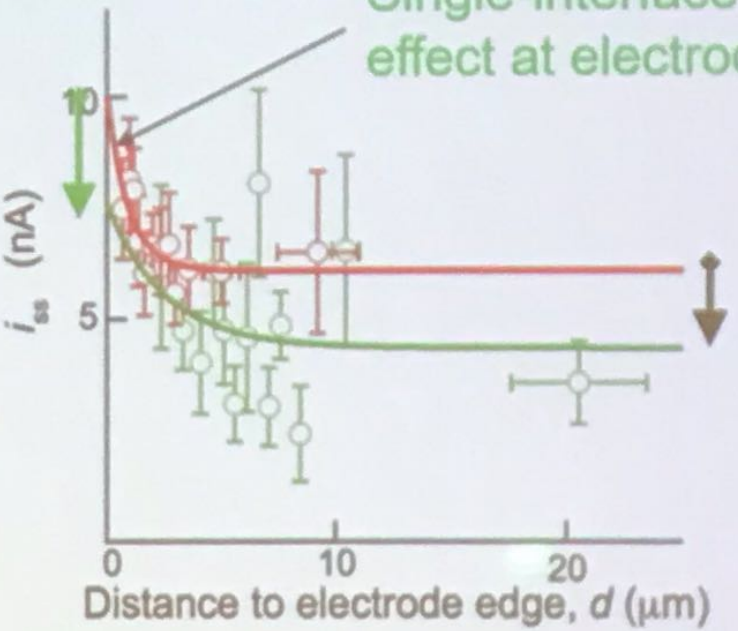


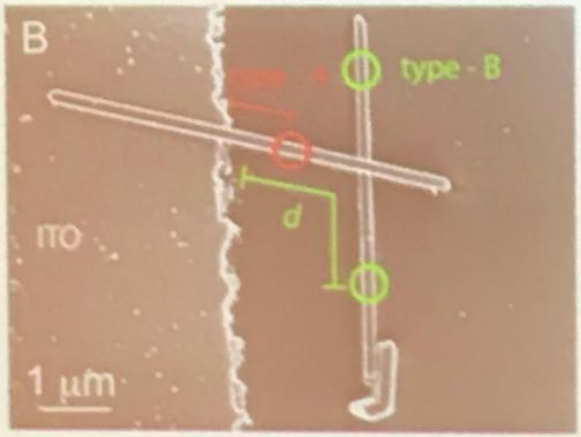
Current Loss from a Single Interface ⇒ Bench Mark

Single spot i_{ss} vs. d



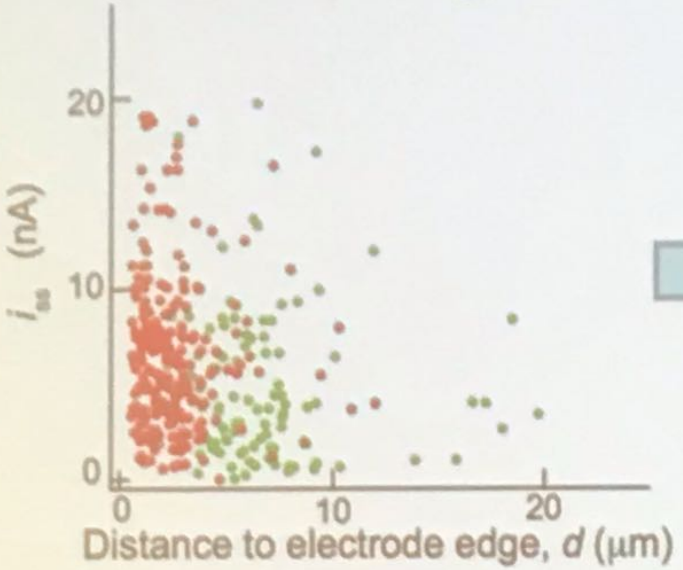
Single-interface effect at electrode!



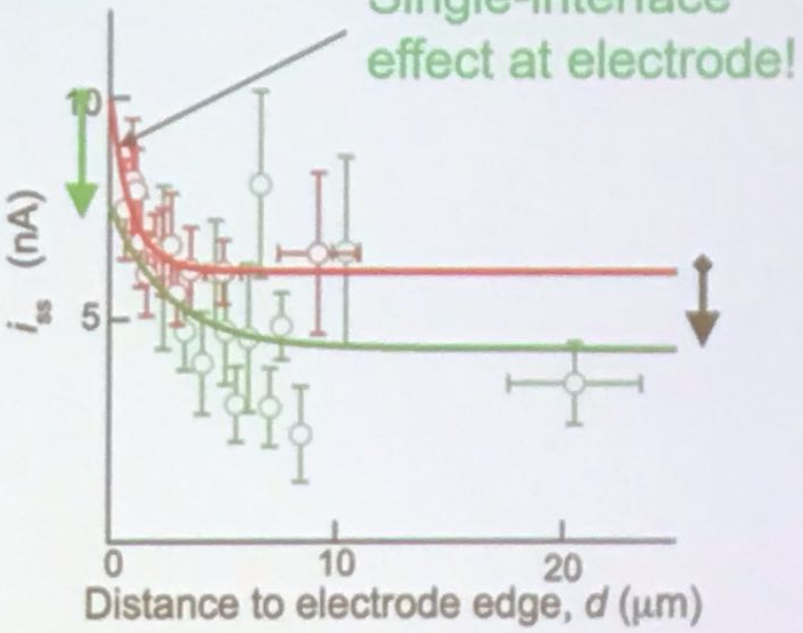


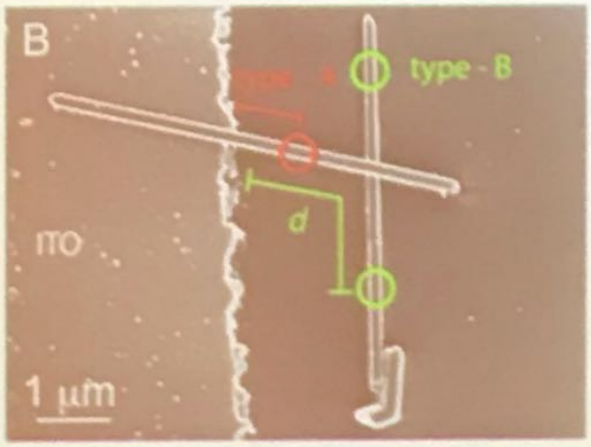
Current Loss from a Single Interface ⇒ Bench Mark

Single spot i_{ss} vs. d

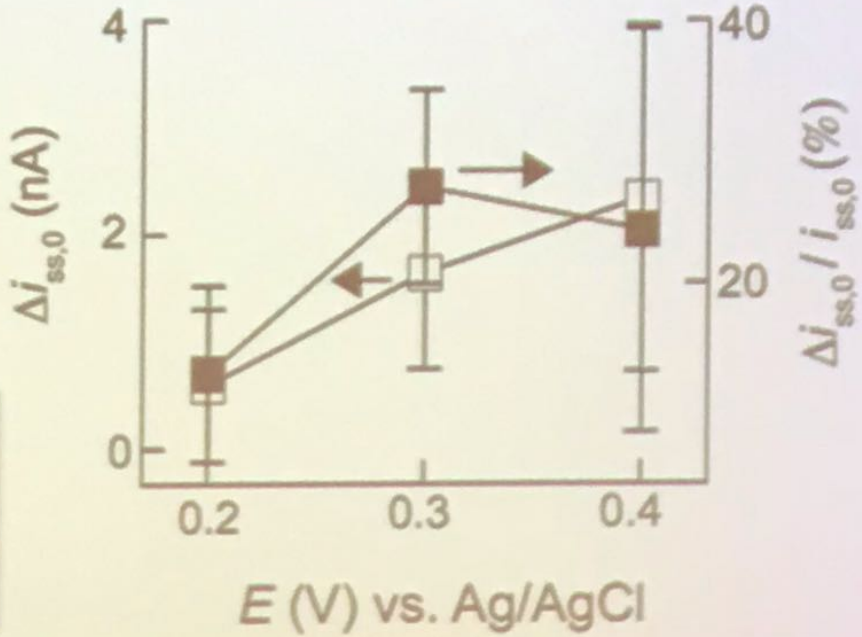


Single-interface effect at electrode!





Loss from single interface vs. E

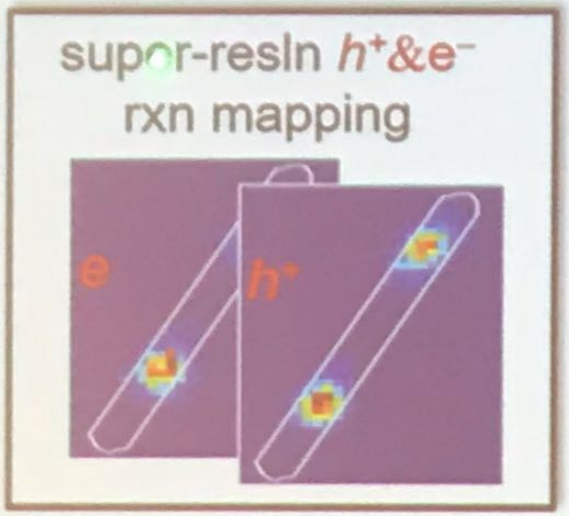


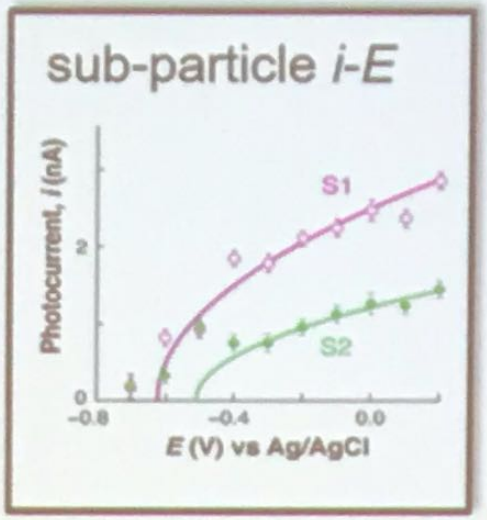
Loss from a single interface:

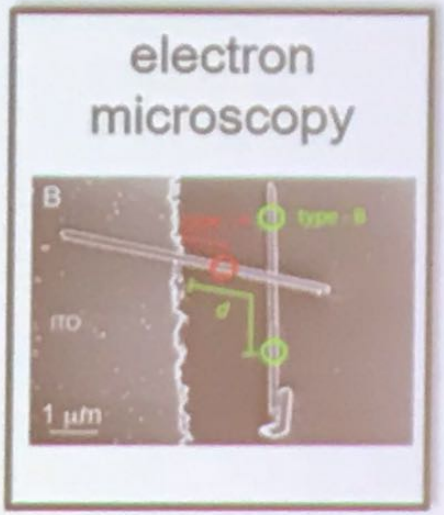
- $\Delta \approx 2$ nA and $\Delta\% \approx 20\%$
- 10 interfaces: 10% left

Summary – Subparticle Photoelectrochemistry

Approaches





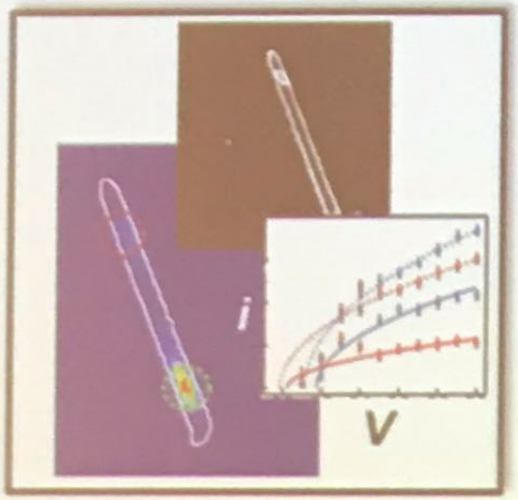


Scientific insights

1. Nature of surface active sites
2. Surface activity ↔ performance correlation
3. Definition of single interface effects

Single-molecule Catalysis

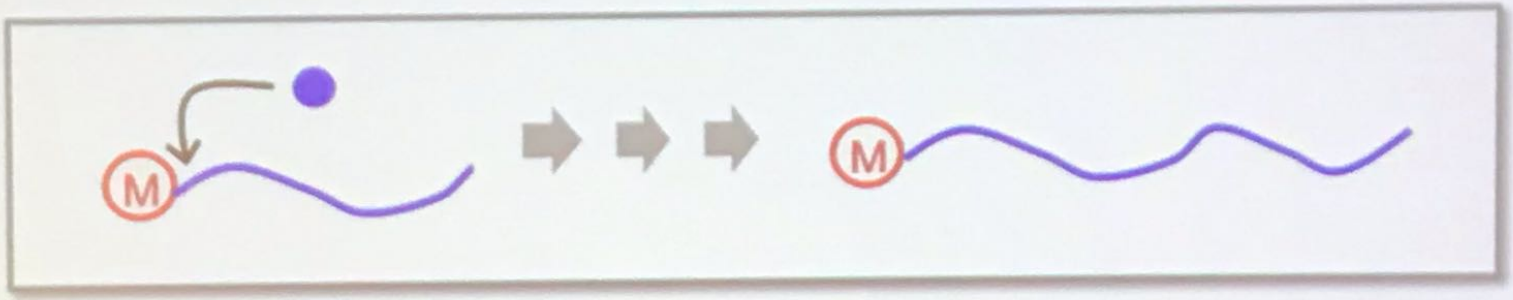
Photoelectrodes



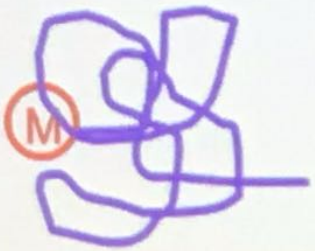
Polymers

Peng Chen
Cornell University
Department of Chemistry and Chemical Biology

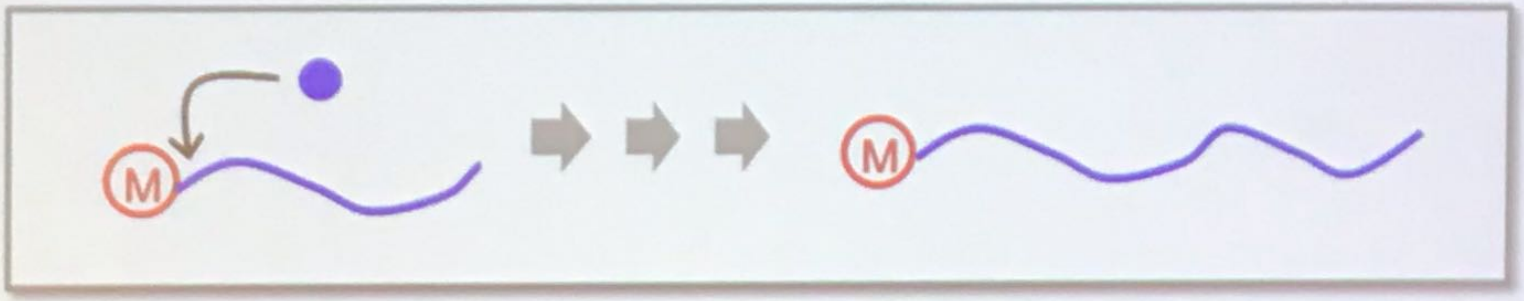
Chain-Growth Polymerization

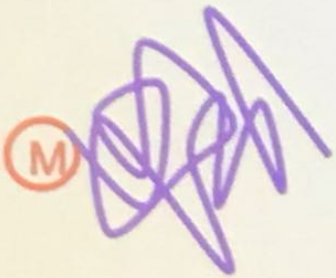


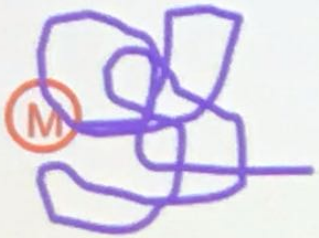
Chain-Growth Polymerization

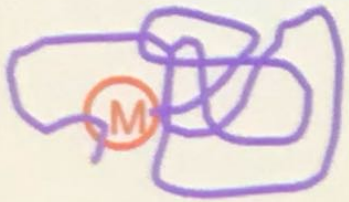


Chain-Growth Polymerization



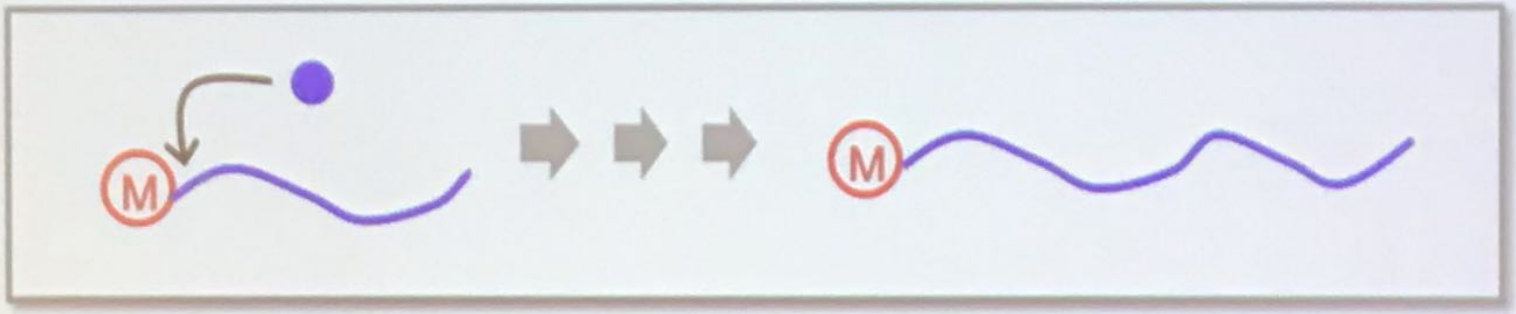


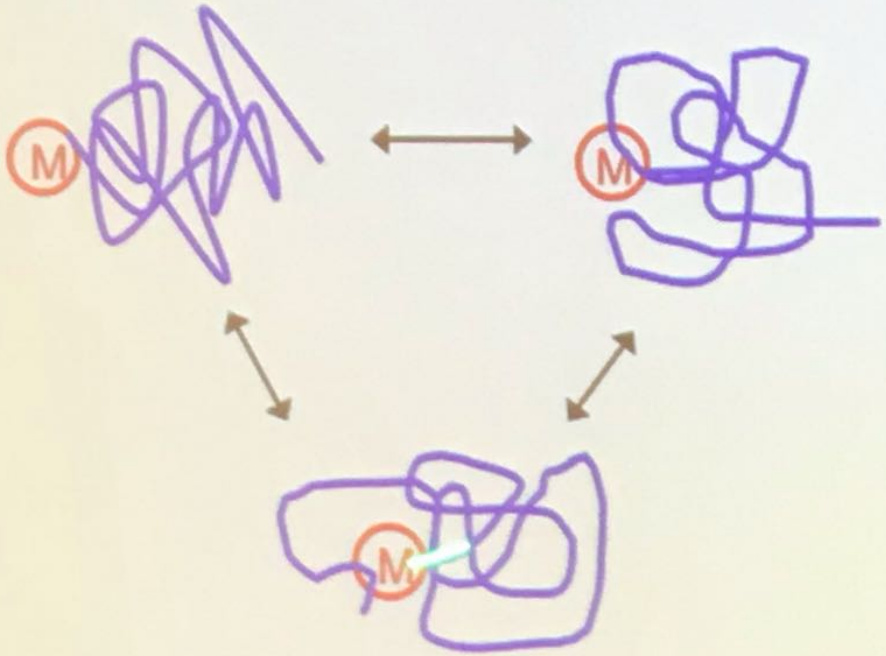




- Differences in catalyst microenvironment

Chain-Growth Polymerization



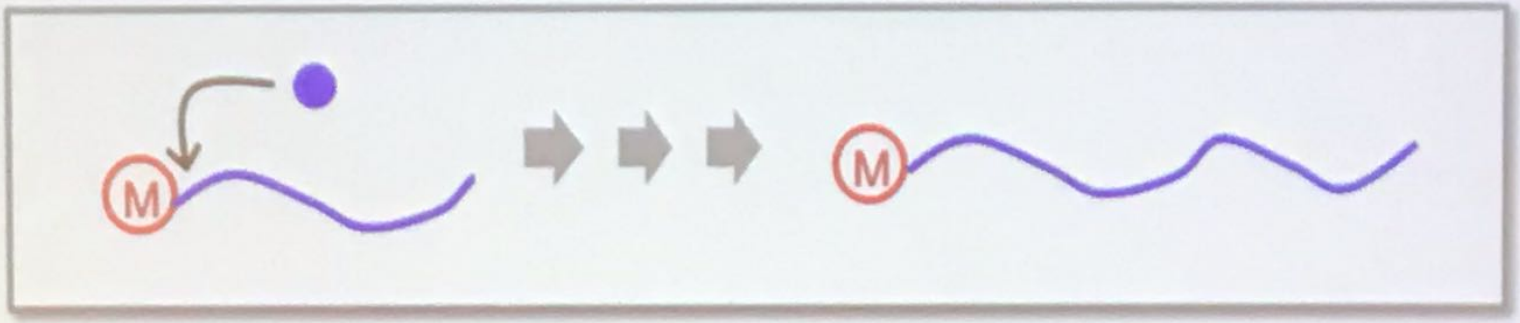


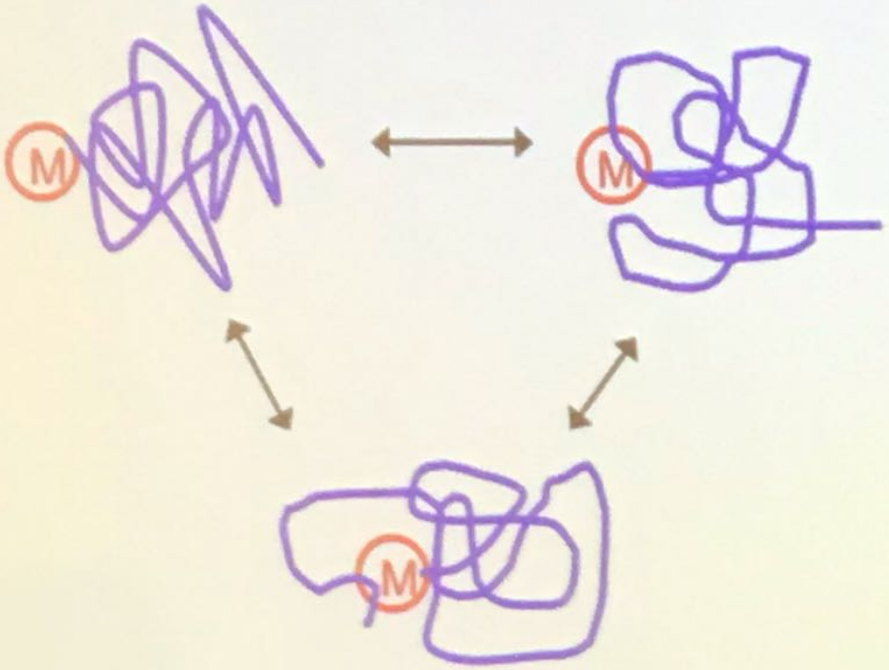
- Differences in catalyst microenvironment
- Inter- and intra-chain rxns

⇒ Each polymer should grow differently.

But, **how?**

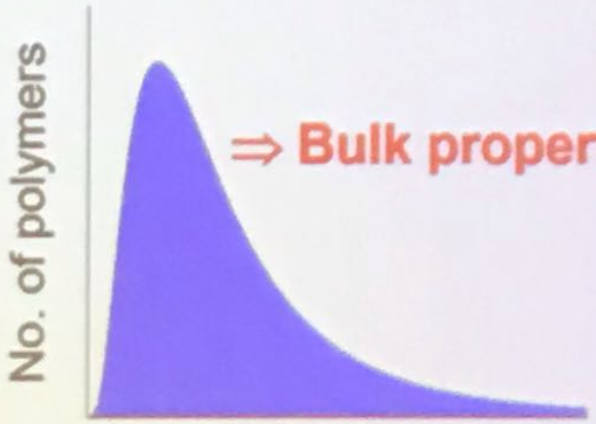
Chain-Growth Polymerization





How?

Molecular distribution



structure
(Chain length, tacticity, sequence, etc.)

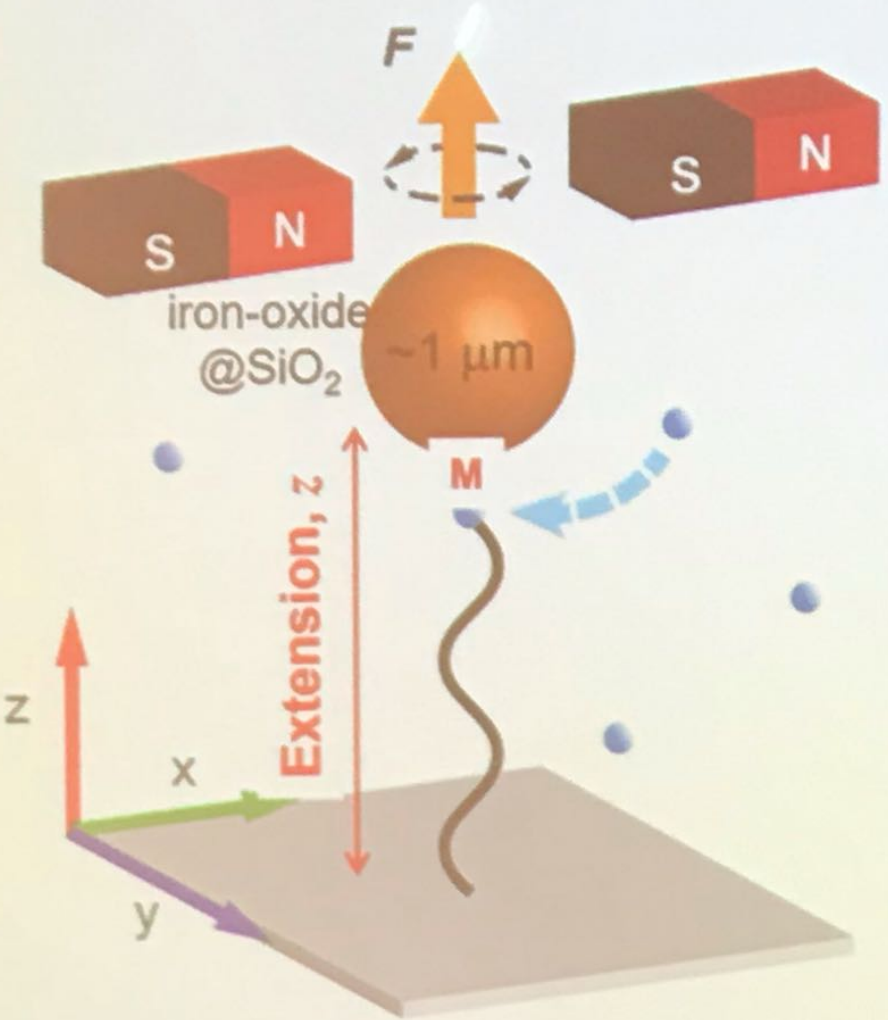
- Differences in catalyst microenvironment
- Inter- and intra-chain rxns

⇒ Each polymer should grow differently.
But, **how?**

⇒ Need to track single polymer growth in real time!

Monitor real-time growth of single polymers

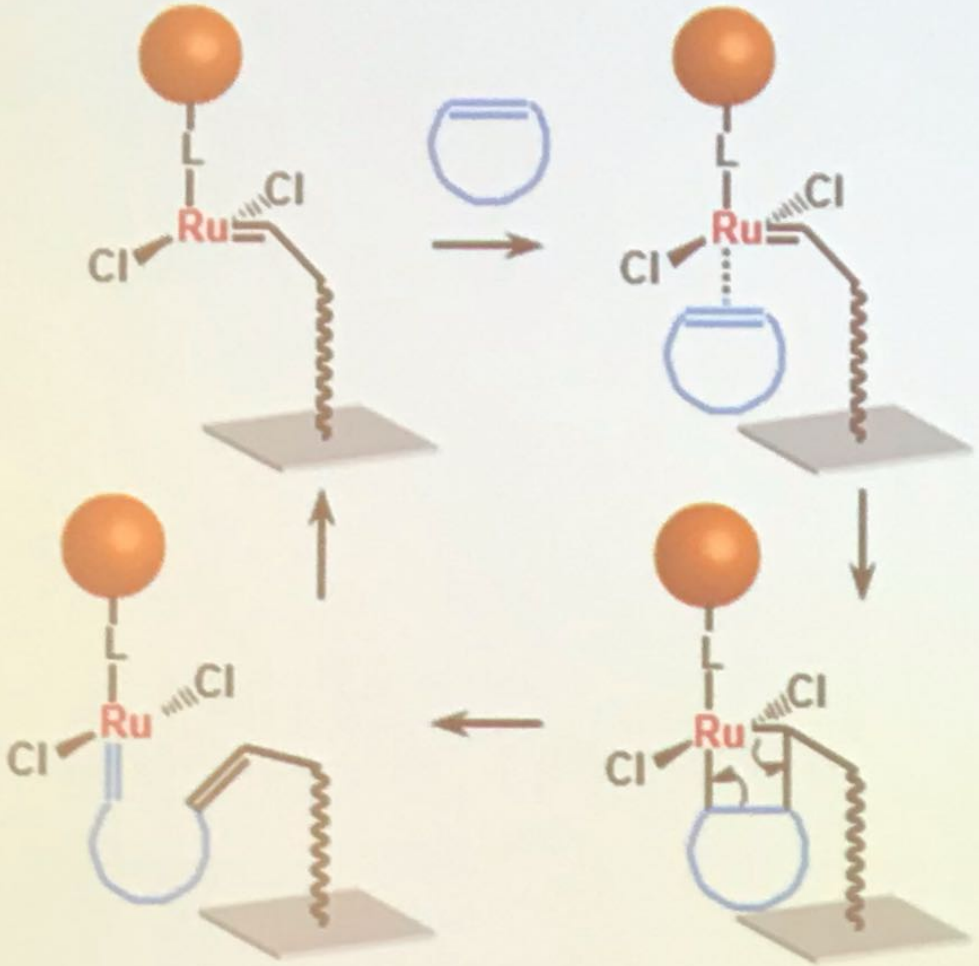
Magnetic tweezers (MT) measurements

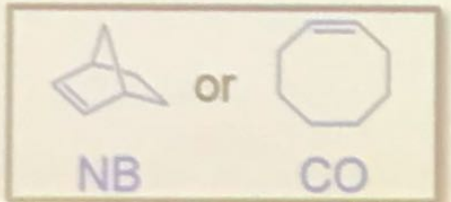


- **Real time extension:** chain length → rate
- **Torsional manipulation** (around *z*-axis): identify single polymers
- **Force-extension curve:** mechanical properties
- **Vary force:** mechano-catalysis coupling

C. Liu, K. Kubo, E. Wang, K.-S. Han, F. Yang, G. Chen, F. A. Escobedo, G. W. Coates, P.C., *Science* **2017**, *358*, 352-355.

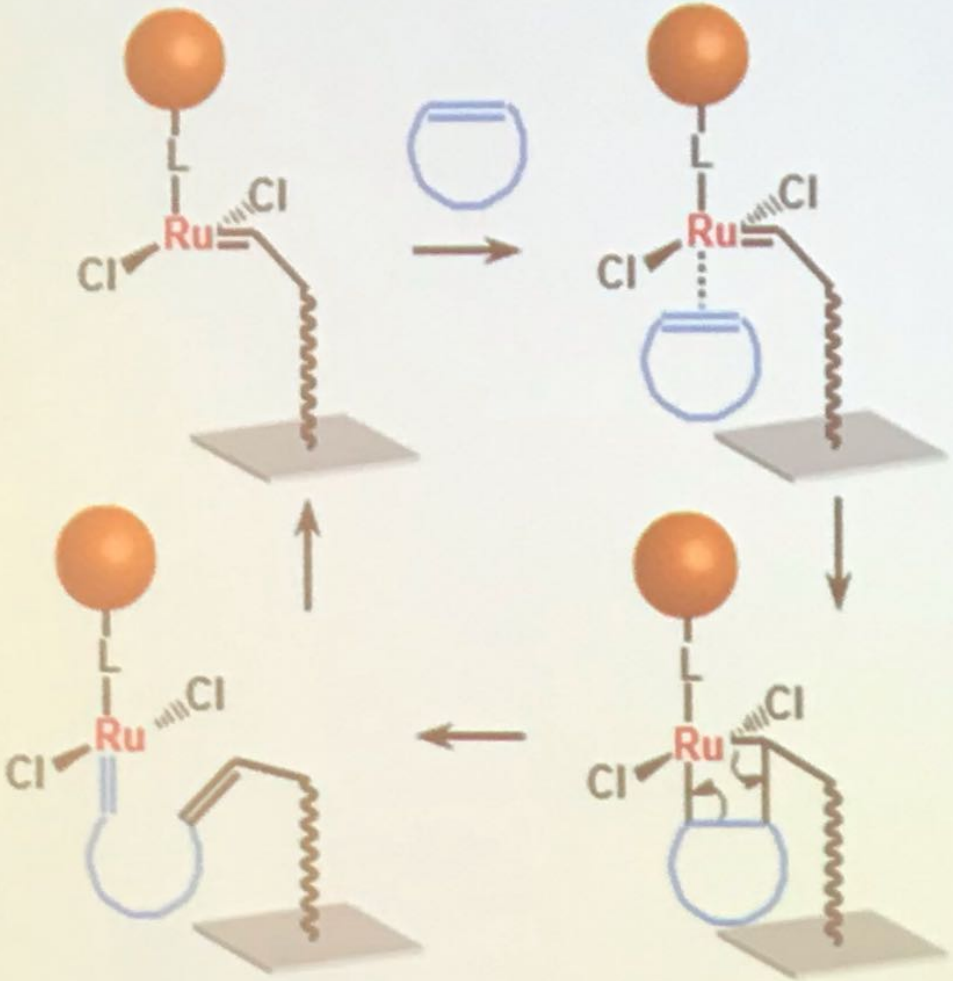
Ring Opening Metathesis Polymerization (ROMP)



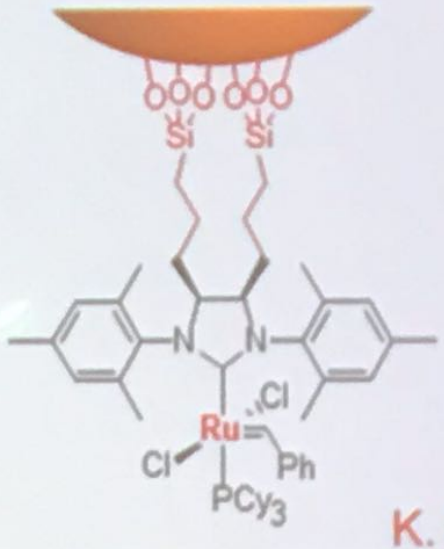


G. Coates

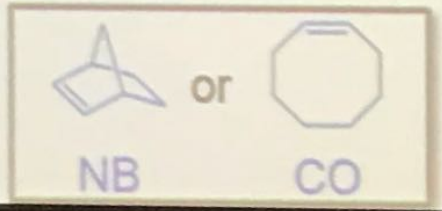
Ring Opening Metathesis Polymerization (ROMP)



Immobilized Grubbs 2nd Generation Catalyst (G2)

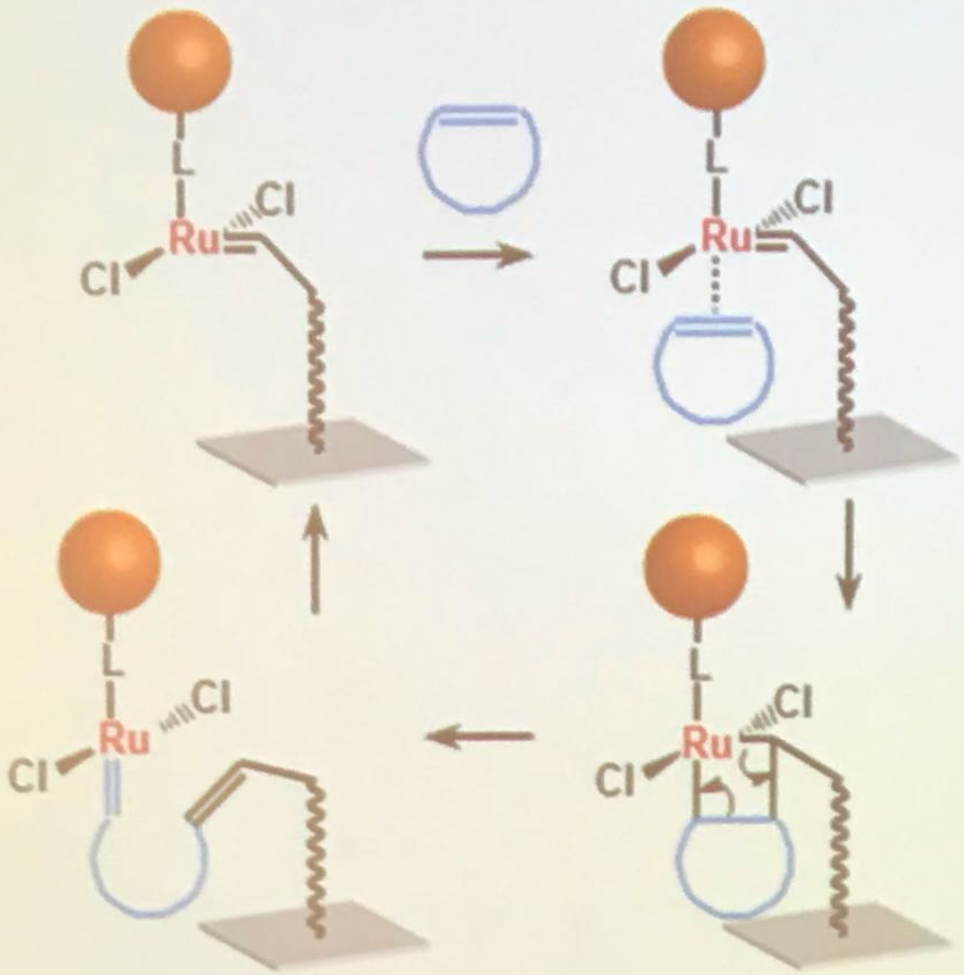


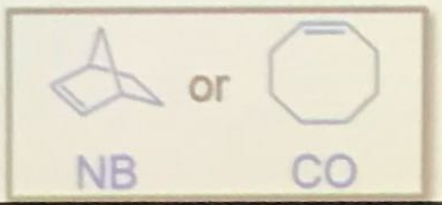
K. Kubo



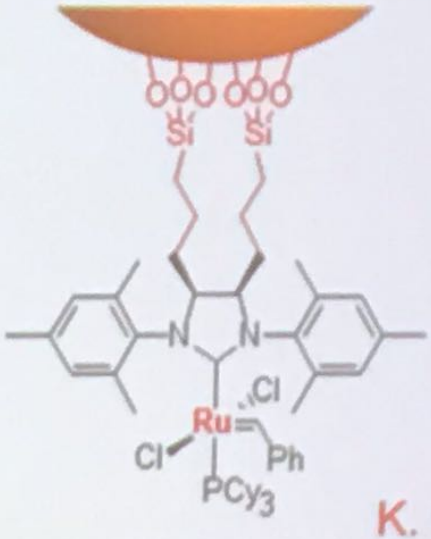
G. Coates

Ring Opening Metathesis Polymerization (ROMP)



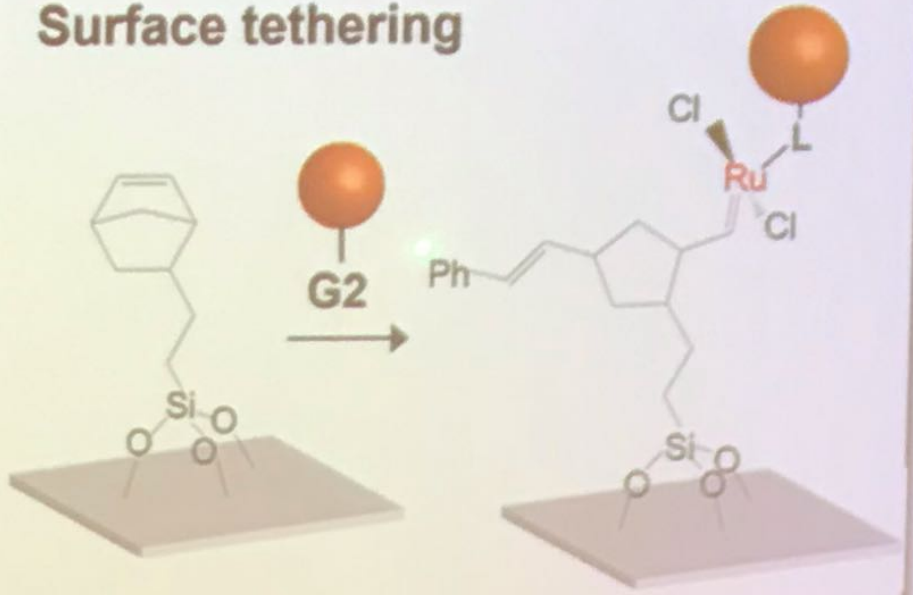


Immobilized Grubbs 2nd Generation Catalyst (G2)



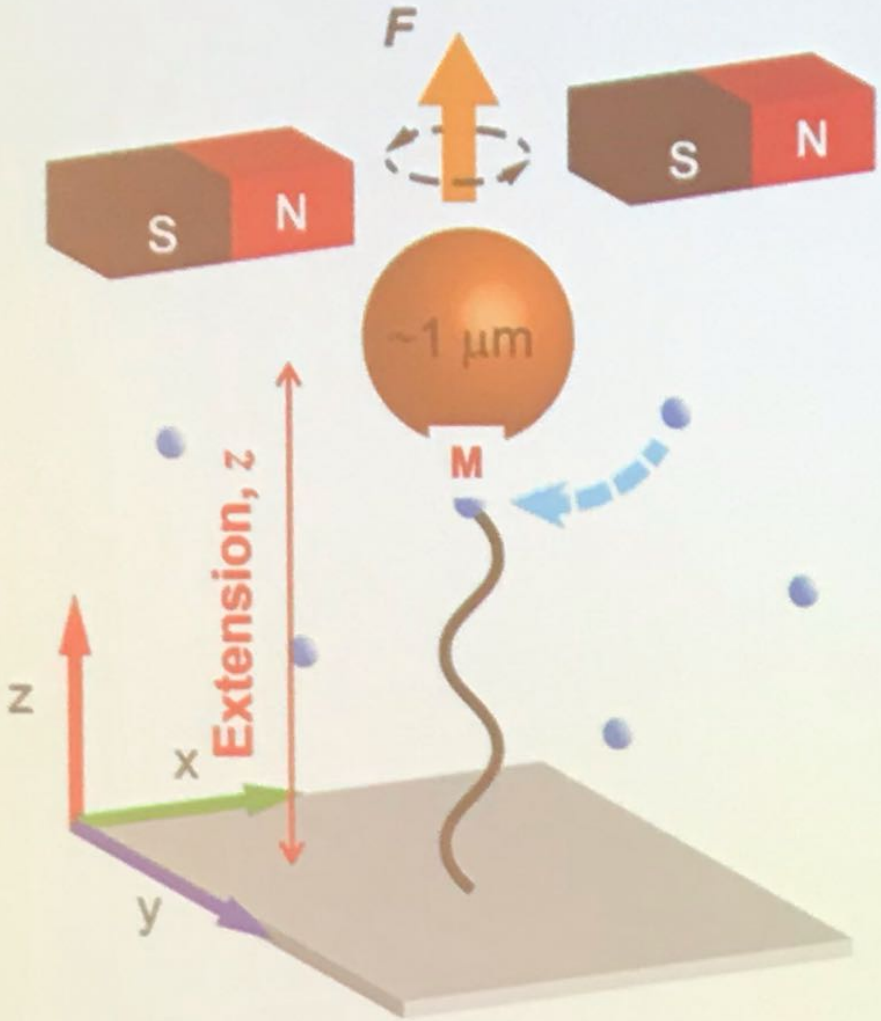
K. Kubo

Surface tethering



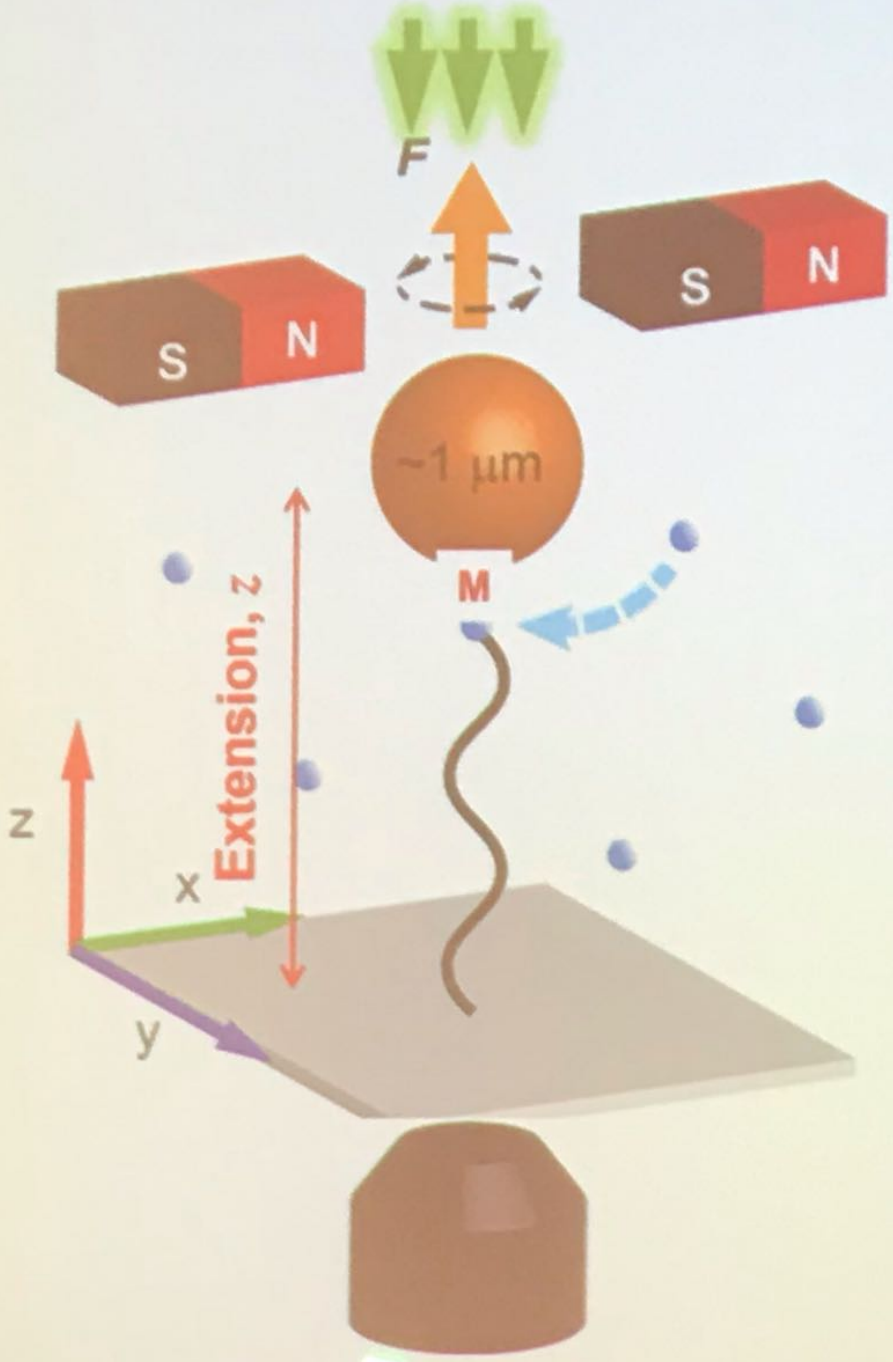
G. Coates

Magnetic Tweezers



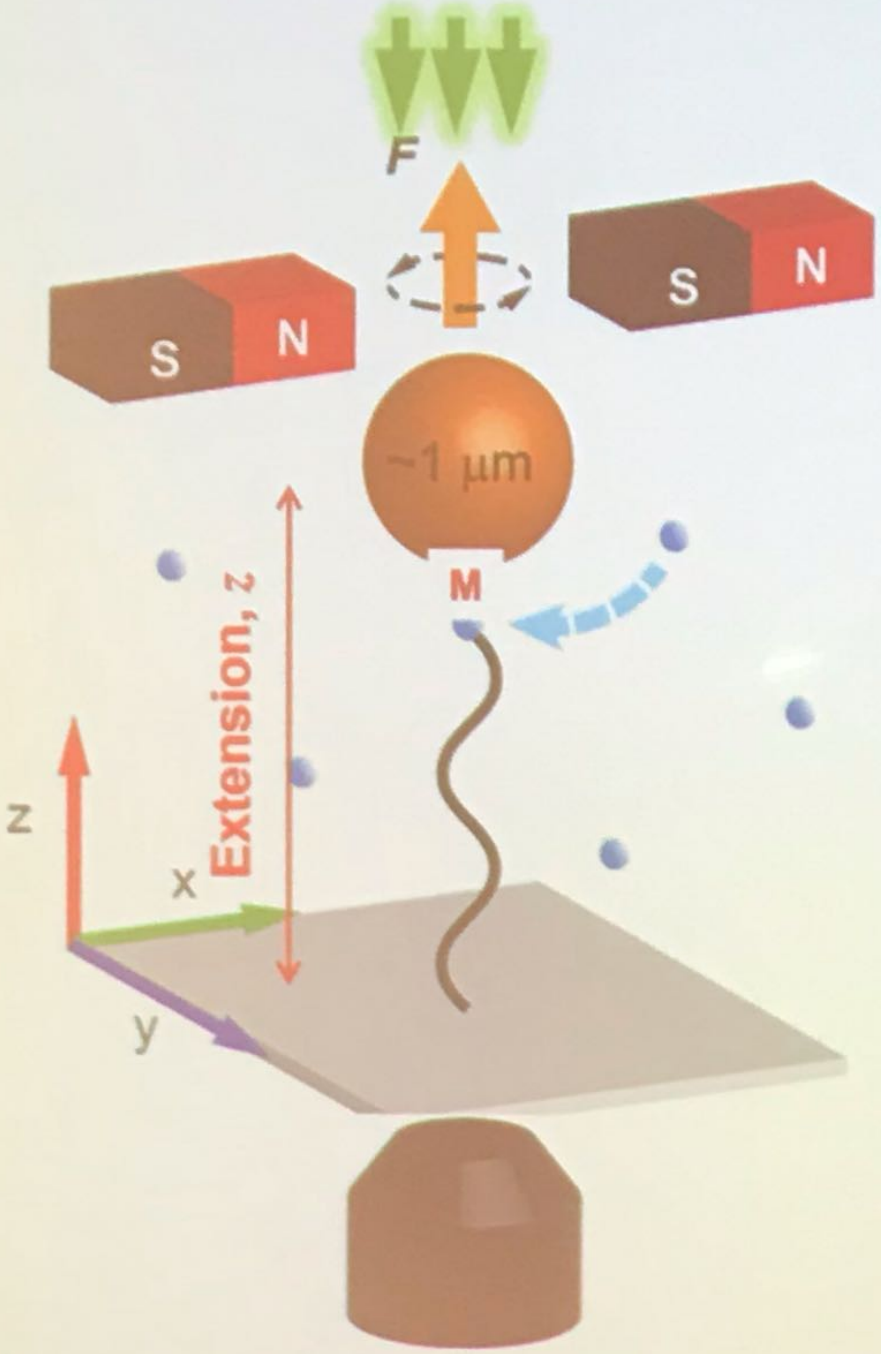
Liu, Kubo, Wang, Han, Yang, Chen,
Escobedo, Coates, P.C., *Science* **2017**, *358*, 352.

Magnetic Tweezers

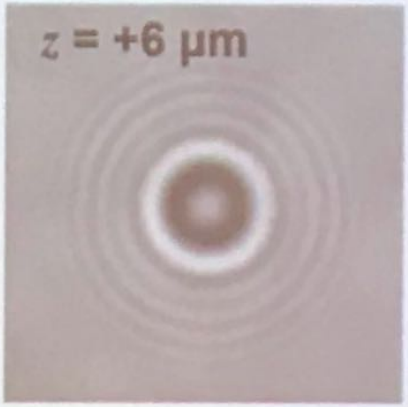


Liu, Kubo, Wang, Han, Yang, Chen, Escobedo, Coates, P.C., *Science* **2017**, *358*, 352.

Magnetic Tweezers



Transmission image
at different z



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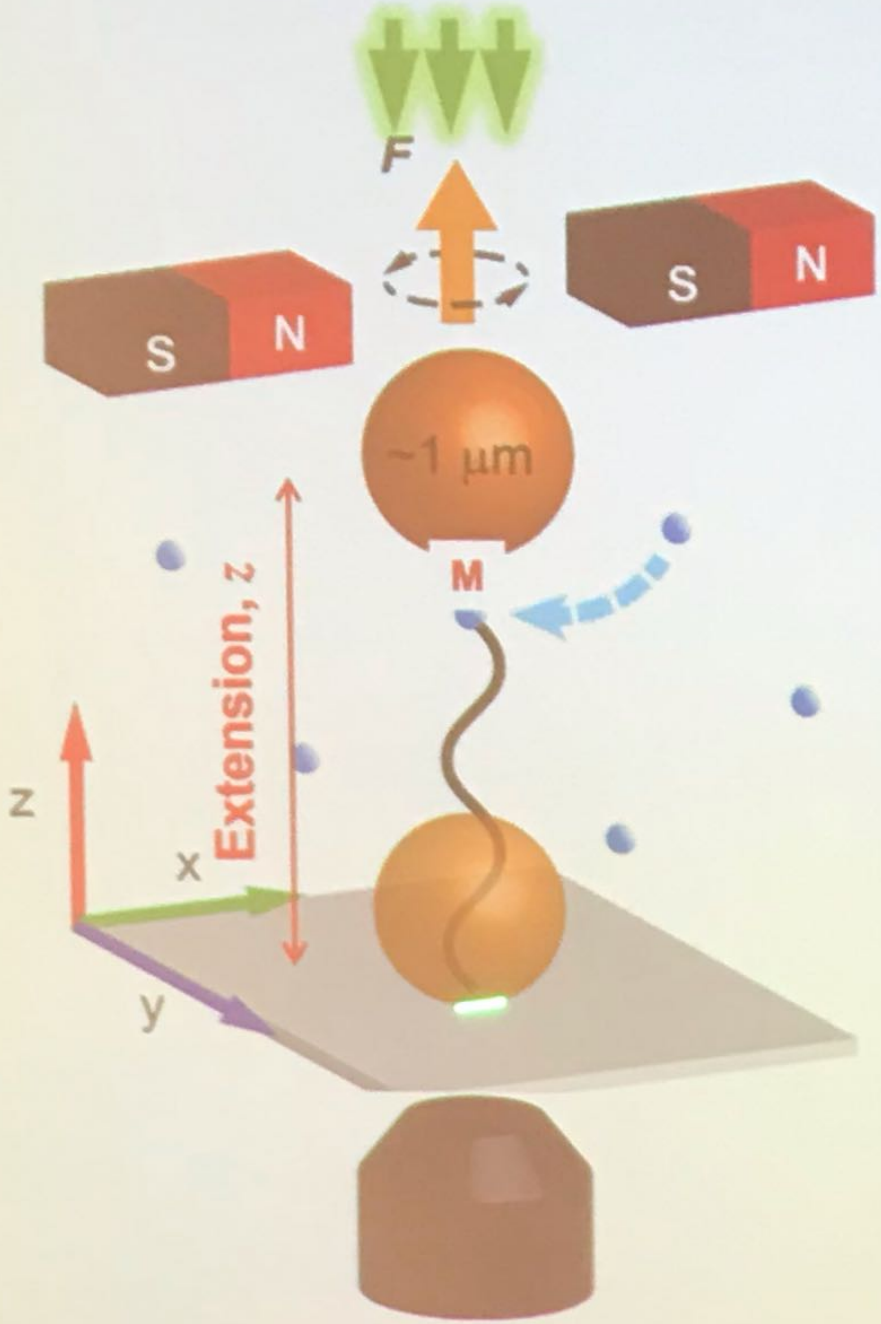
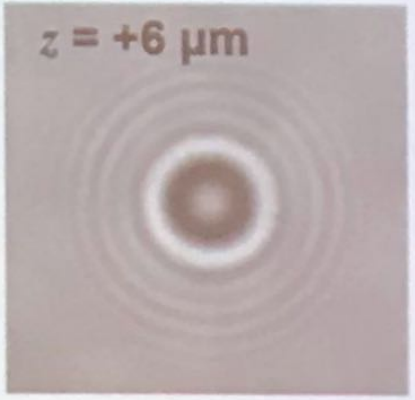
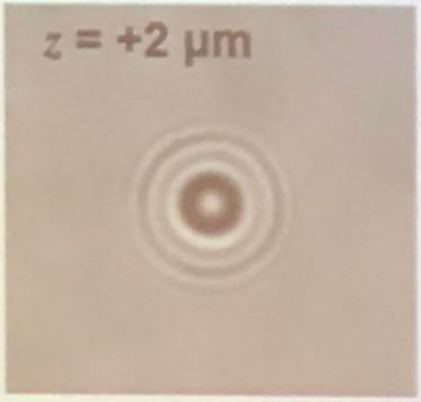
Escobedo, Coates, P.C., *Science* **2017**, *358*, 352.

Magnetic Tweezers



Transmission image at different z

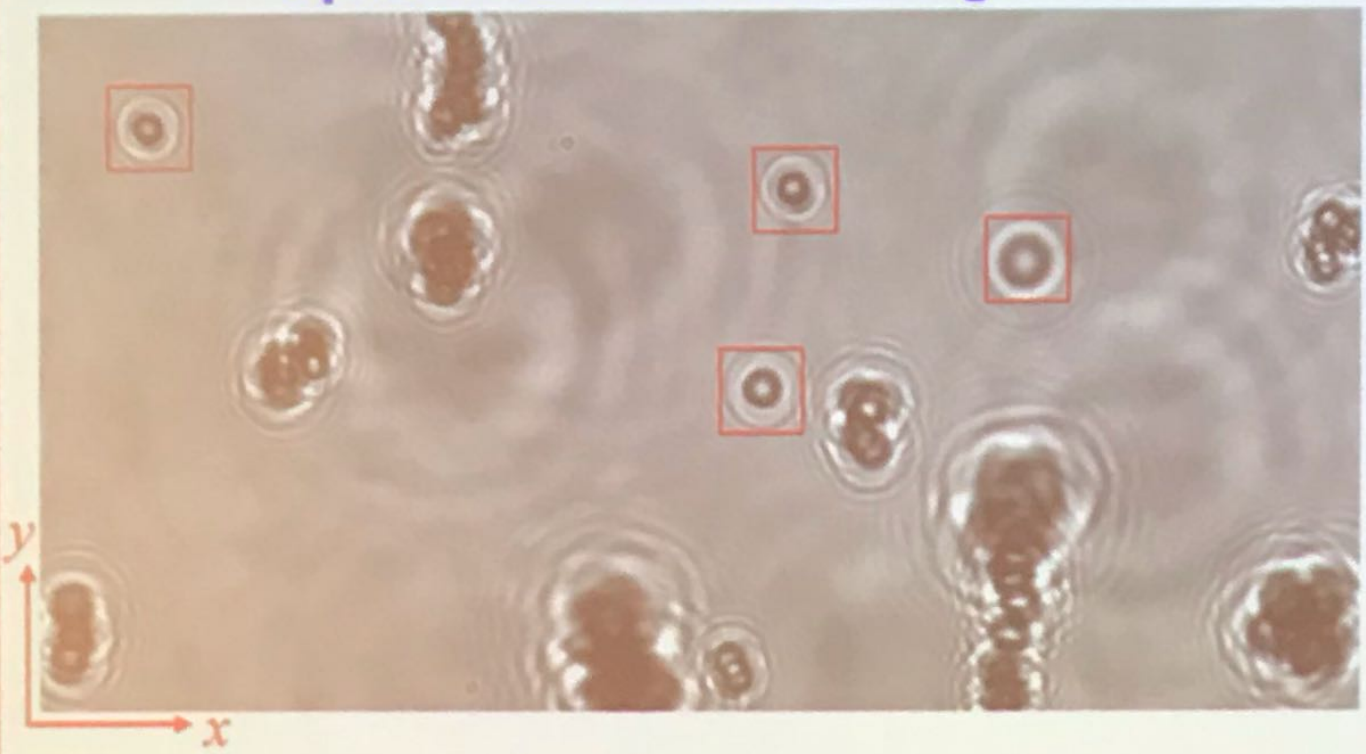




Liu, Kubo, Wang, Han, Yang, Chen, Escobedo, Coates, P.C., *Science* **2017**, *358*, 352.

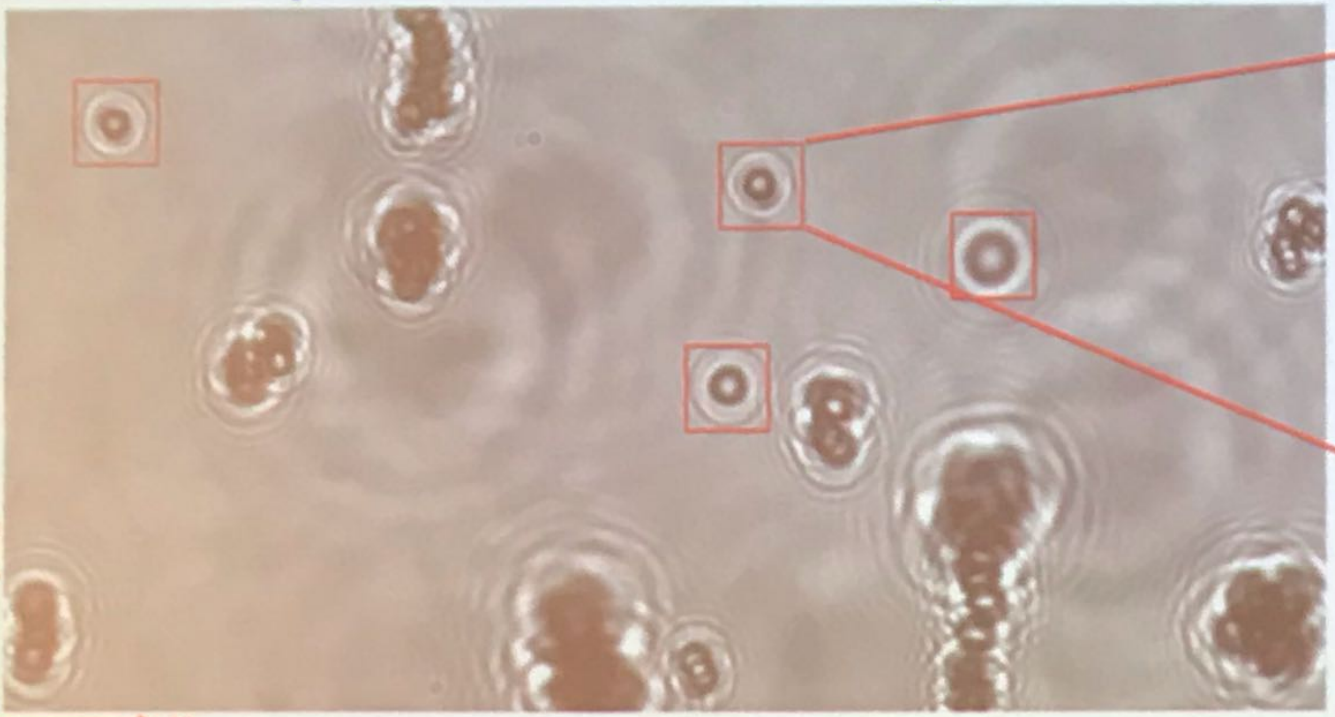
Real-time movie of single polymer growth

Optical transmission image

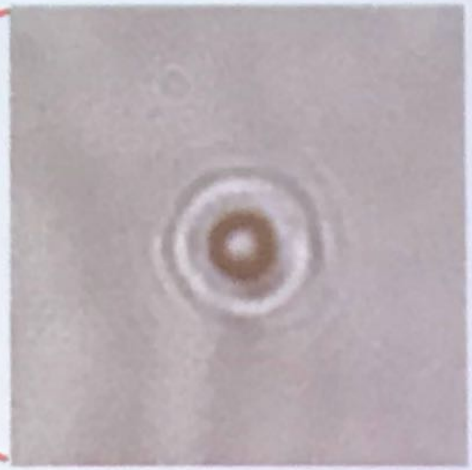


Real-time movie of single polymer growth

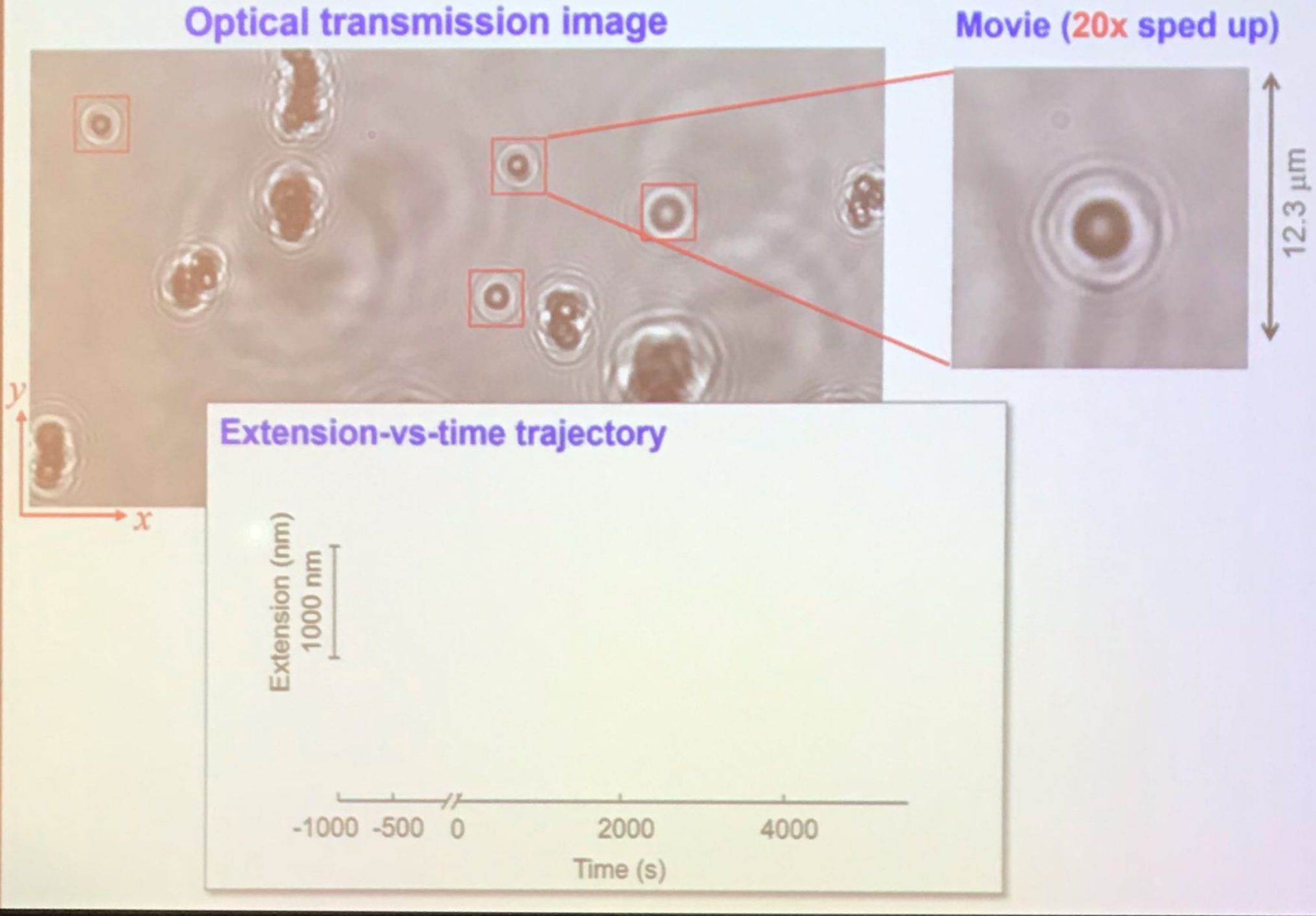
Optical transmission image



Movie (20x sped up)

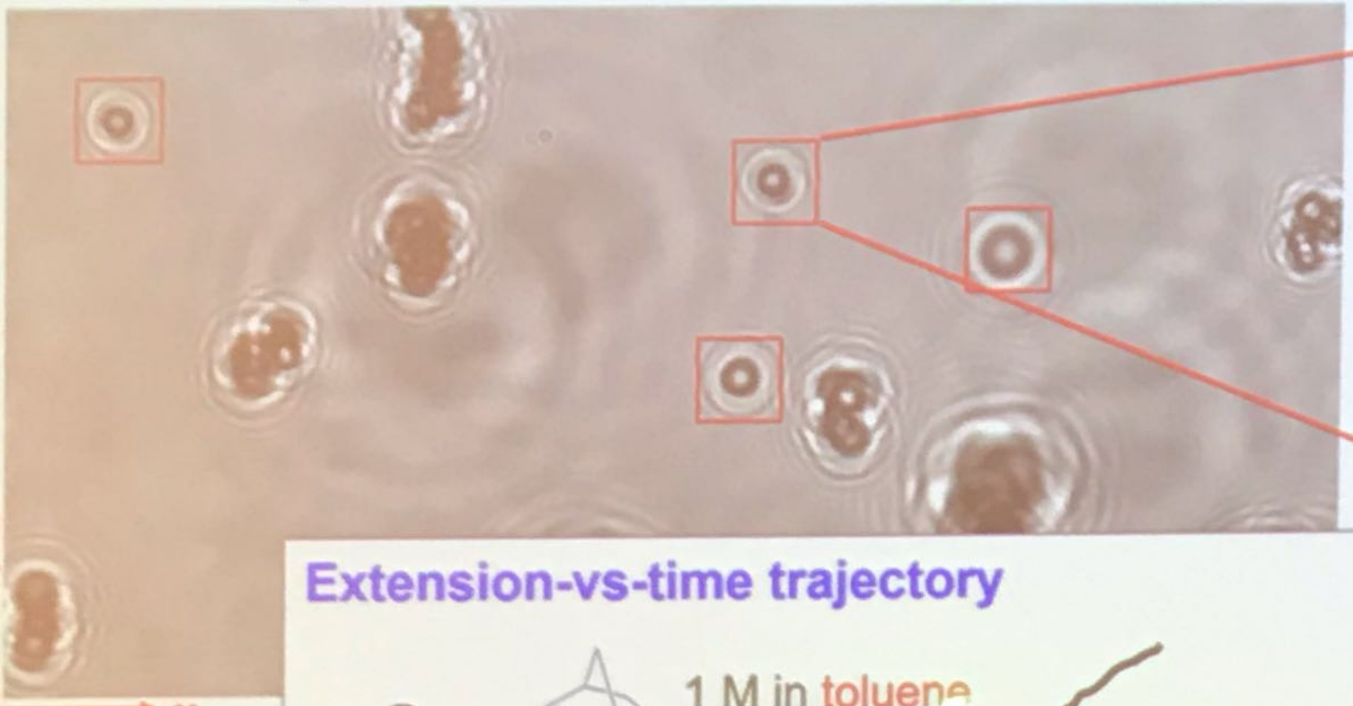


Real-time movie of single polymer growth

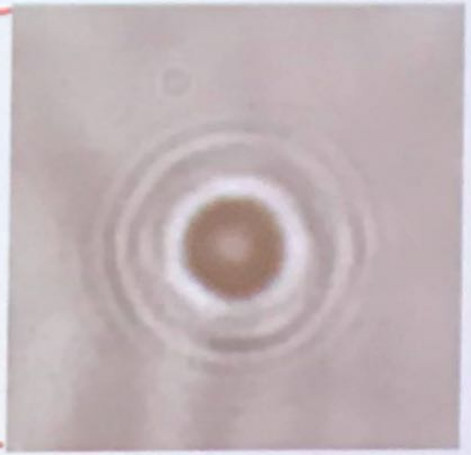


Real-time movie of single polymer growth

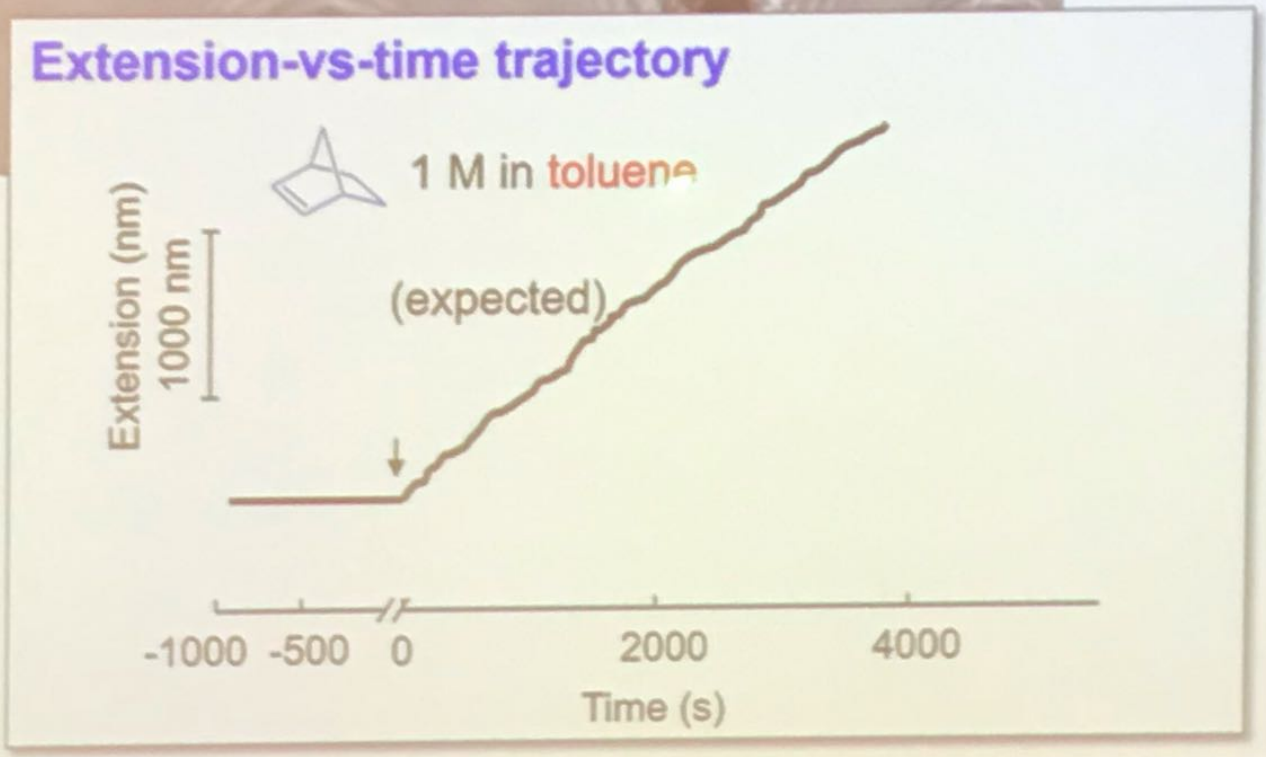
Optical transmission image



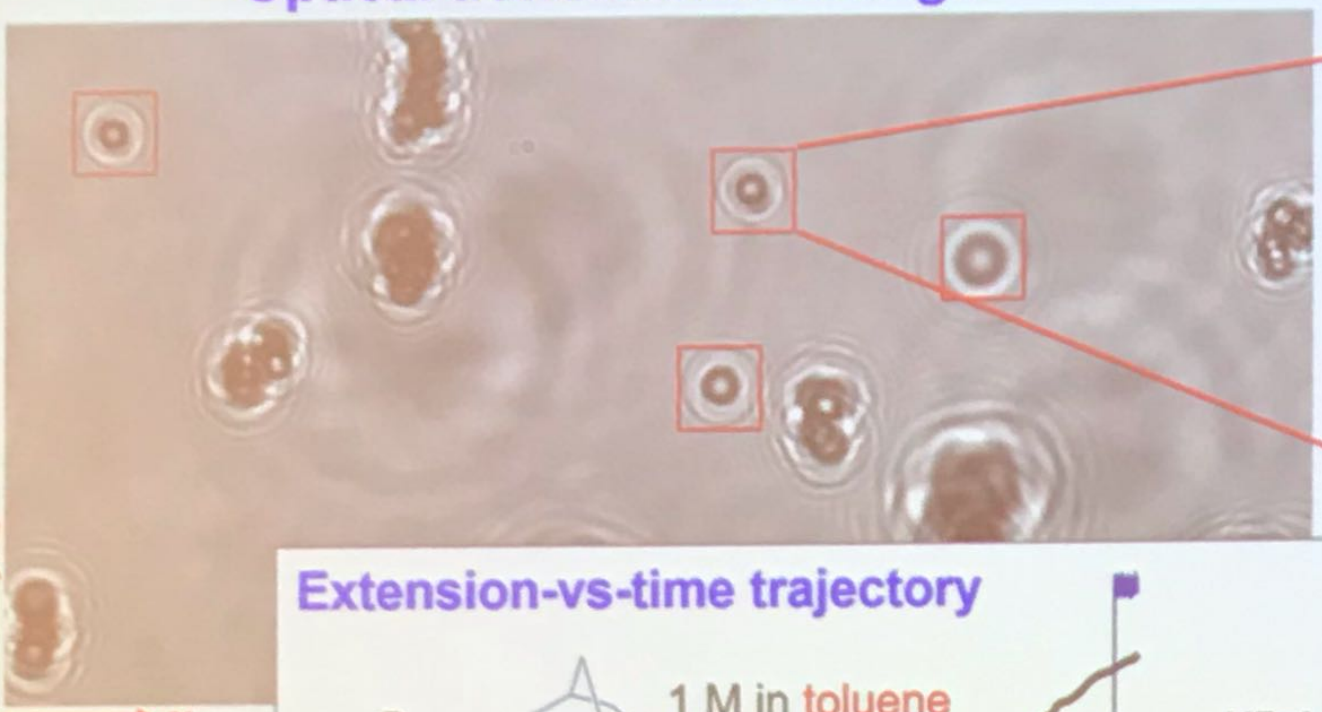
Movie (20x sped up)

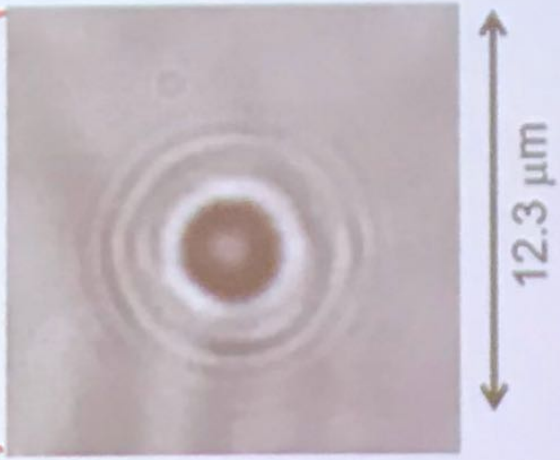


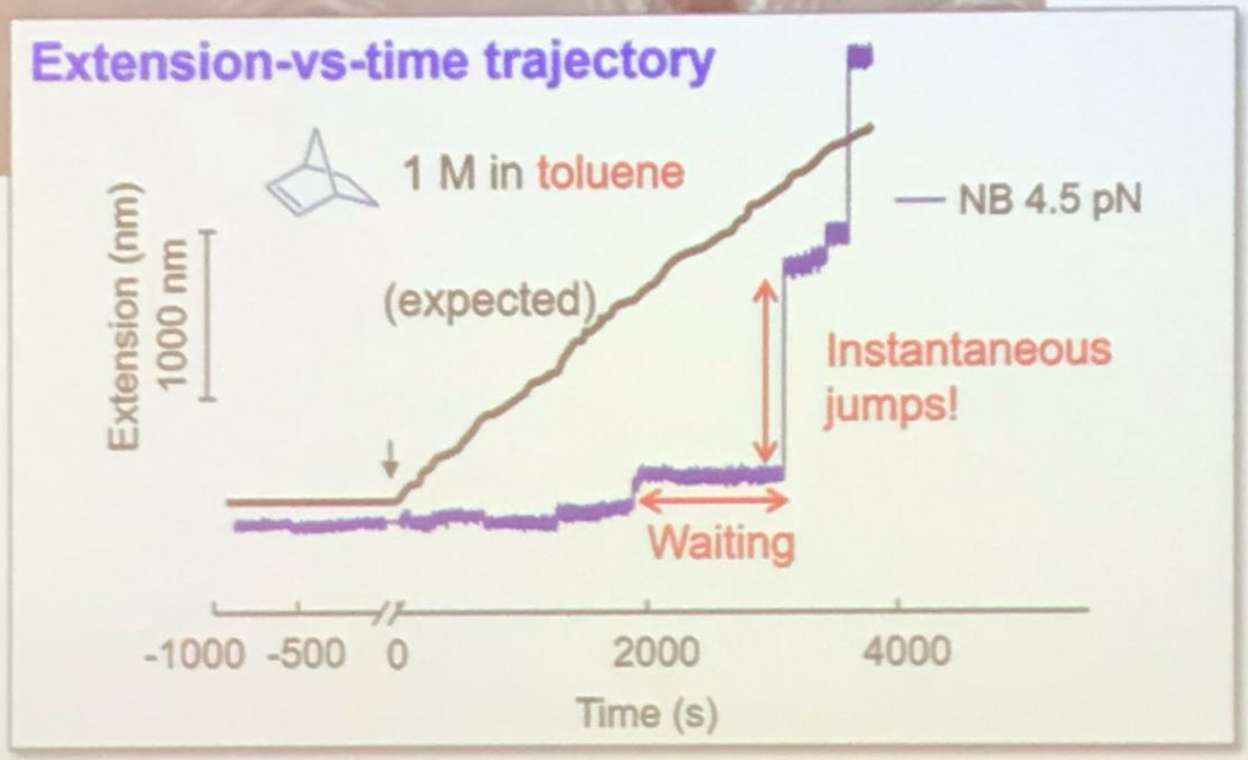
Extension-vs-time trajectory



Real-time movie of single polymer growth



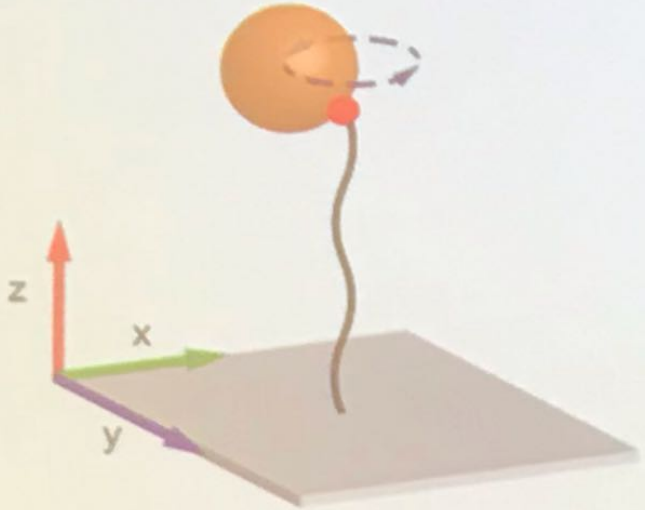


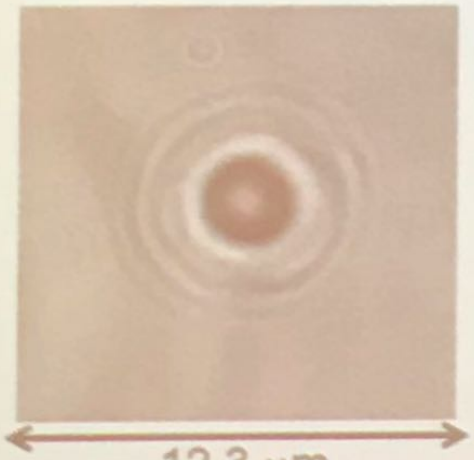


⇒ Single polymer?

How do we know it is a single polymer?

Rotational manipulation





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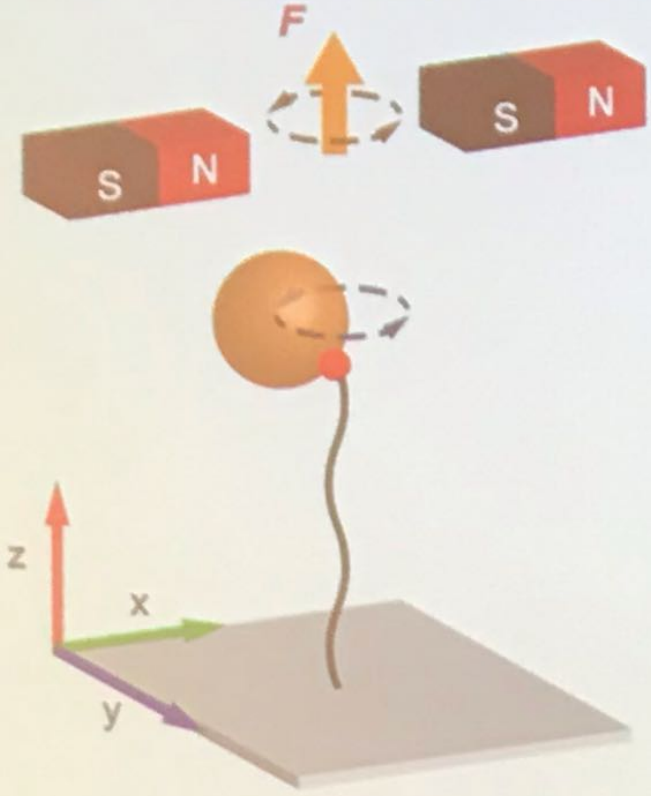
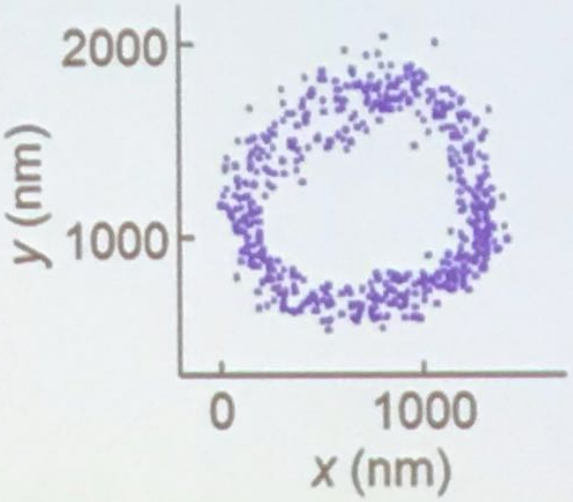
Rotational manipulation



Single-tether: circular procession



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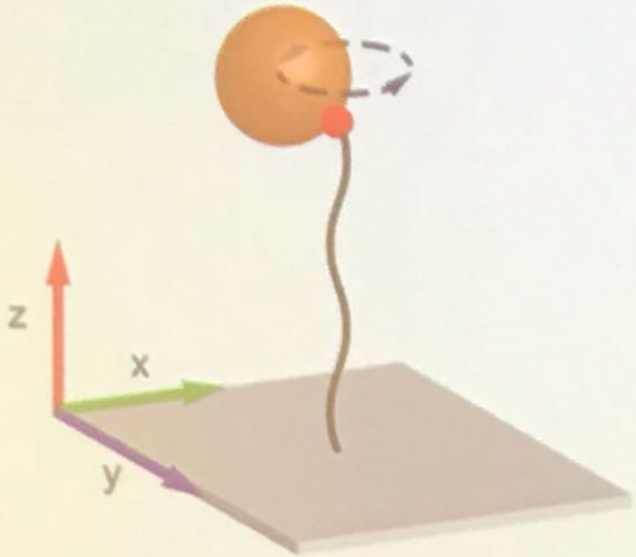
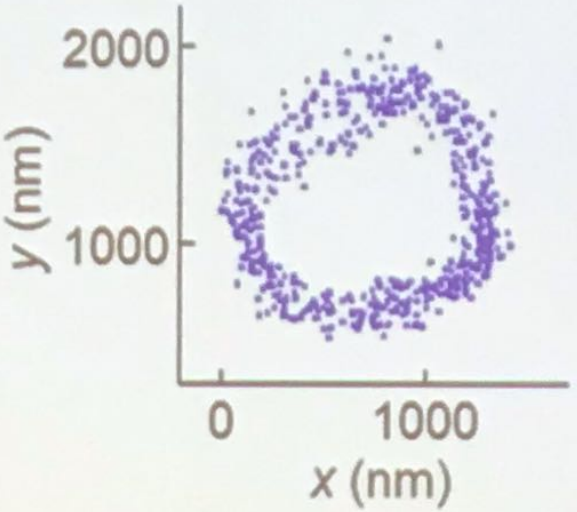
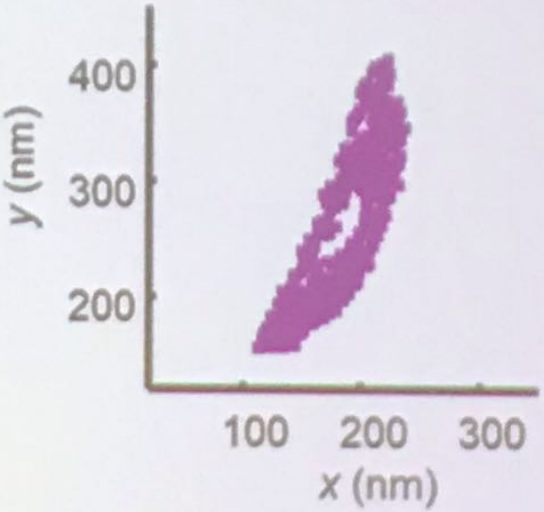


Single-tether: circular procession

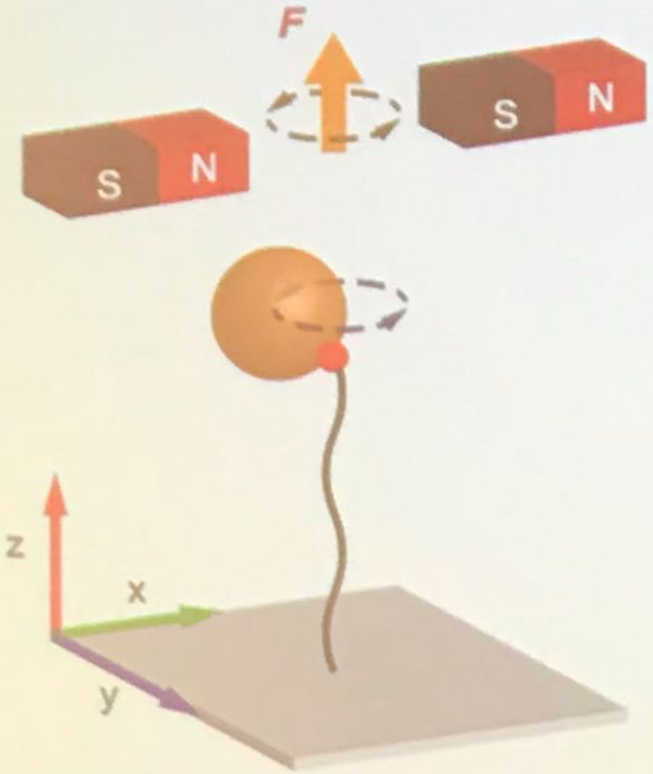


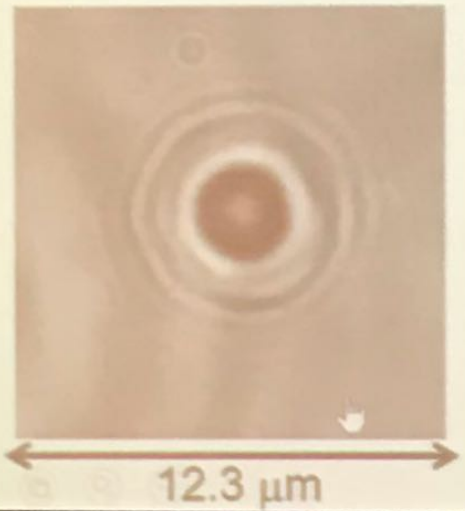
Multi-tether: irregular



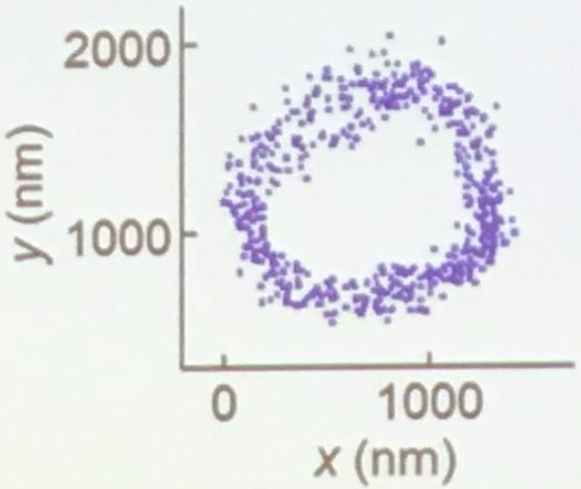
How do we know it is a single polymer?

Rotational manipulation

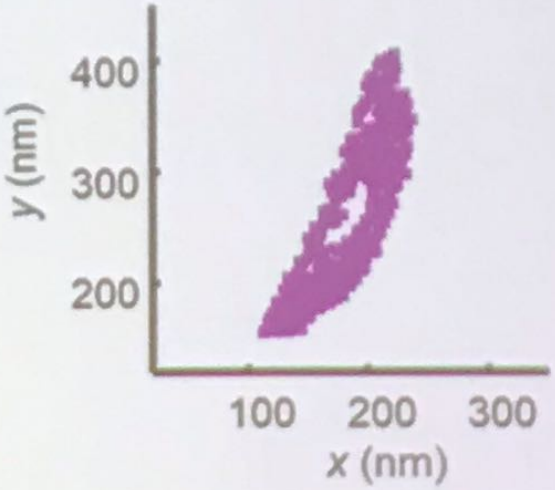




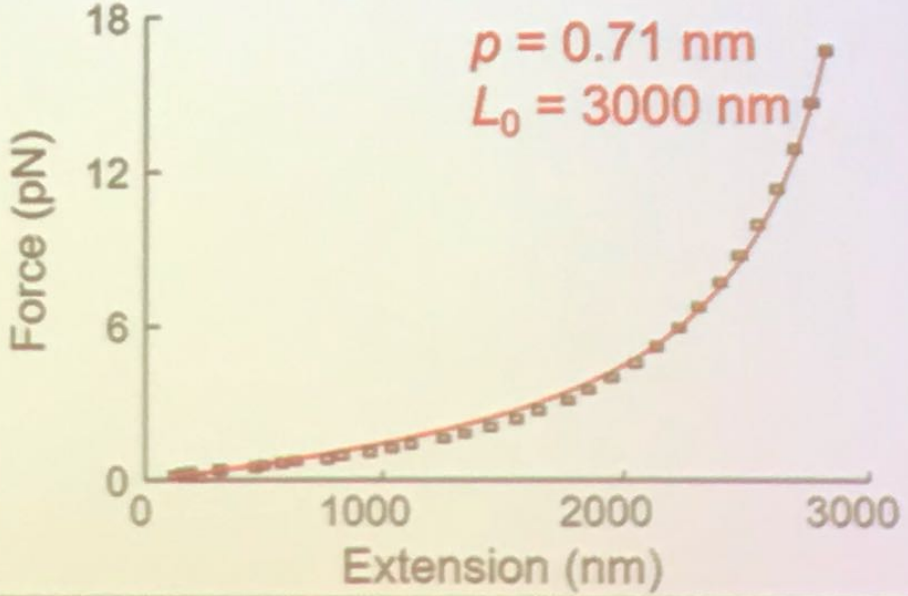
Single-tether: circular procession



Multi-tether: irregular

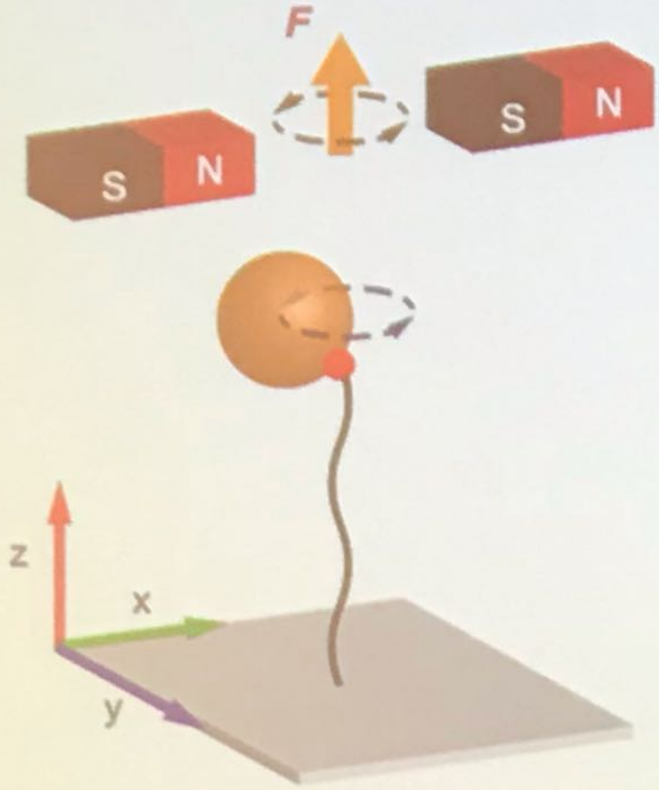


Force-extension afterward = WLC

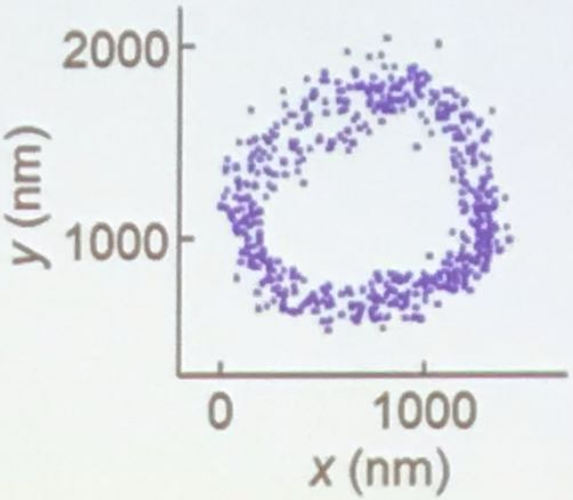


How do we know it is a single polymer?

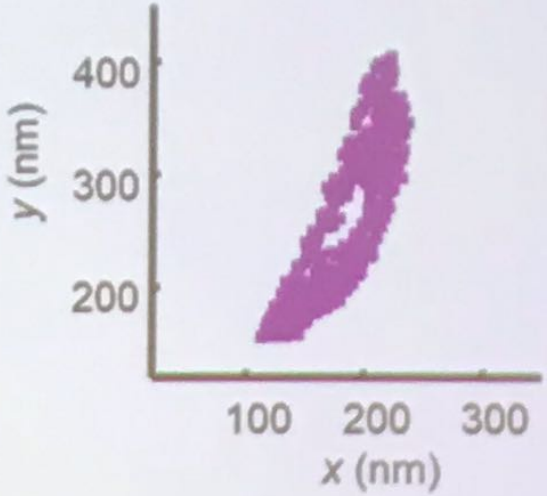
Rotational manipulation



Single-tether: circular procession



Multi-tether: irregular



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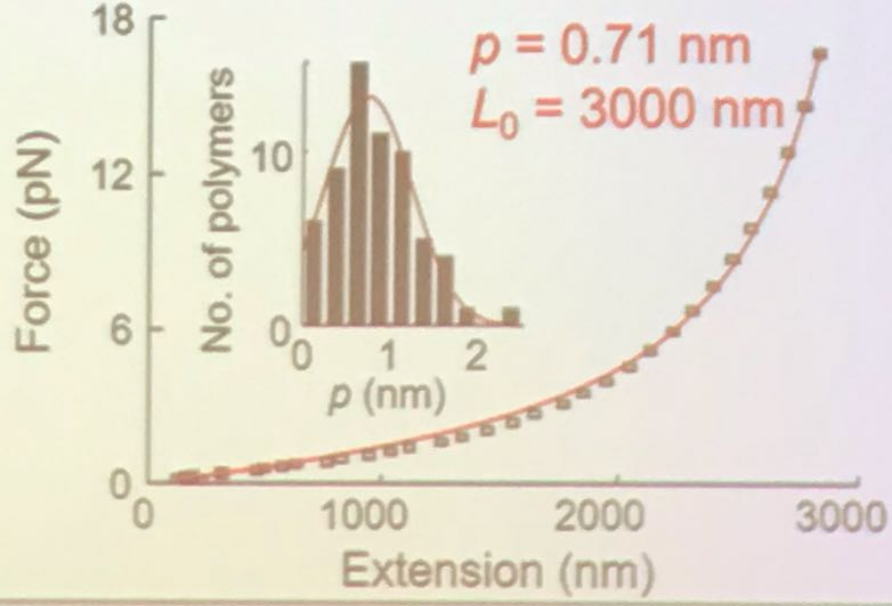
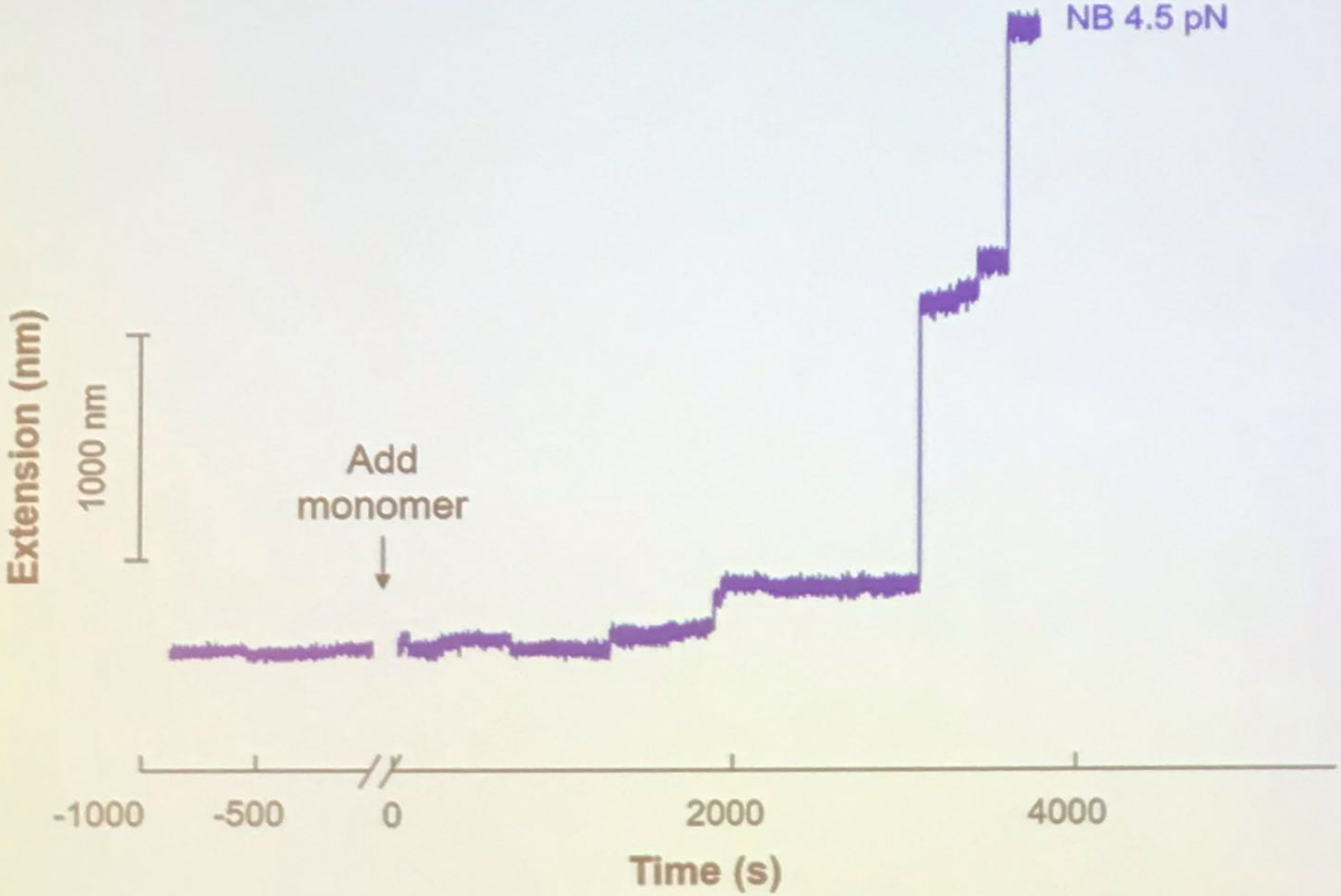
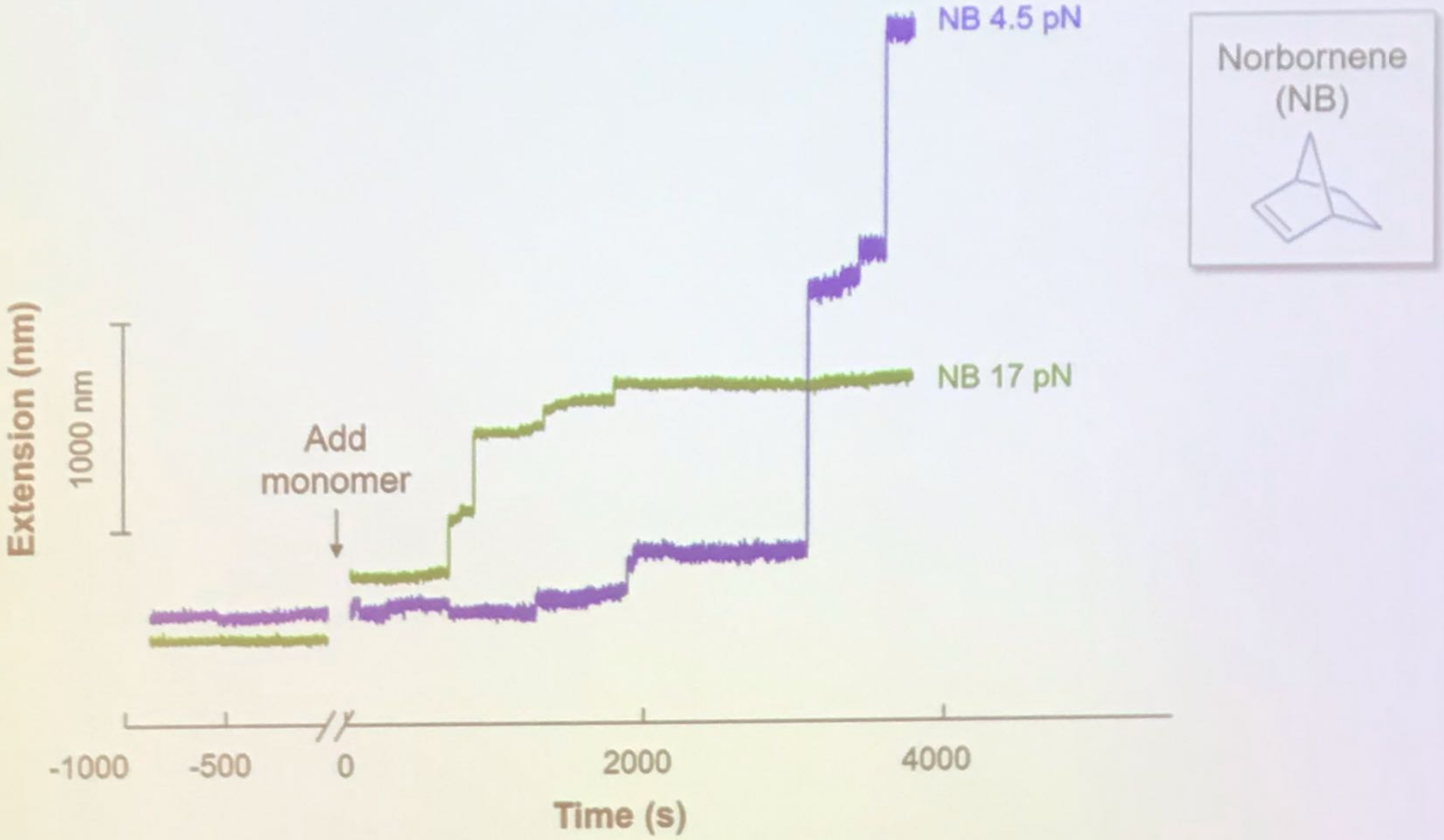


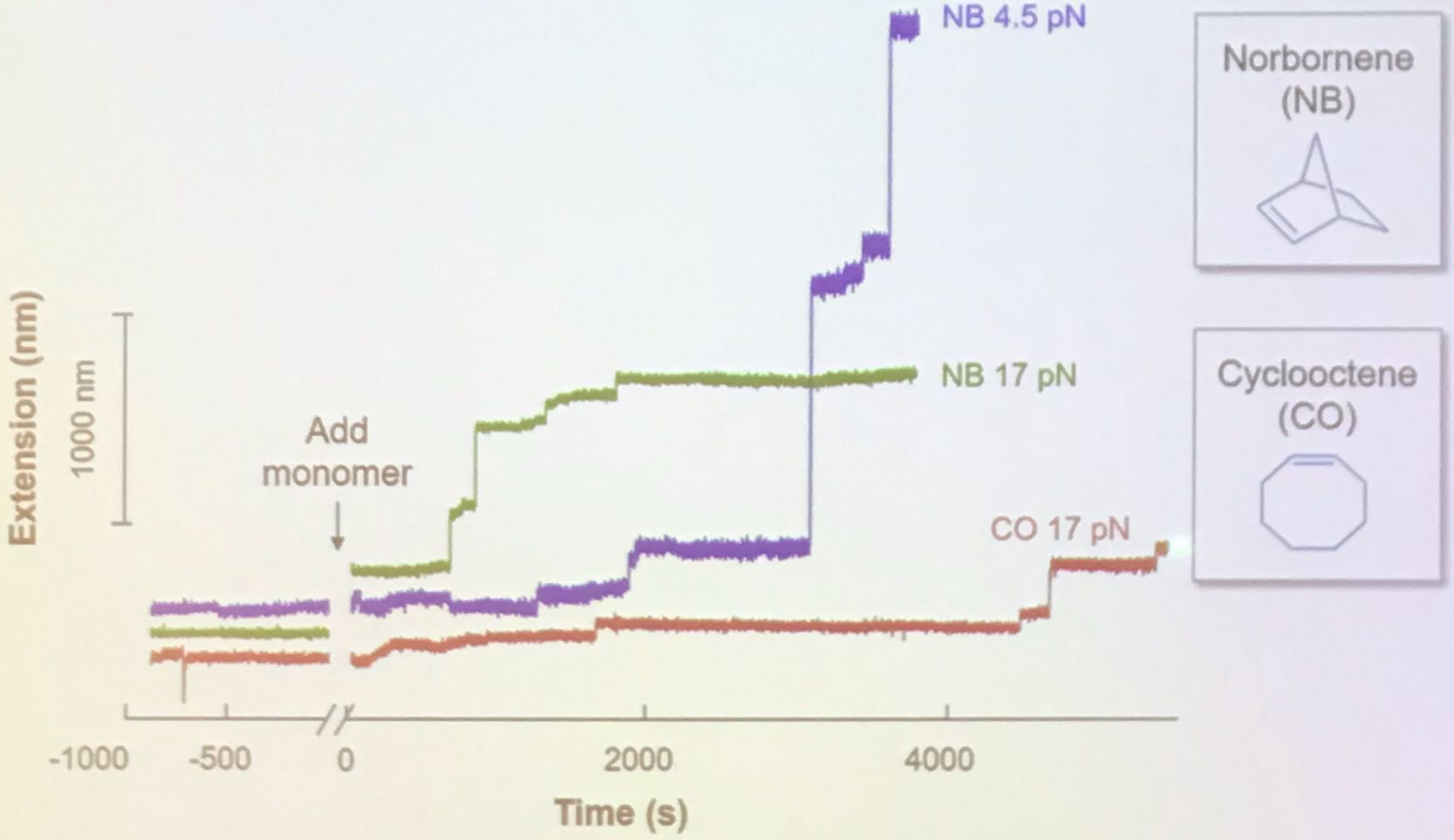
Real-time extension trajectory of single polymer growth



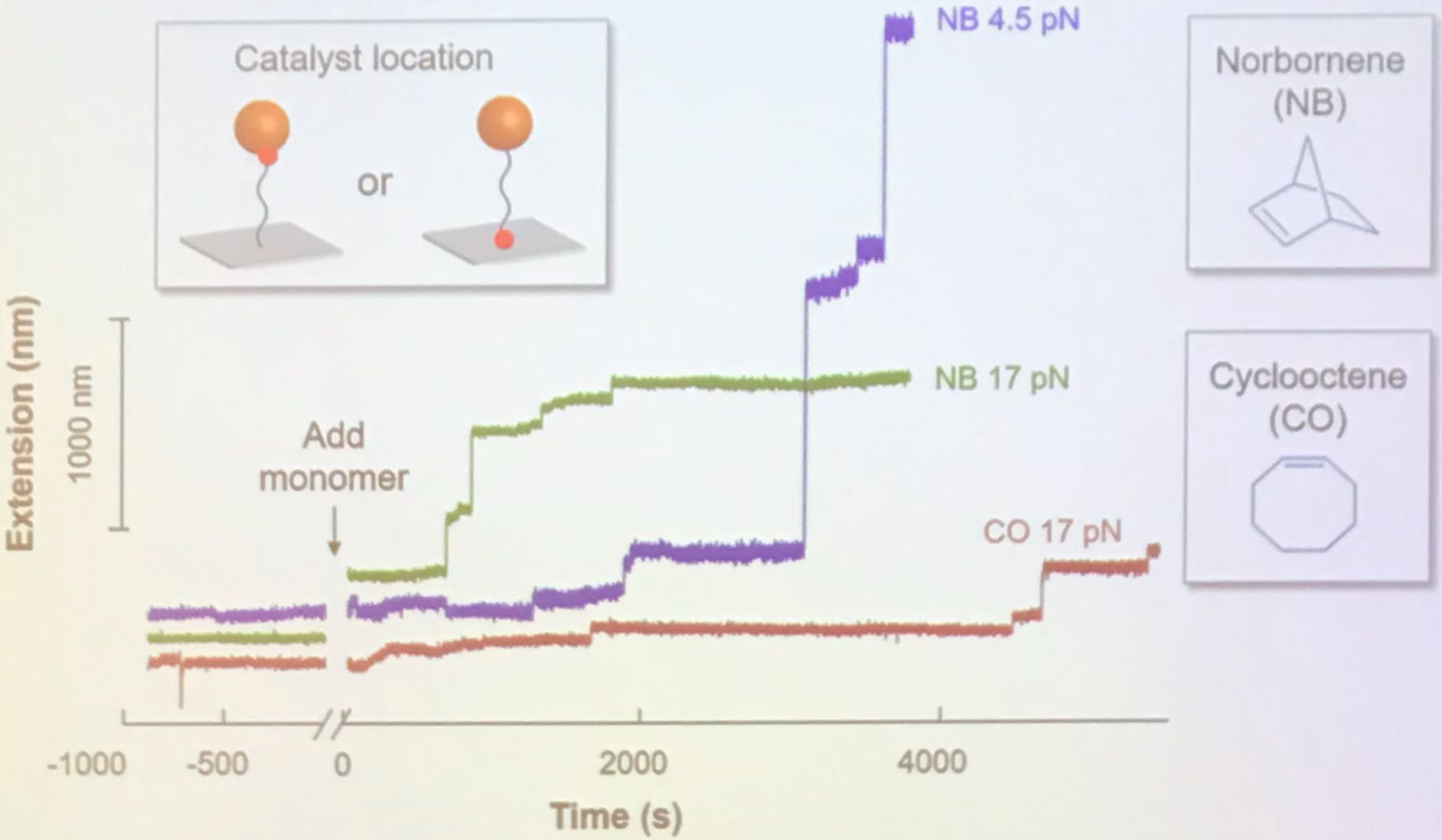
Real-time extension trajectory of single polymer growth



Real-time extension trajectory of single polymer growth



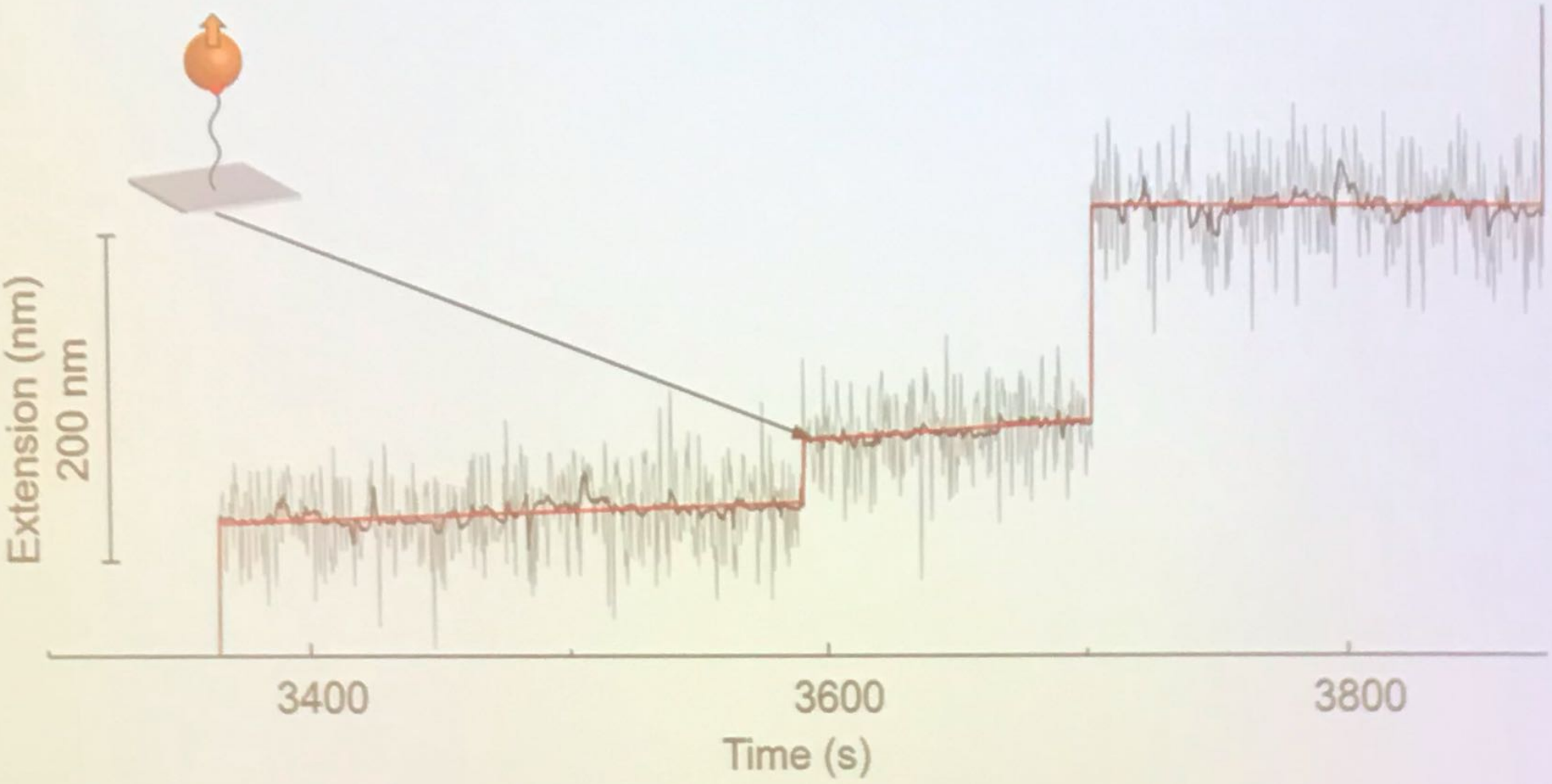
Real-time extension trajectory of single polymer growth



- **Waiting periods:** ~10^2 s
- **Jumps (instantaneous):** 10^2-10^3 nm = 10^2-10^3 monomers

⇒ **Too fast for polymer growth! What & how?**

Hypothesis: torsional strain from living polymerization → entanglements ("hairballs")



Science **2017**, *358*, 352.

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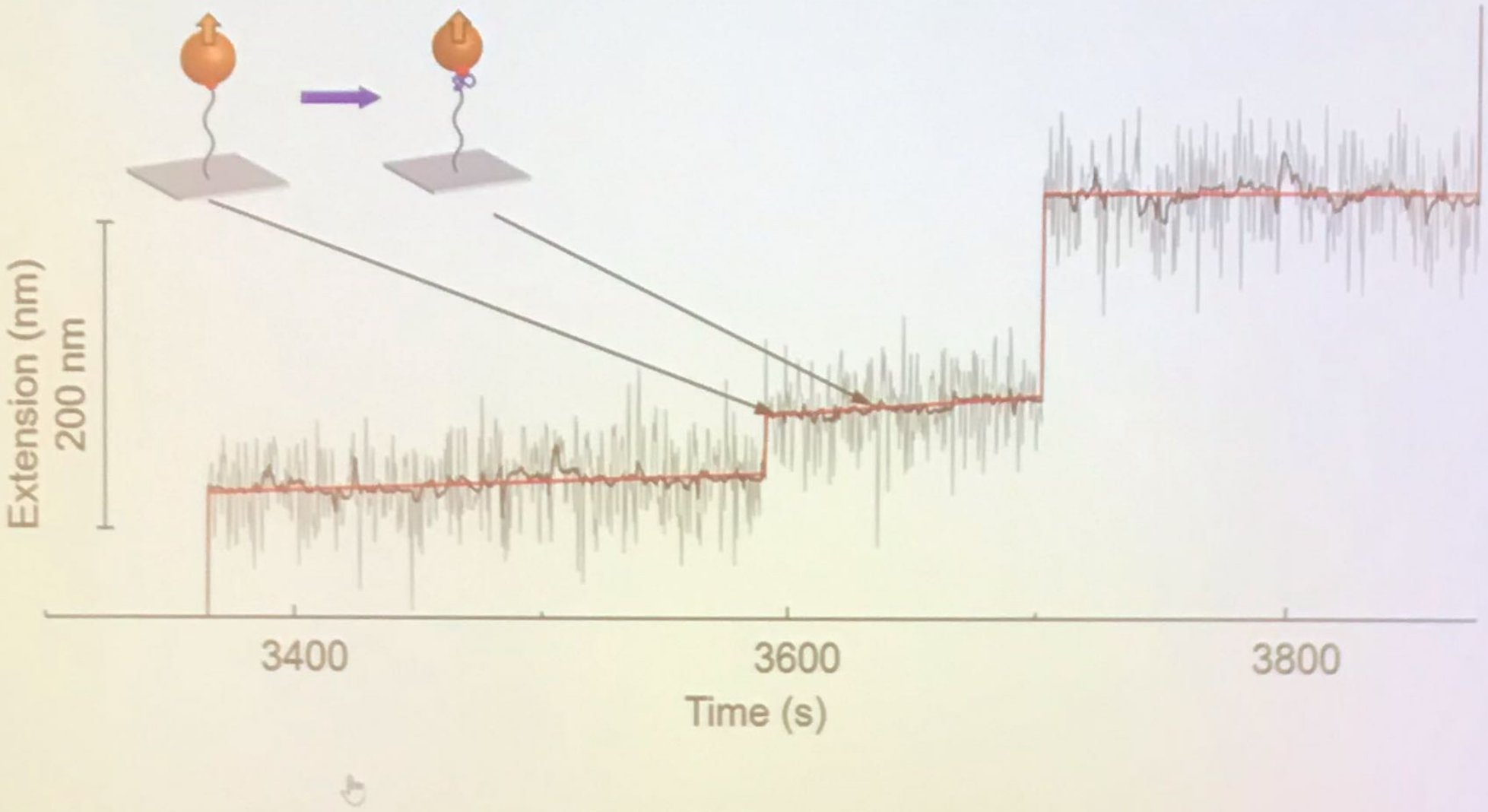

Science **2017**, *358*, 352.

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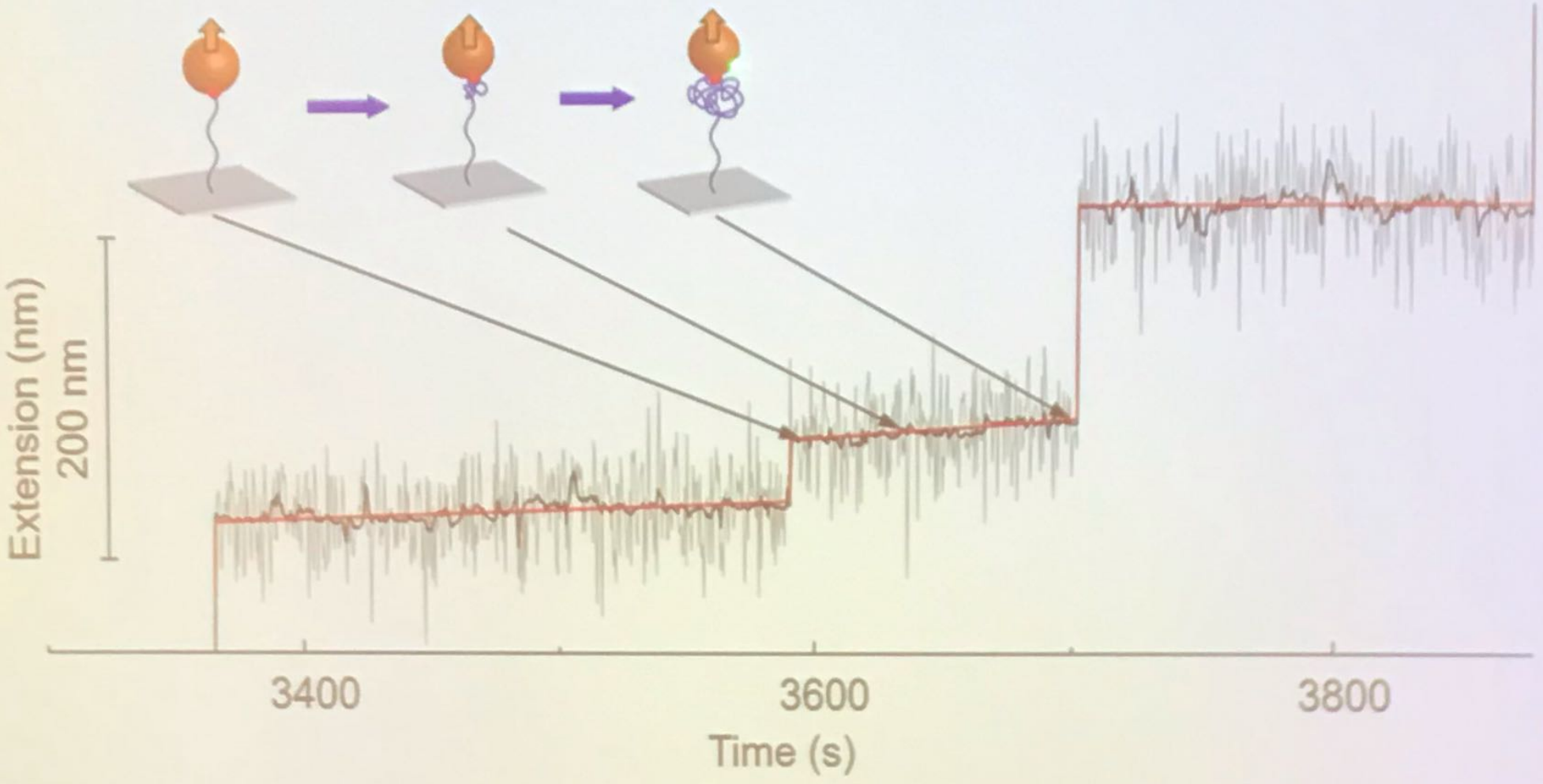

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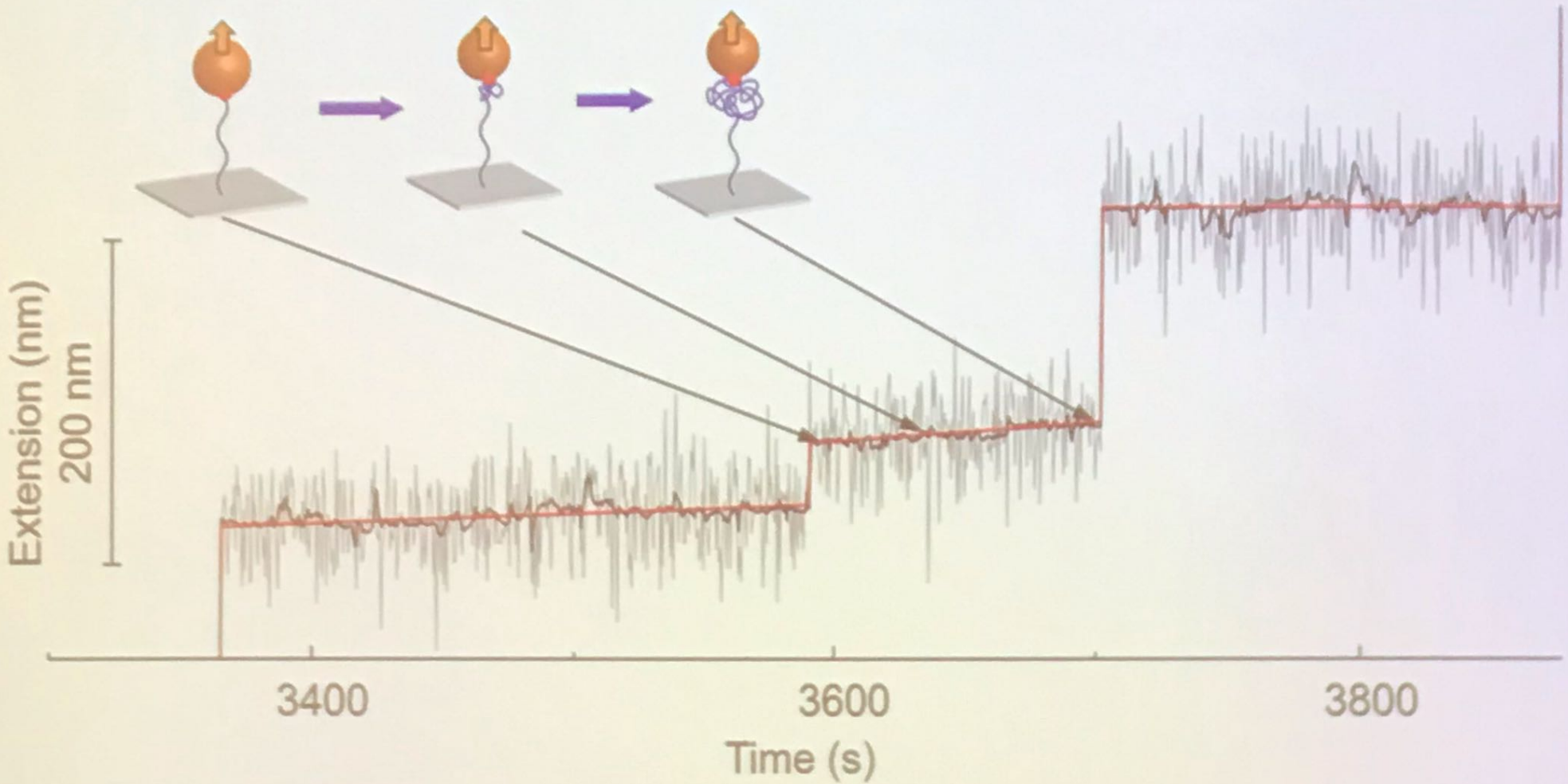

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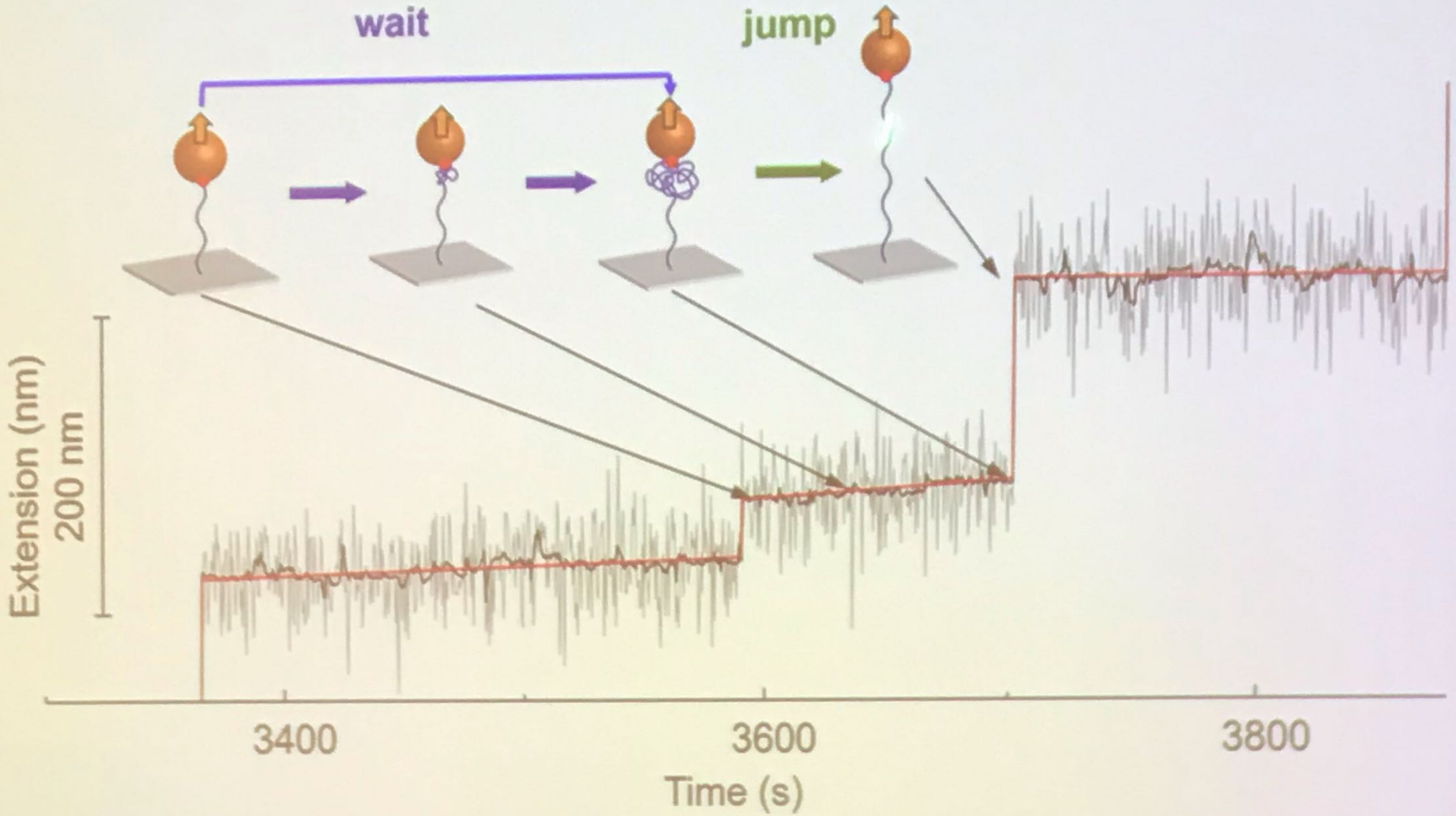

Science **2017**, *358*, 352.

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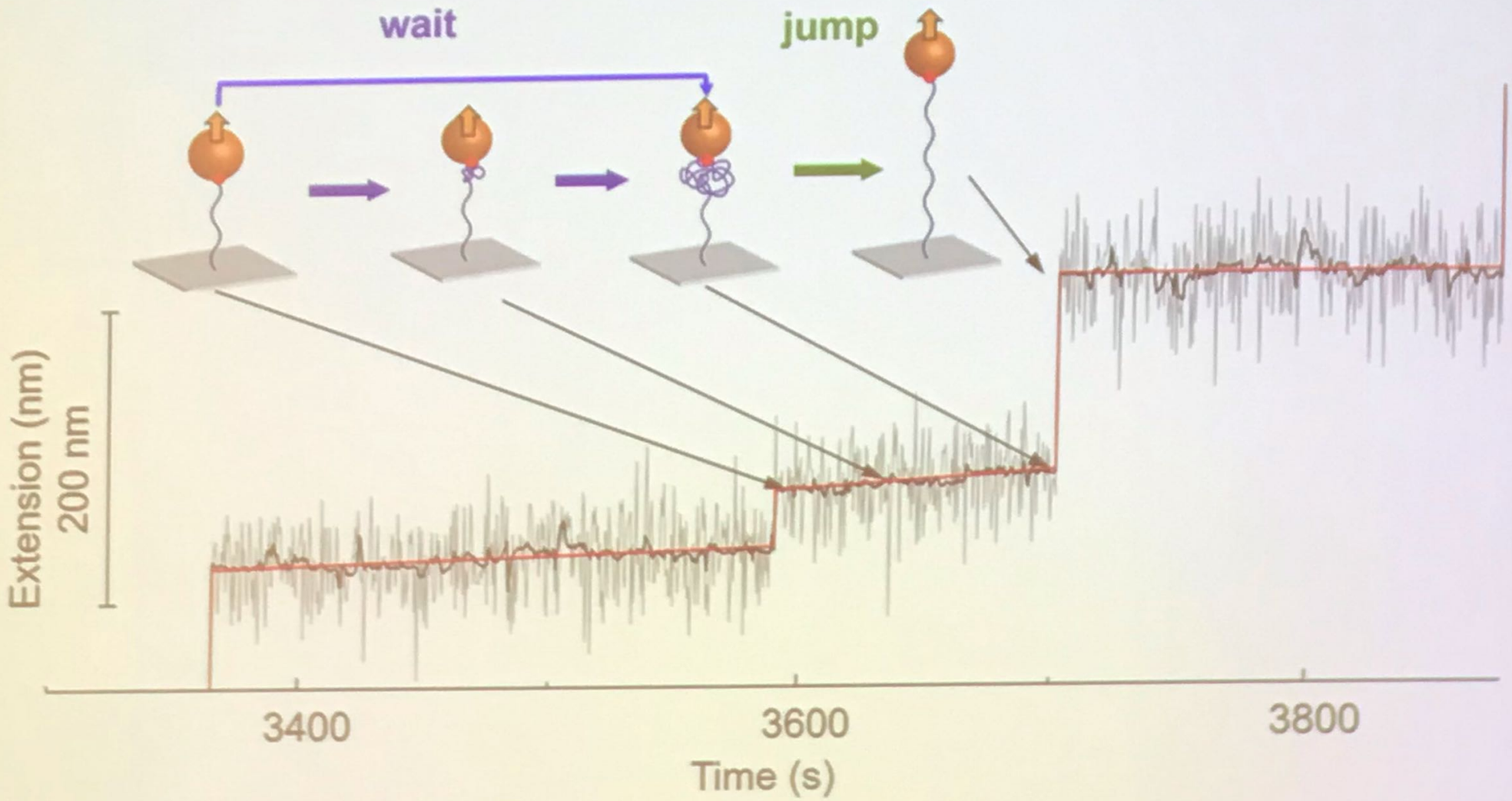

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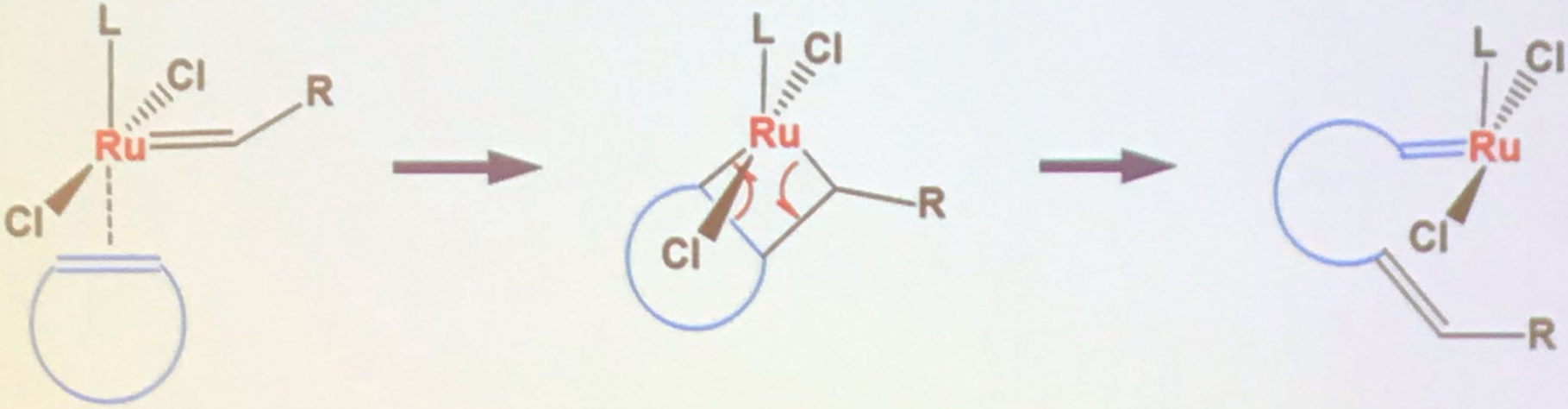
Torsional Strain → Entanglements (Hairball)

But, how could torsional strain be generated during polymerization?

Torsional strain generation during ROMP

(1) Ru=C bond rotation (Grubbs, Chen, et al.)



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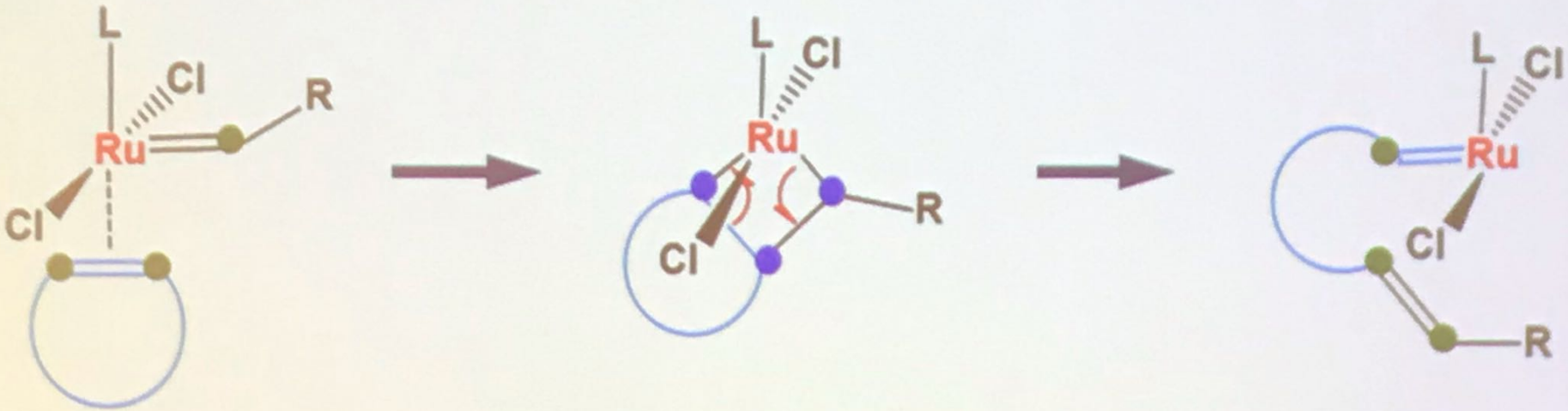


Dihedral strain

sp^2 carbon: ●

Preferred dihedral: 0°

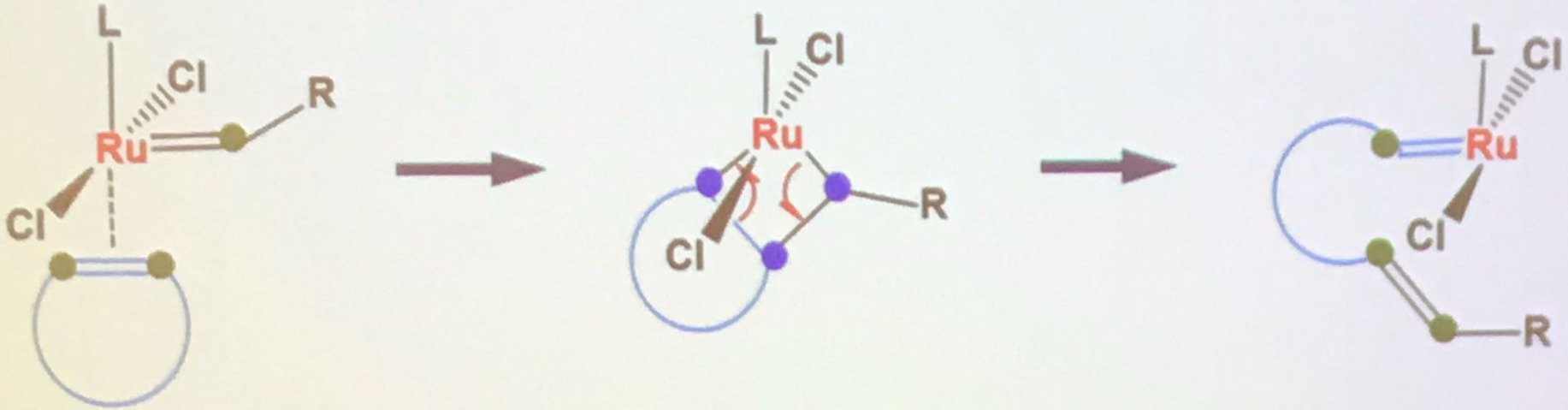
sp^3 carbon: ●

Preferred dihedral: 60°

(2) Changes in orbital hybridizations

Torsional strain generation during ROMP

(1) Ru=C bond rotation (Grubbs, Chen, et al.)



Dihedral strain

sp^2 carbon: ●

Preferred dihedral: 0°

sp^3 carbon: ●

Preferred dihedral: 60°

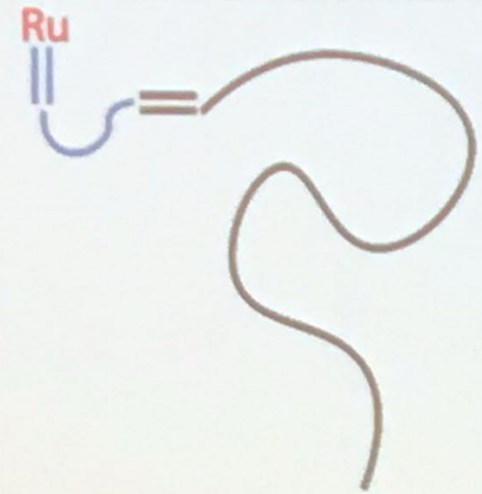
(2) Changes in orbital hybridizations

Model: Torsional strain induced conform. entanglement

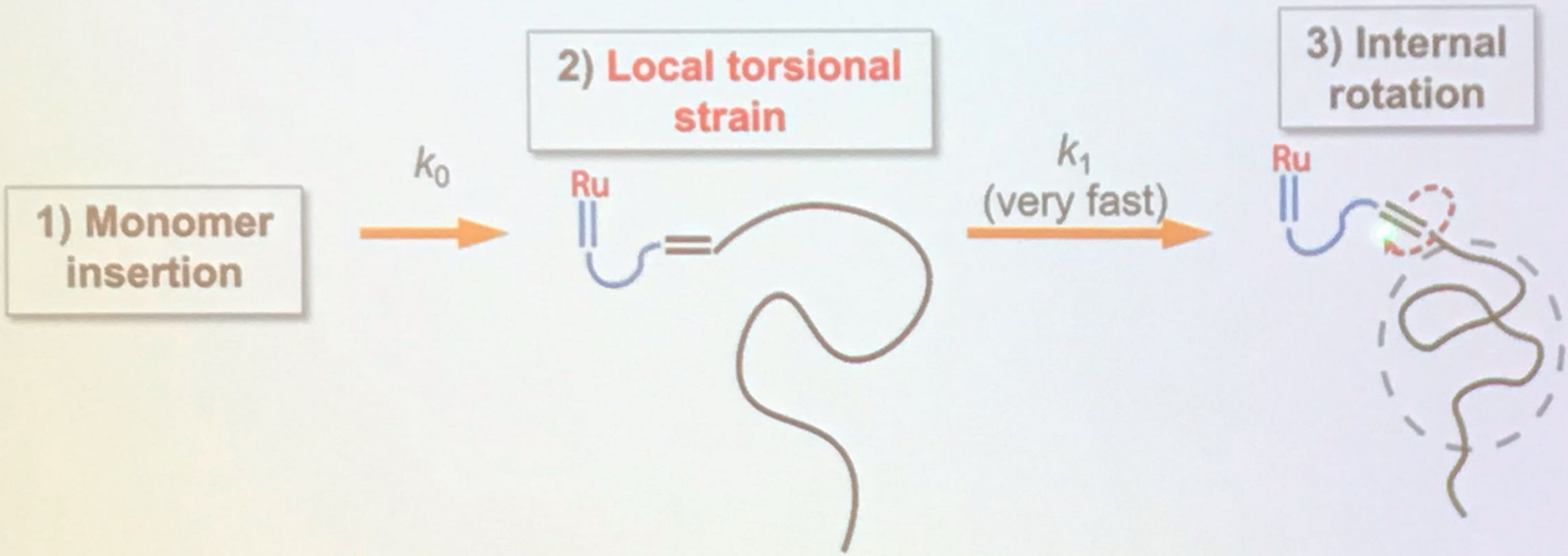
1) Monomer insertion

k_0

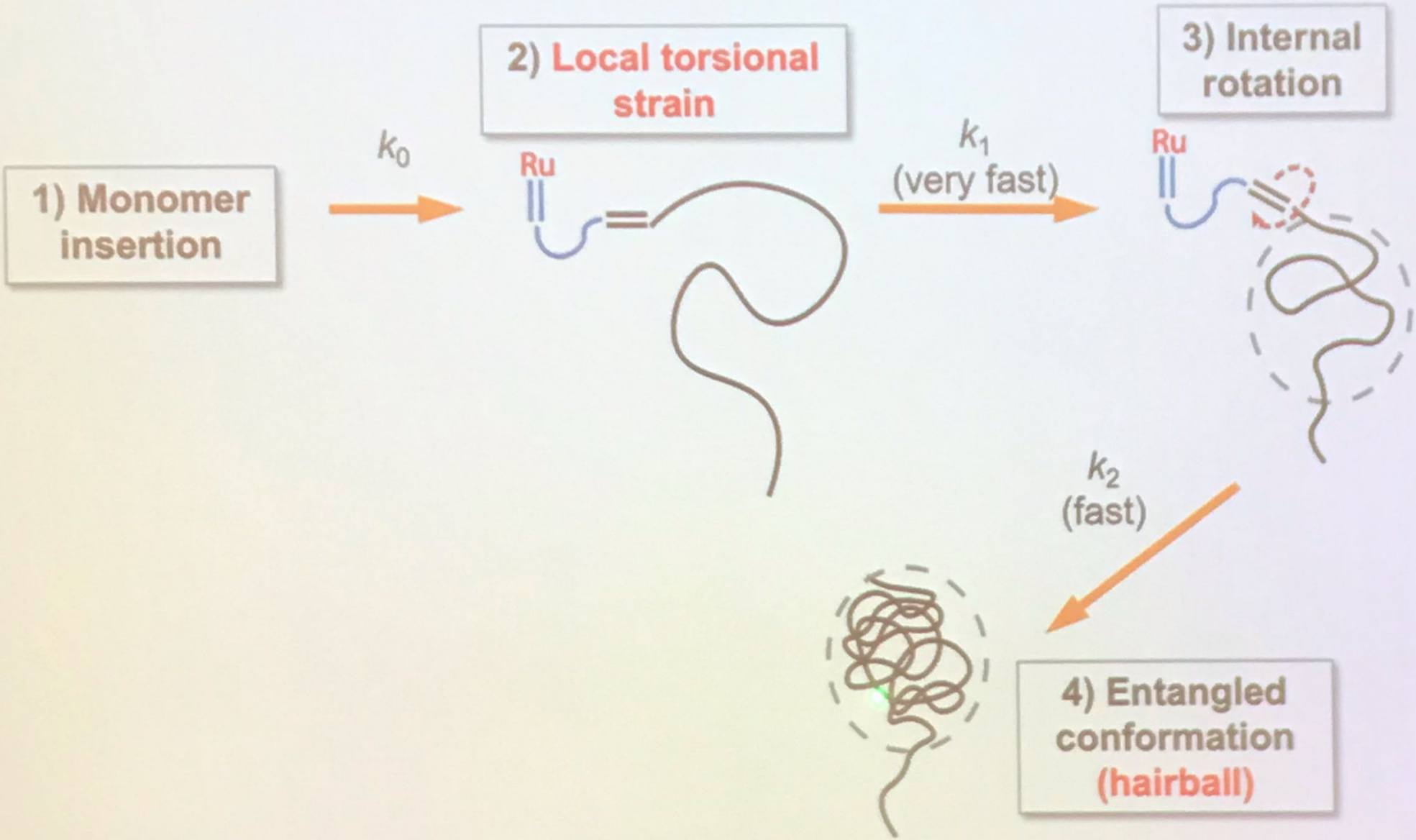
2) Local torsional strain



Model: Torsional strain induced conform. entanglement



Model: Torsional strain induced conform. entanglement



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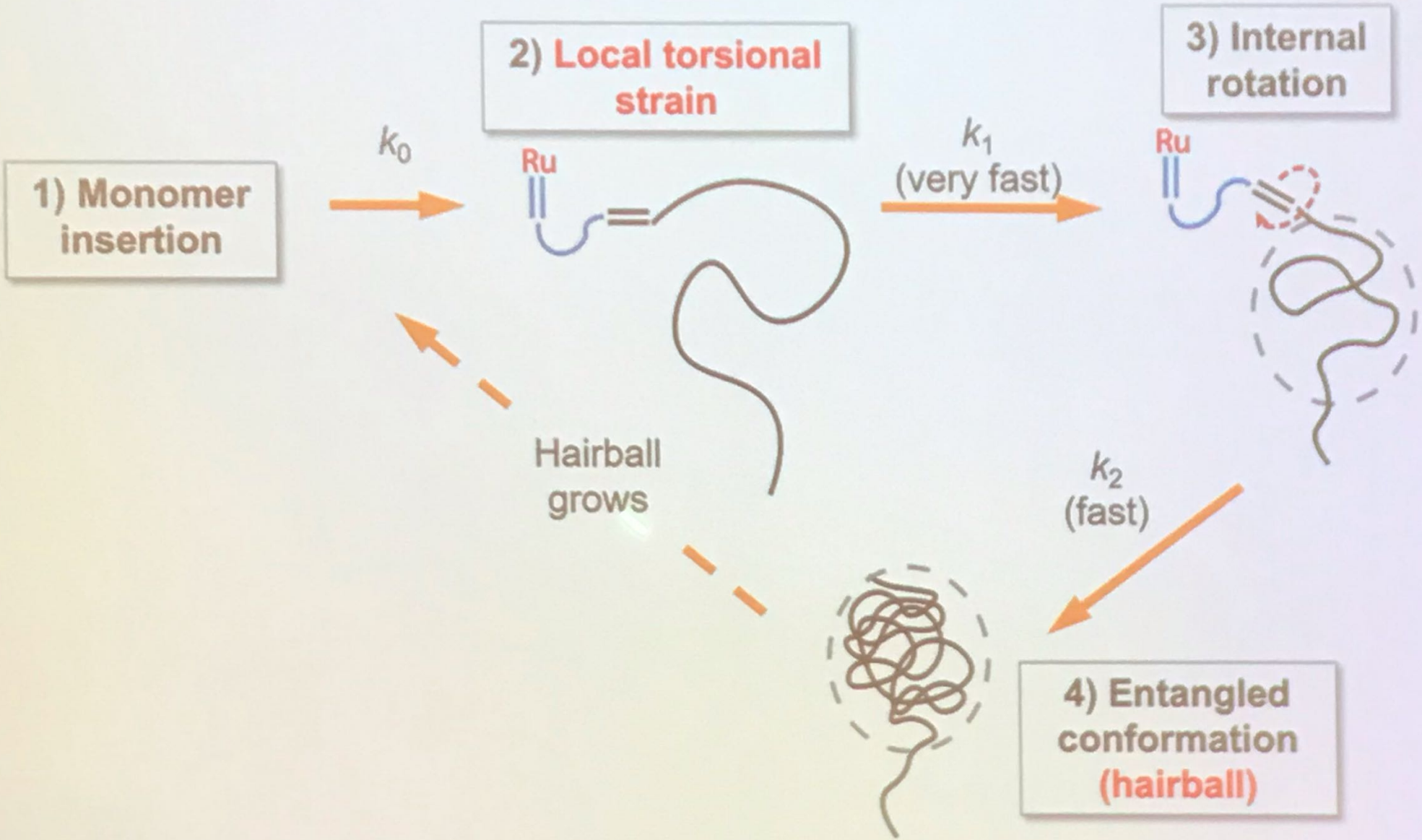

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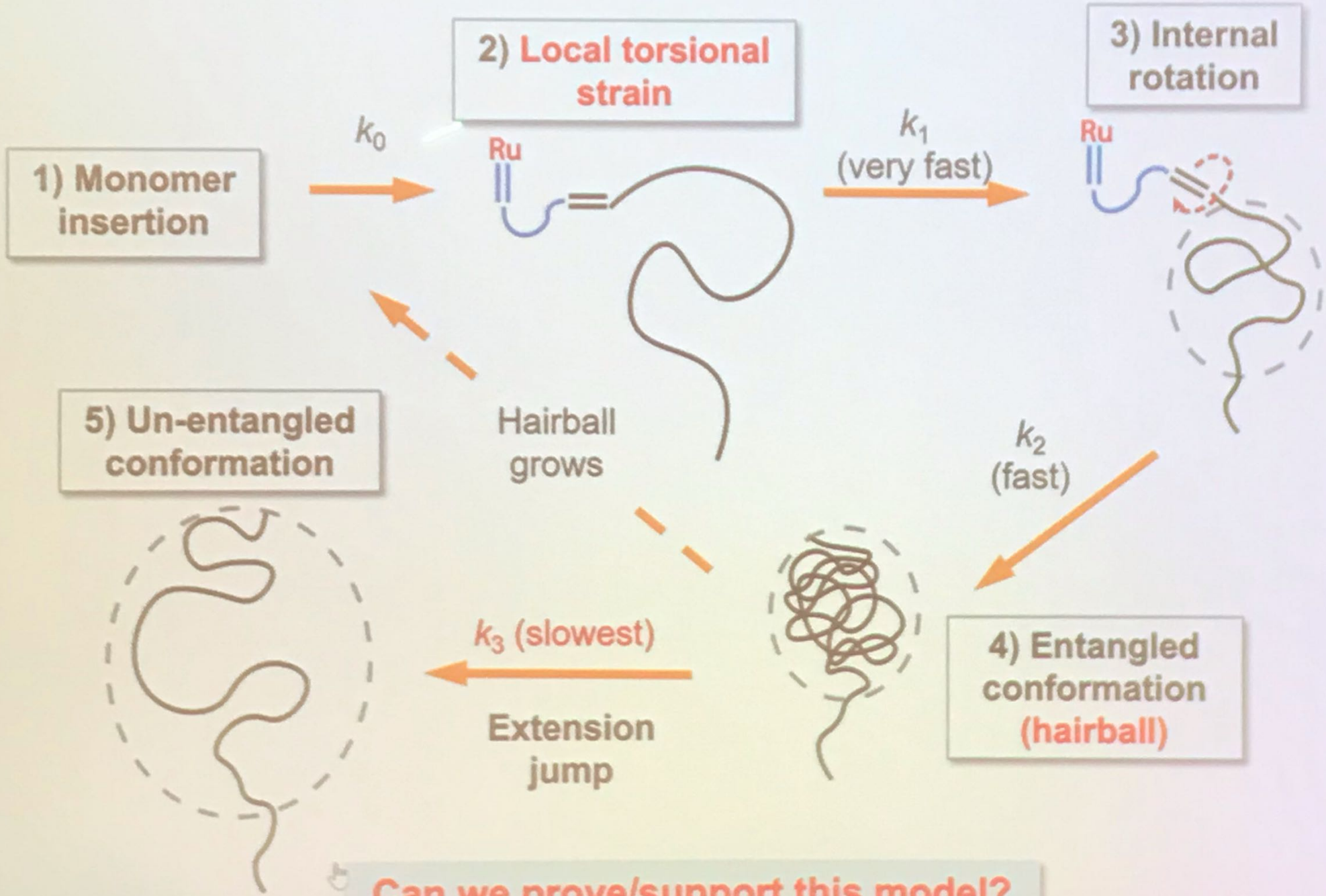
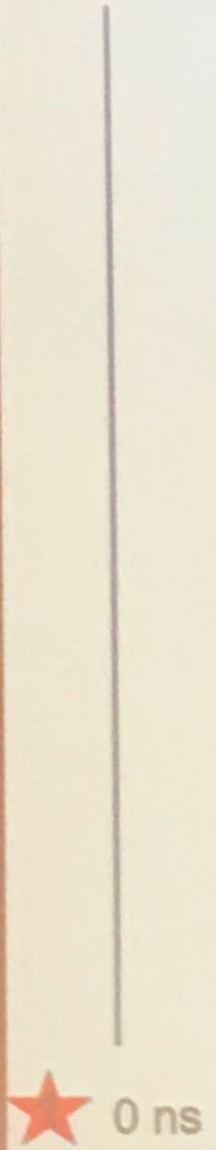


Can we prove/support this model?

Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

Built-in torsional strain (artificial)



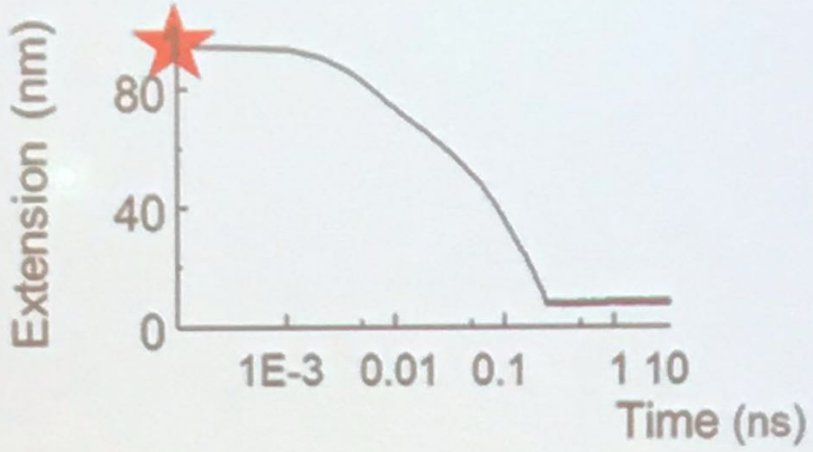
0 ns

146 monomer

F. Escobedo

Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

Built-in torsional strain (artificial)



0 ns

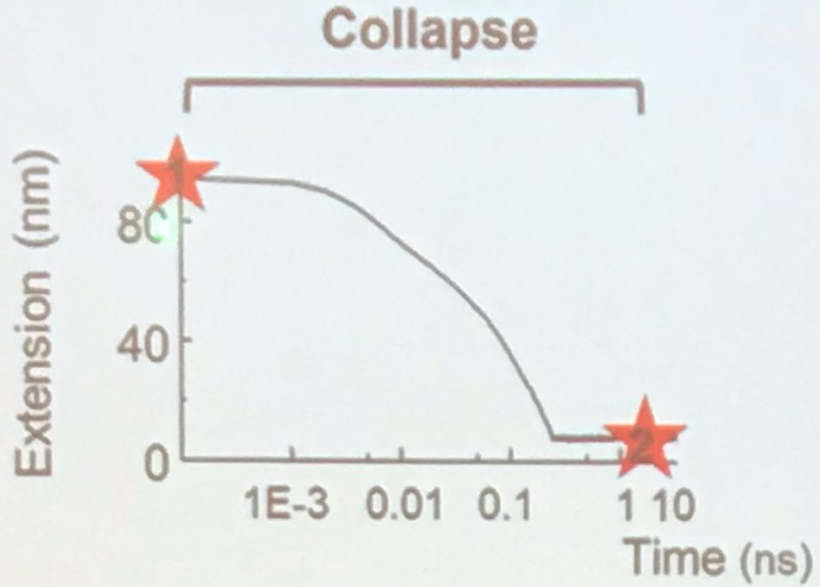
146 monomer

F. Escobedo

Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

Built-in torsional strain (artificial)

Force



0 ns

2 ns

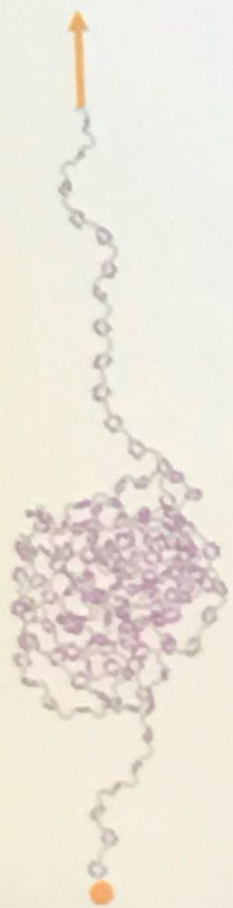
146 monomer

F. Escobedo

Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

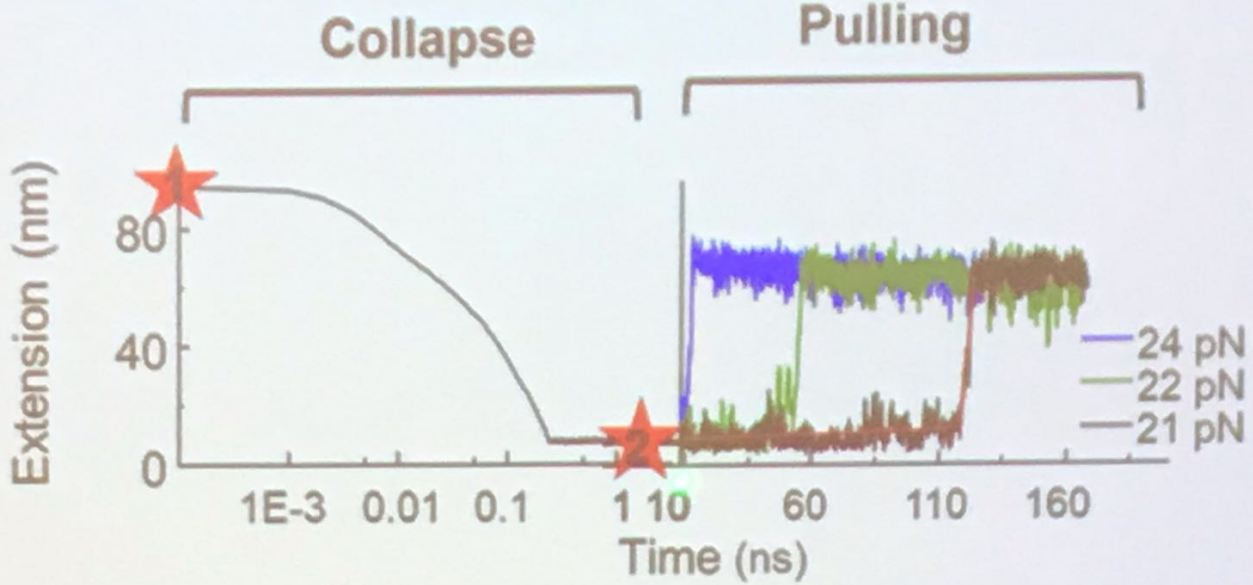
Built-in torsional strain (artificial)

Force



0 ns

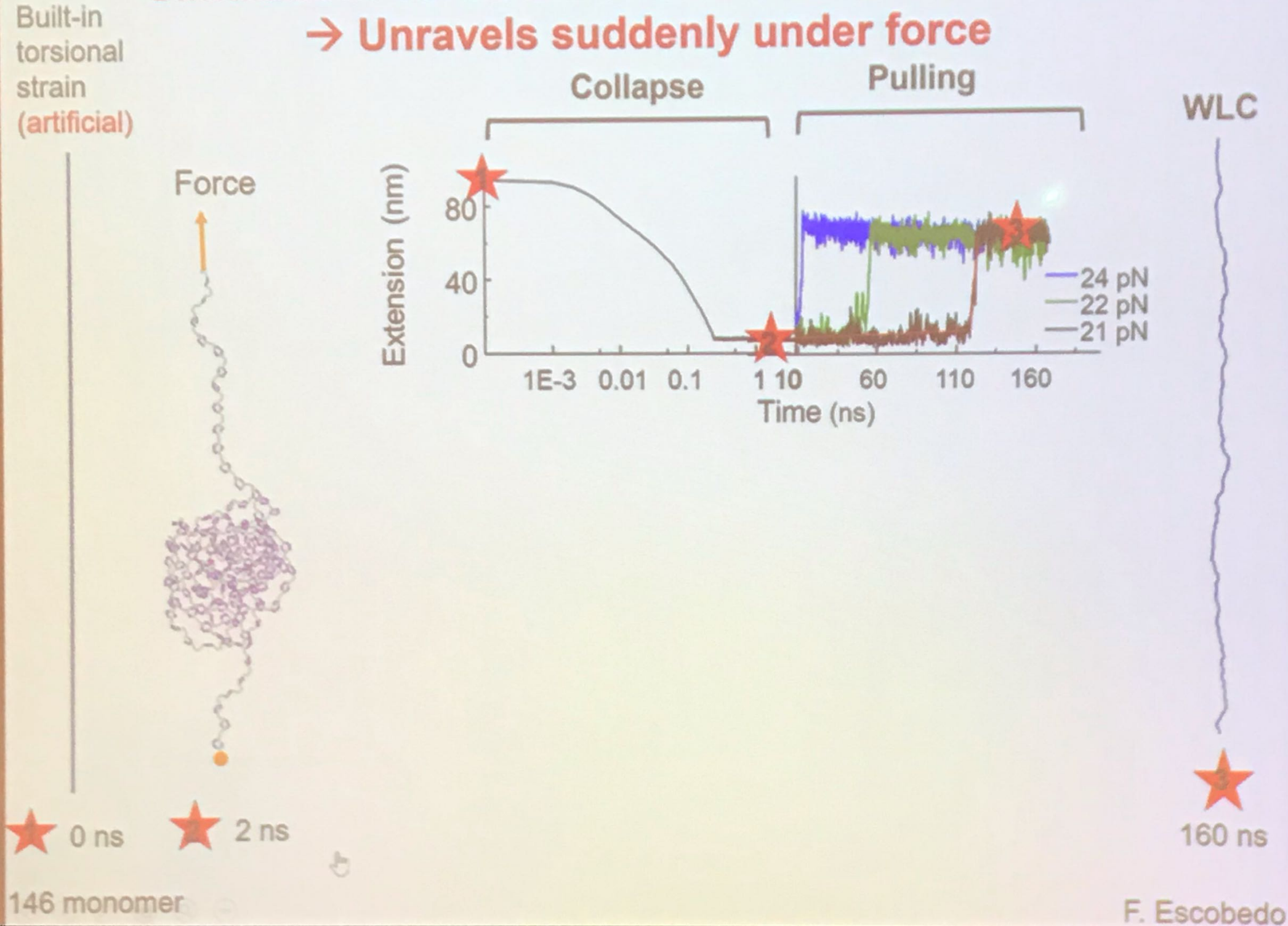
2 ns



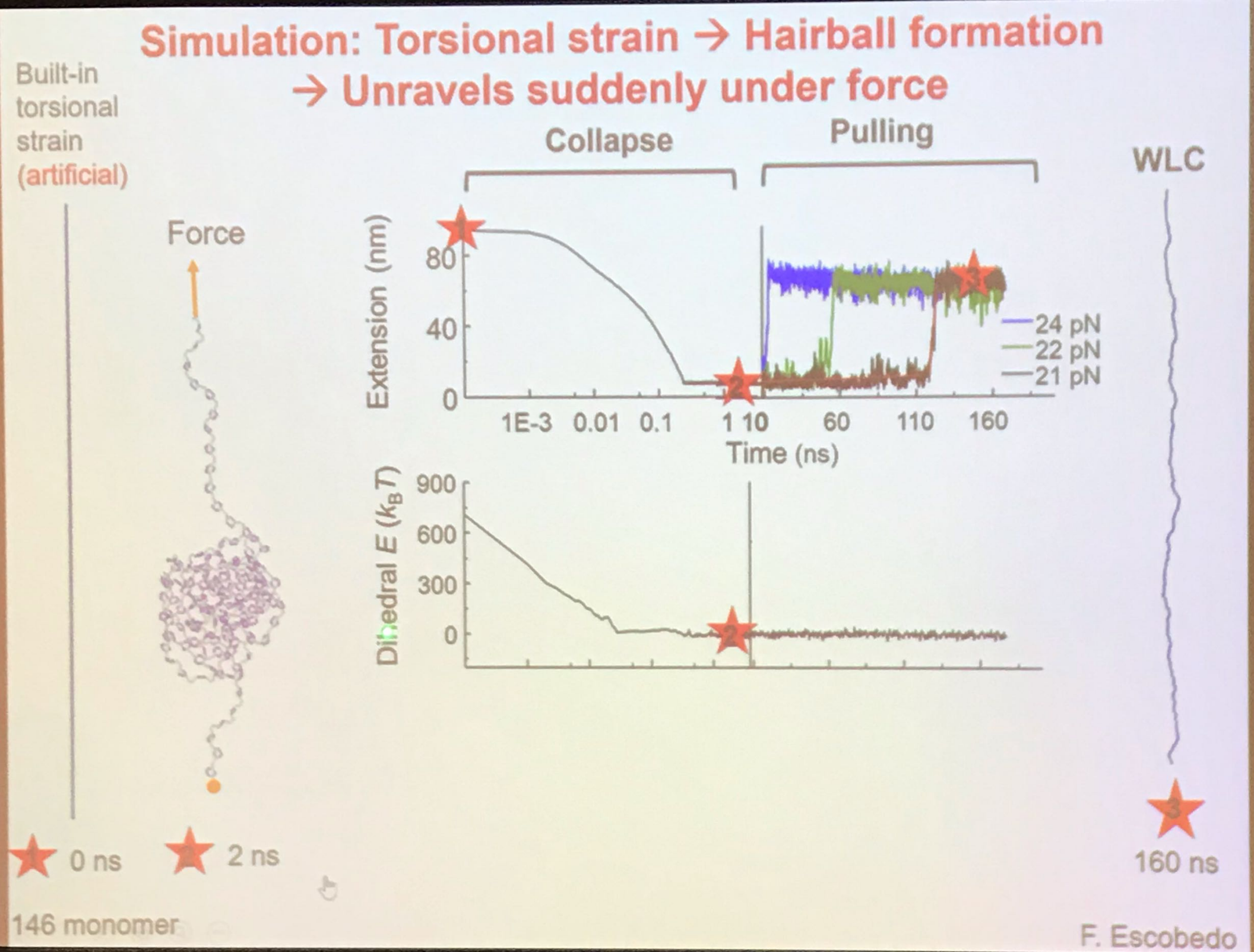
146 monomer

F. Escobedo

Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

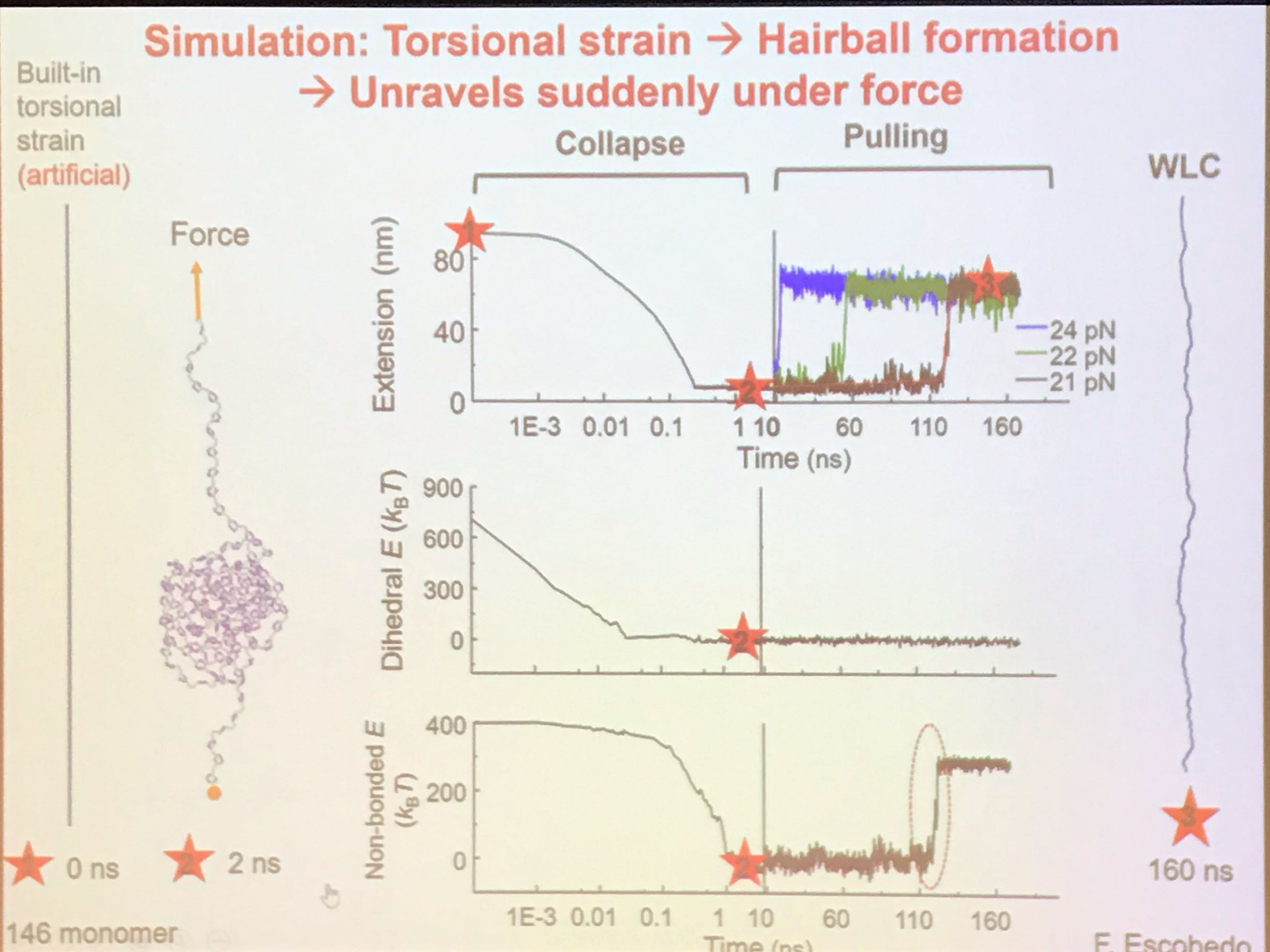


Simulation: Torsional strain → Hairball formation → Unravels suddenly under force

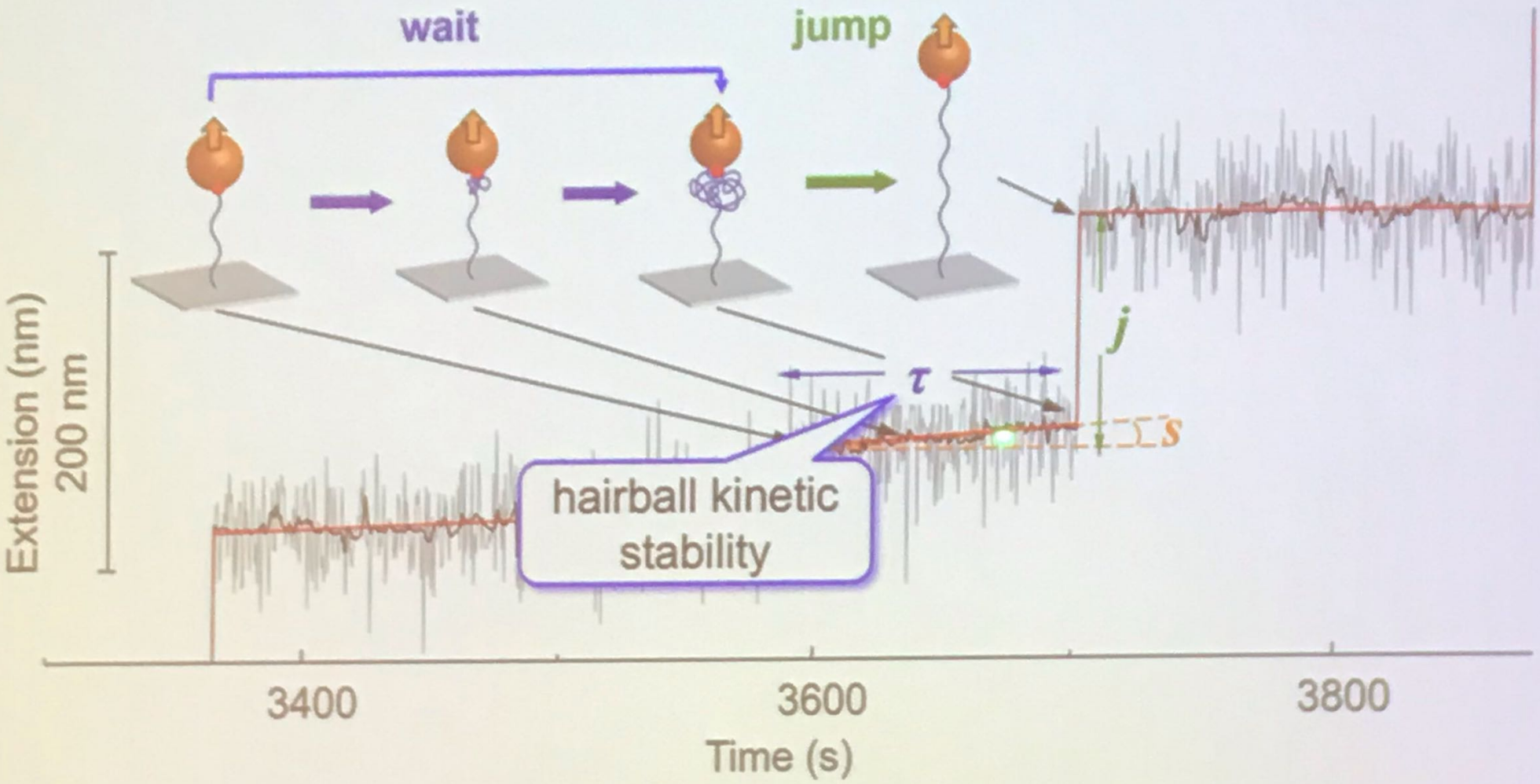


F. Escobedo

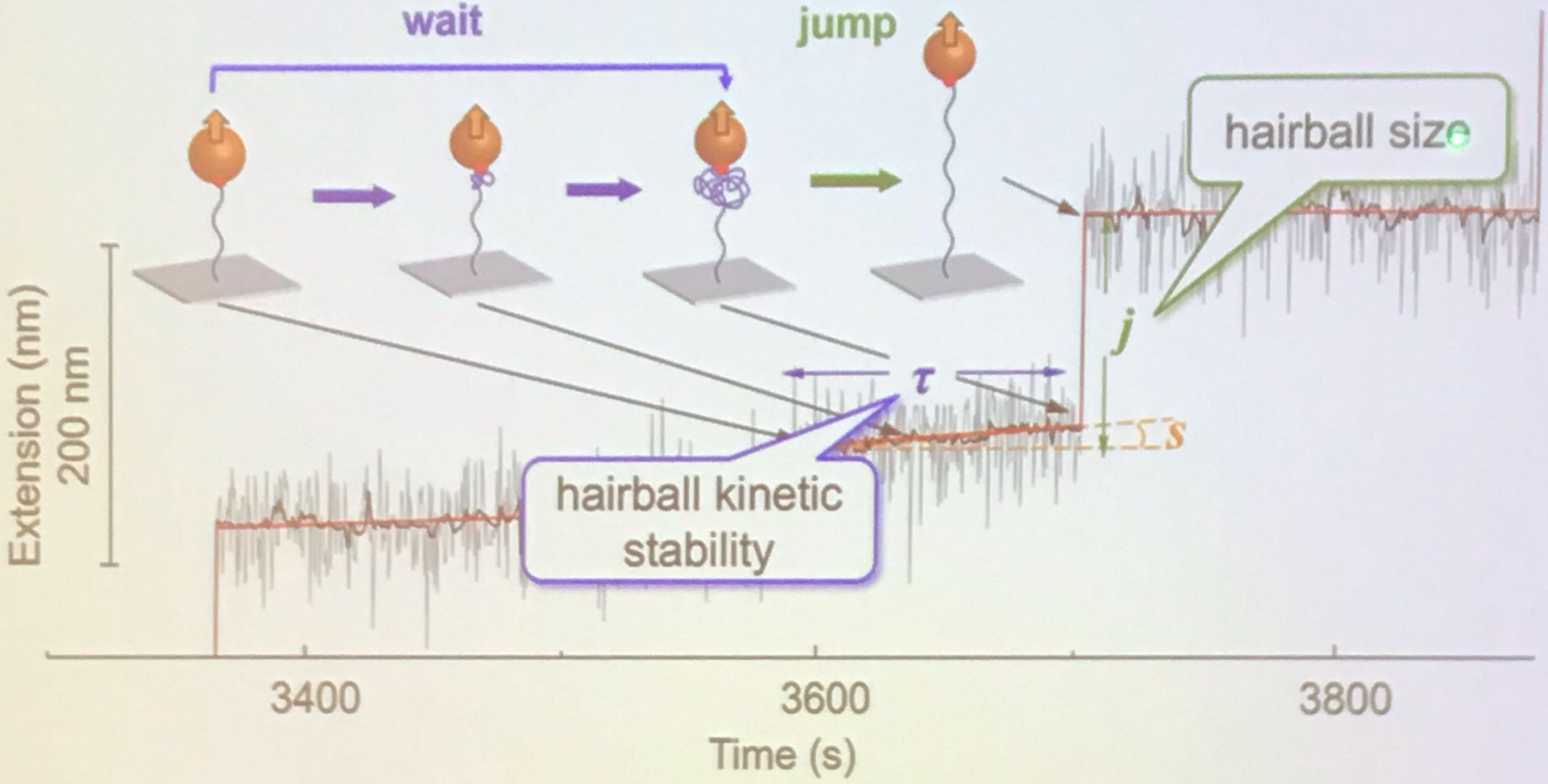
Simulation: Torsional strain → Hairball formation → Unravels suddenly under force



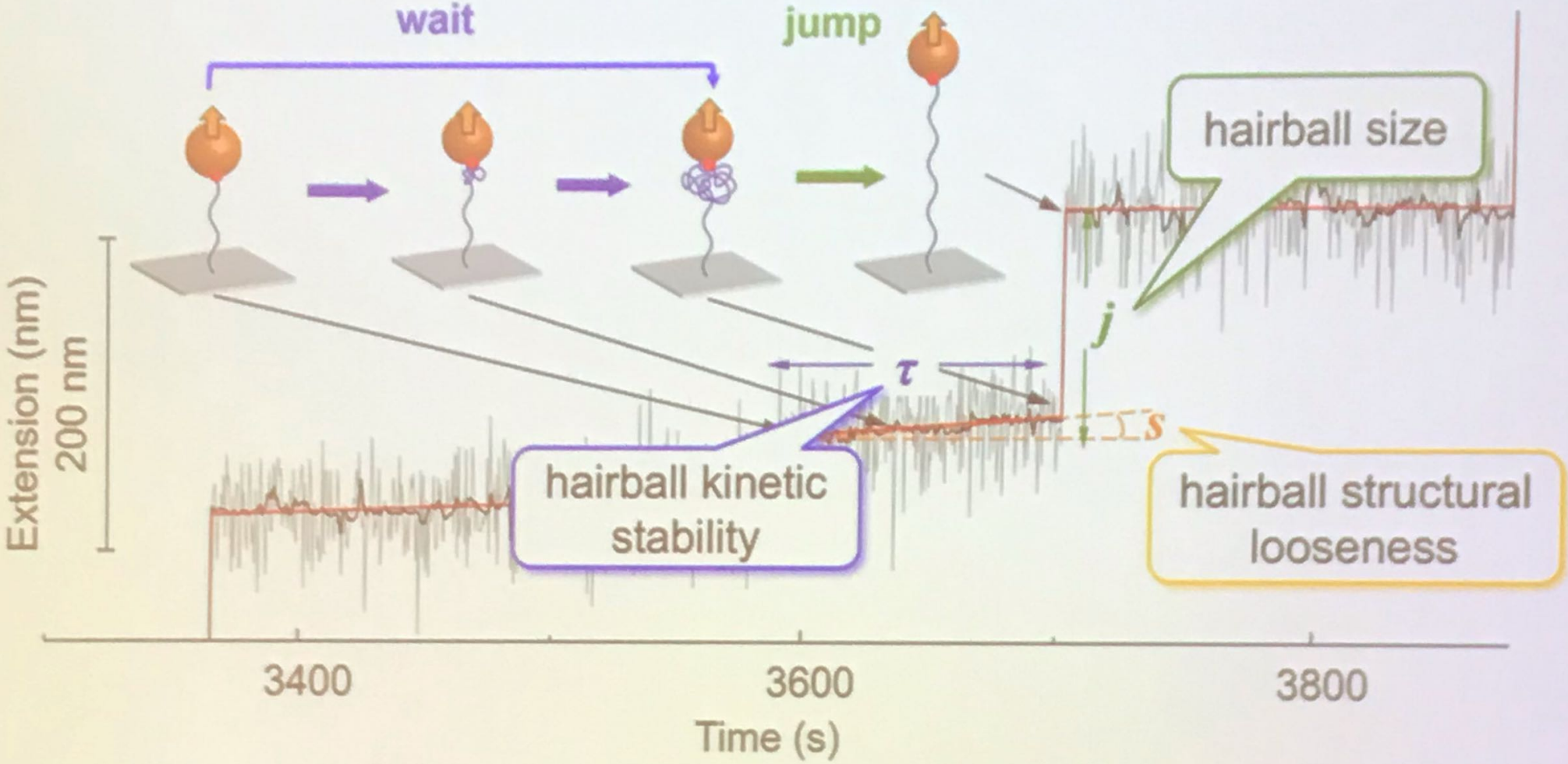
Hairball: Microscopic properties



Hairball: Microscopic properties

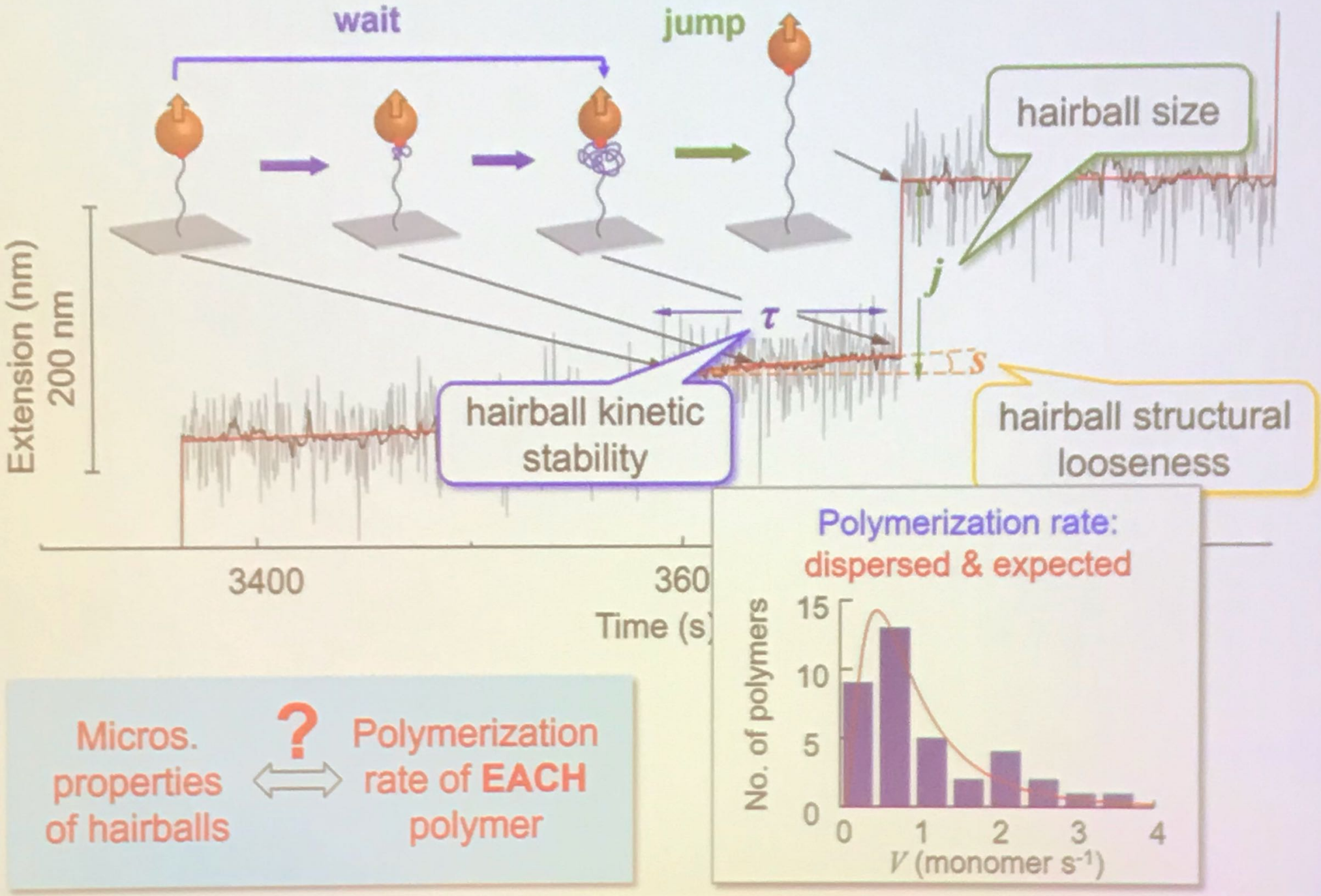


Hairball: Microscopic properties



Micros. properties of hairballs ? Polymerization rate of **EACH** polymer

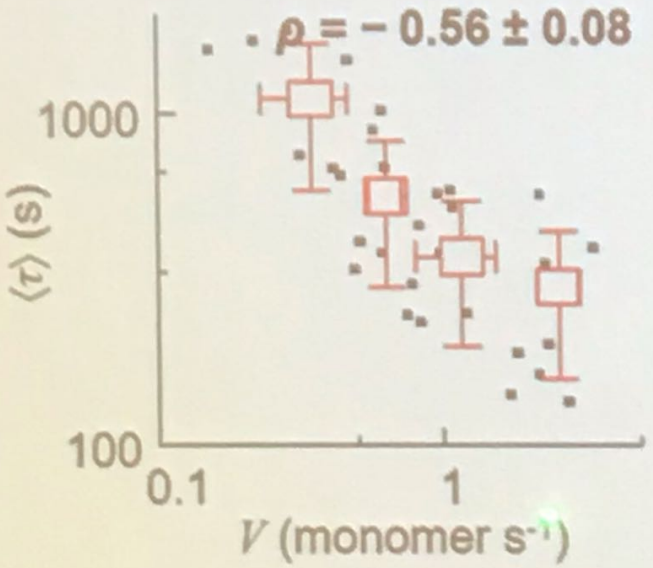
Hairball: Microscopic properties



Micros. properties of hairballs ⟺ ? Polymerization rate of **EACH** polymer

Polymerization Kinetics ⇔ Hairball Micro. Properties

V ↔ ⟨Waiting time⟩
(kinetic stability)



Faster V ↔ Less stable hairball

Polymerization Kinetics ⇔ Hairball Micro. Properties

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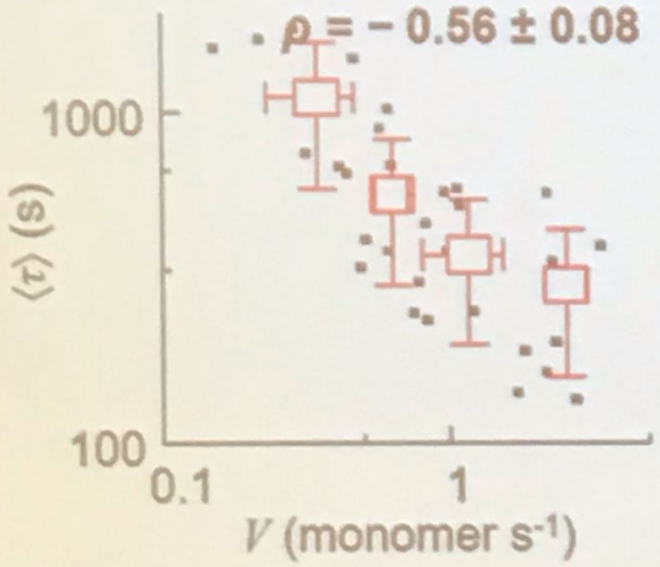
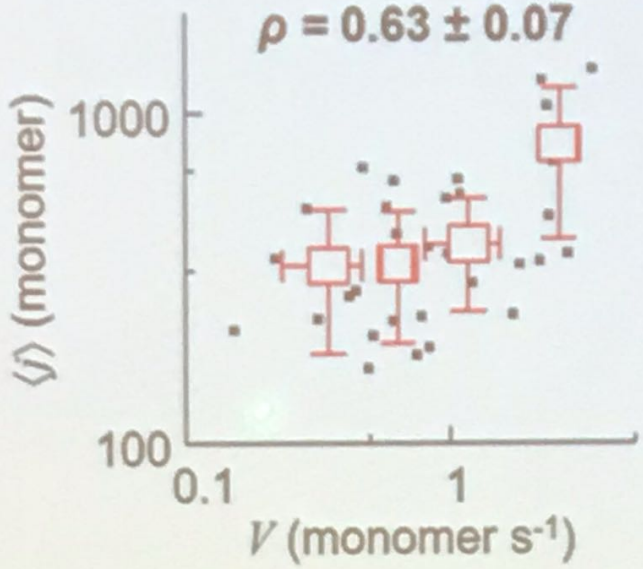


V ↔ ⟨jump length⟩
(hairball size)



Faster V ↔ Less stable hairball

↔ Larger hairballs

Polymerization Kinetics ⇔ Hairball Micro. Properties

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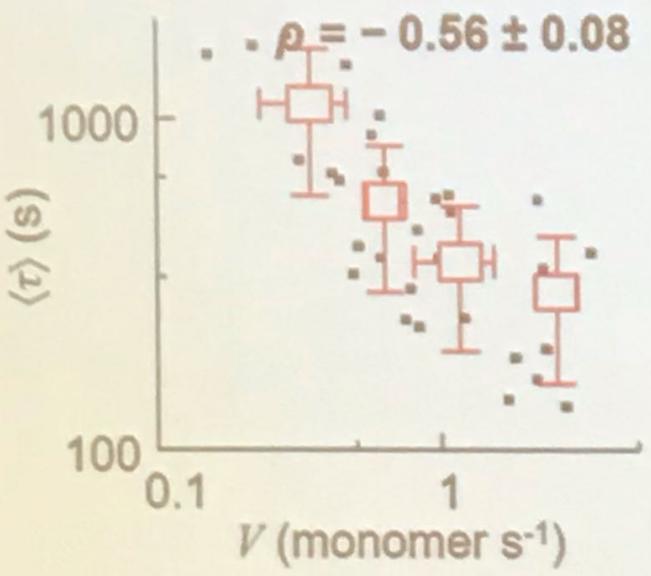

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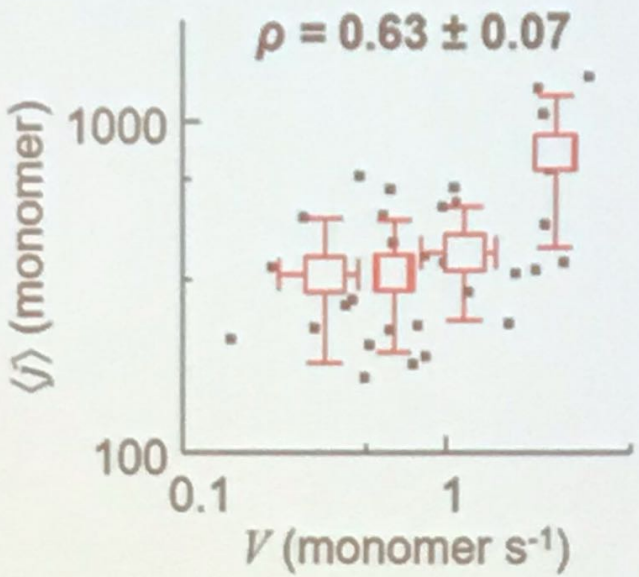
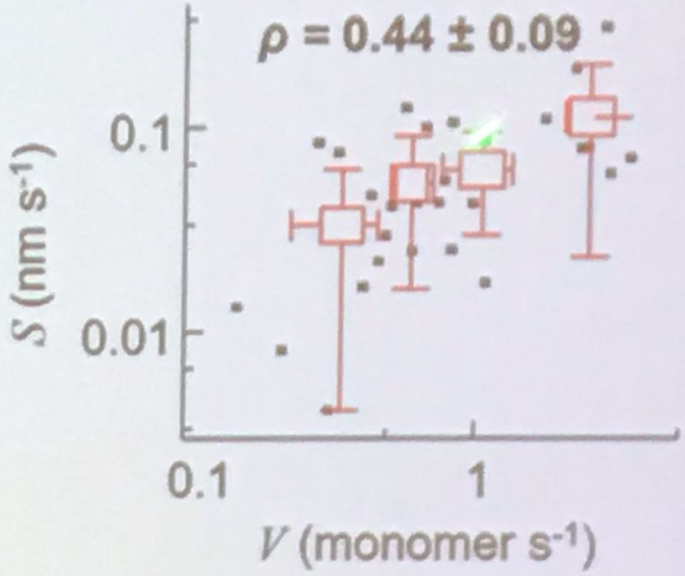


V ↔ ⟨slope⟩
(structural looseness)



Faster V ↔ Less stable hairball

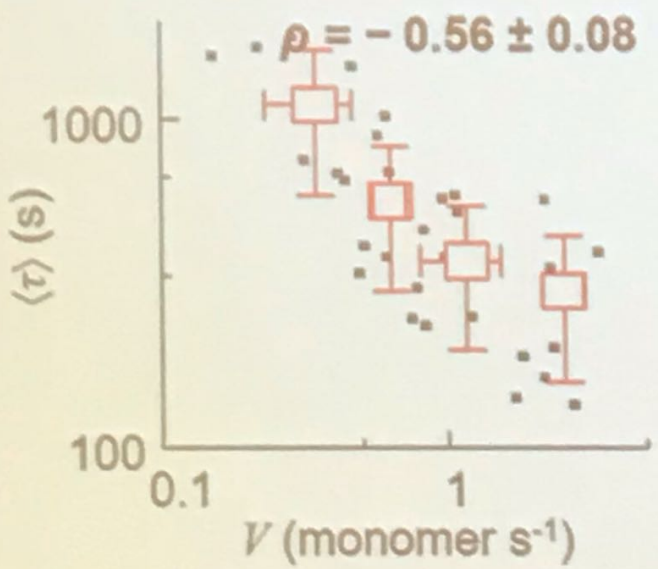
↔ Larger hairballs

↔ Looser hairballs

⇒ Configurations of hairballs control polymerization rate

Polymerization Kinetics ⇔ Hairball Micro. Properties

V ↔ ⟨Waiting time⟩
(kinetic stability)



V ↔ ⟨jump length⟩
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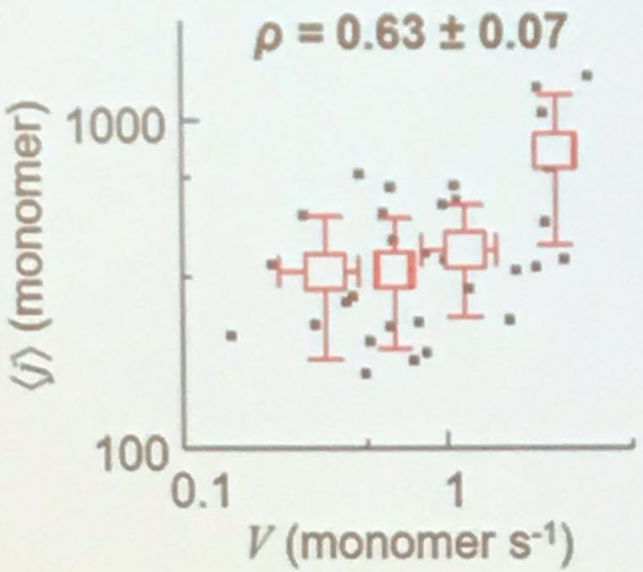

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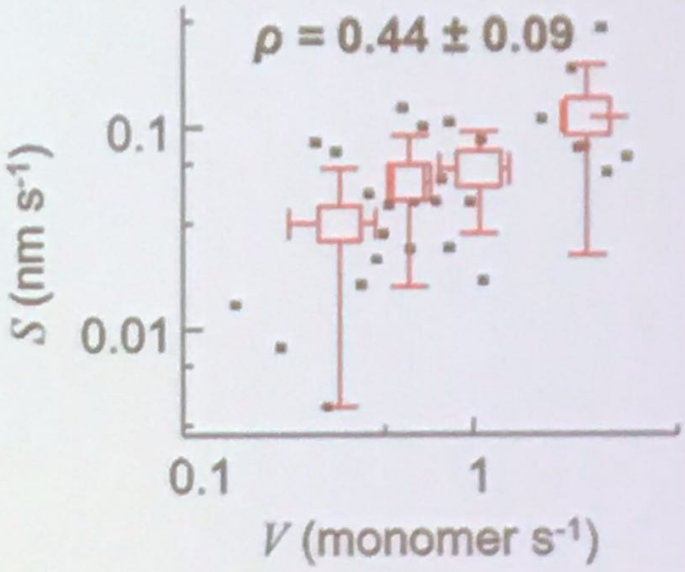

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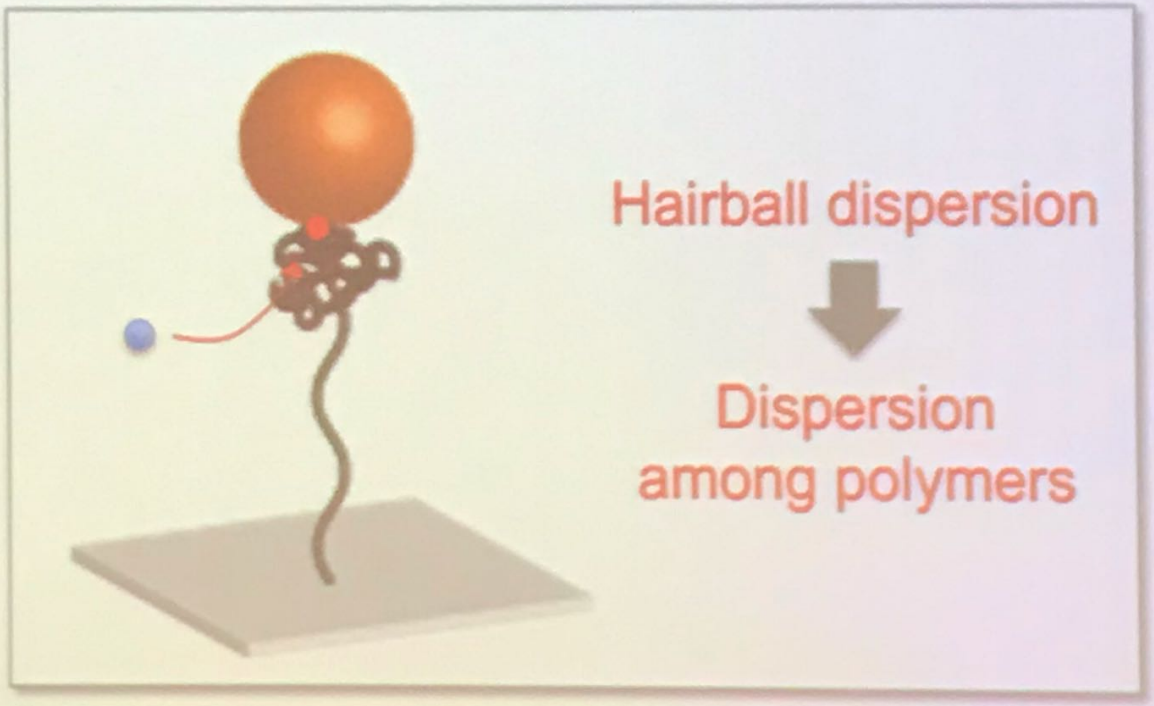
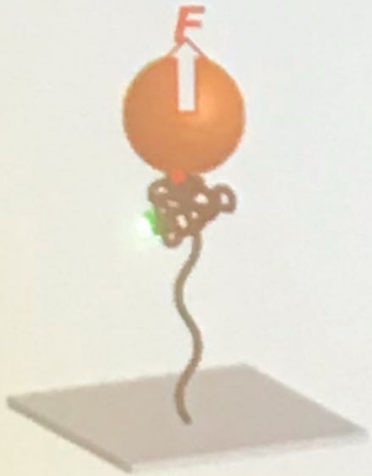


Broad relevance: Non-equil. conform. entanglements

Living polymerization in free solution

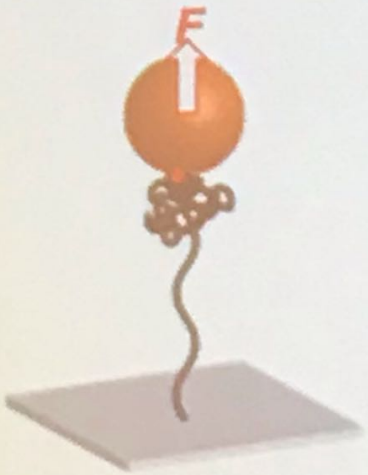


free solution?

- Hairball more likely
- Bigger role in affecting kinetics
- Can we manipulate hairball formation to alter kinetics and dispersion (e.g., shear flow?)

Broad relevance: Non-equil. conform. entanglements

Living polymerization in free solution



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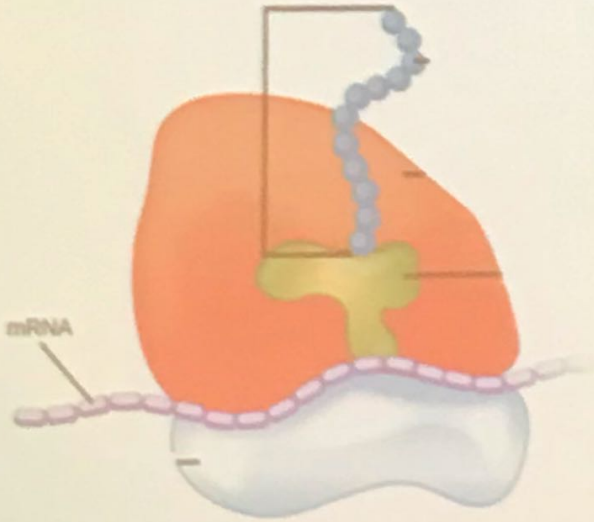
Living bio-polymerization

Protein synthesis



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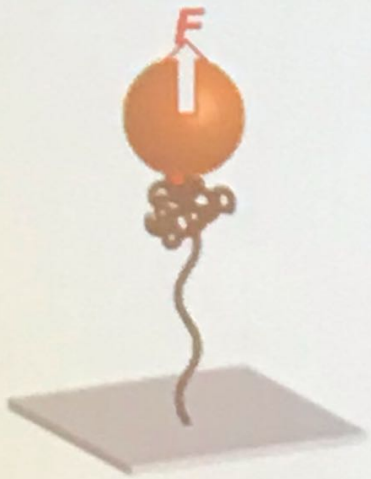

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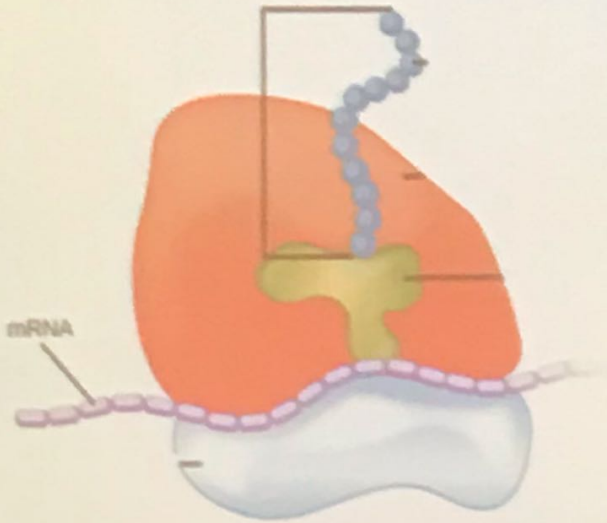
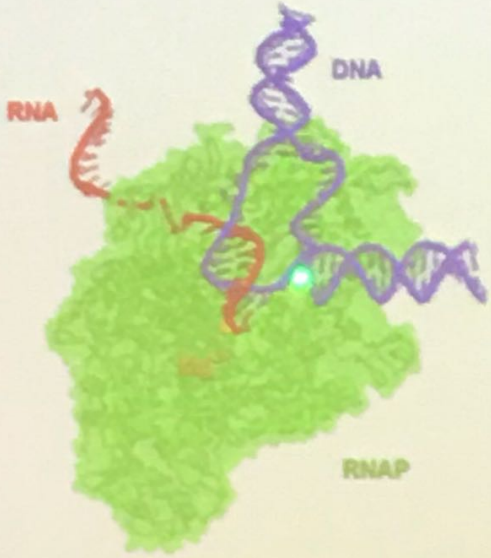


RNA synthesis



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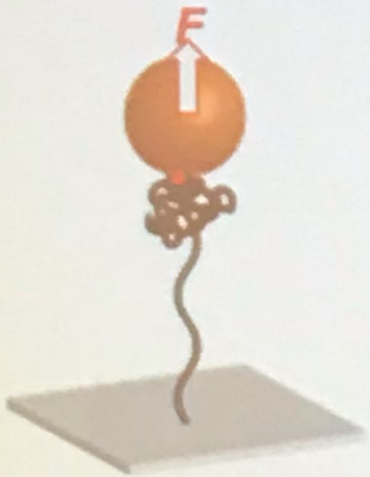
Living polymerization in free solution



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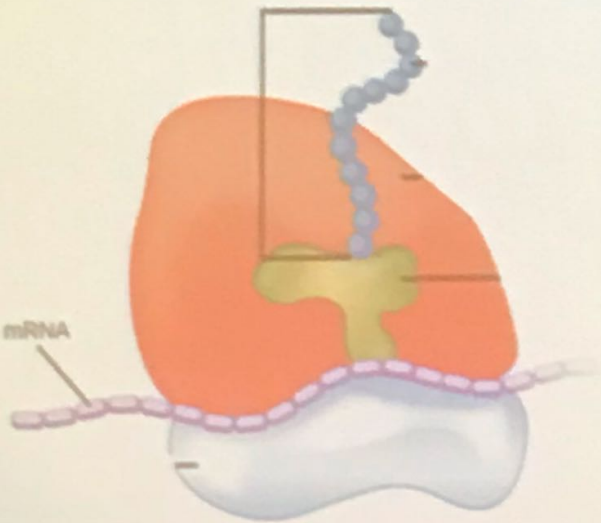
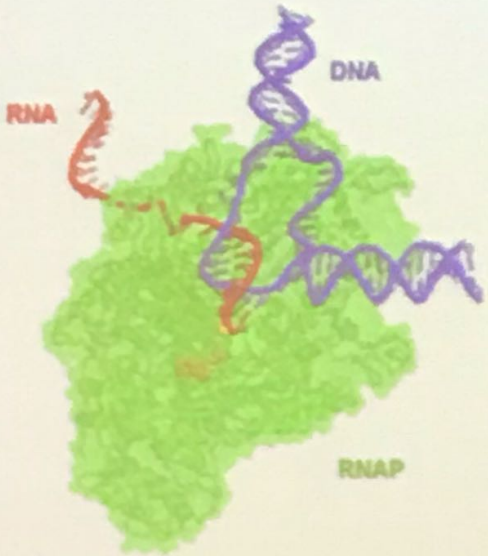
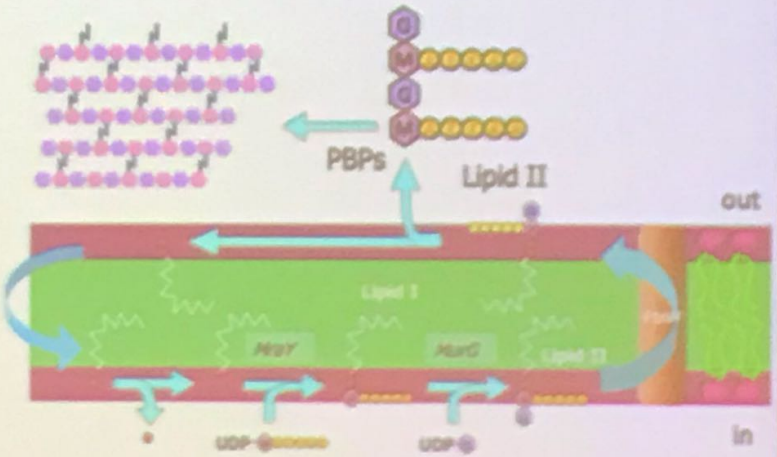


RNA synthesis

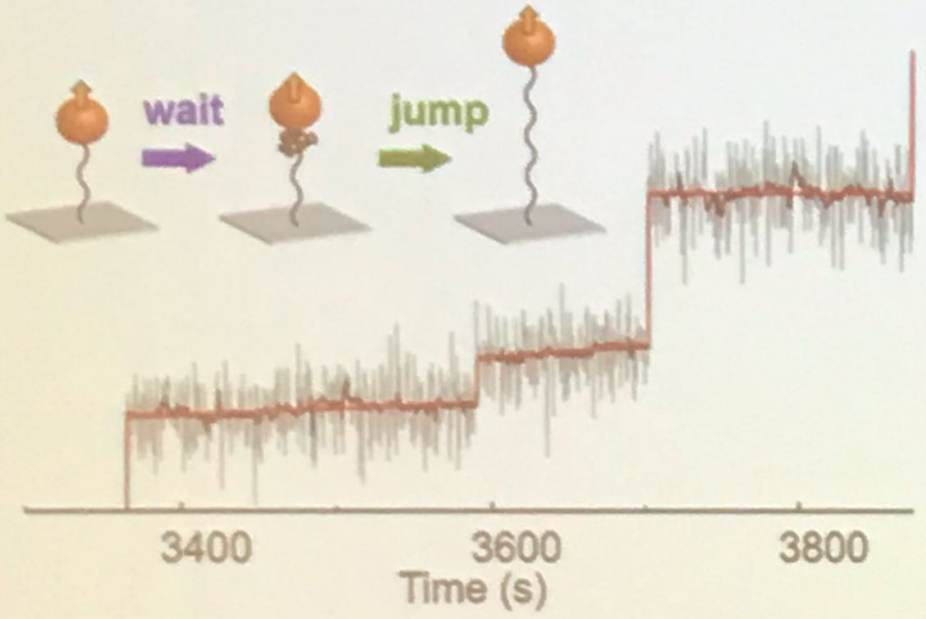


Polysaccharide synthesis



Summary: Single-polymer growth dynamics

MT → Real-time visualization of single-polymer growth



- Discovery of nonequilibrium conformational entanglements
  → step-wise extension
- Entanglement controls polymerization rate and contributes to dispersion
- Broad relevance: Living (bio)polymerization

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