



# Artificial Photosynthesis with Biomimetic Nanomaterials: Self-Repairing Solar Cells

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## Current Photovoltaic & Photo-electrochemical Technologies

- Solar radiation: 120,000 TW constantly strikes the surface of the earth
- Presently, solar energy supplies less than 0.01% of world's energy demand
- Major challenge in solar energy utilization:

Energy harvesting economically competing with cheap fossil fuel

Type of Cell	Cell Efficiency	Current Technology Needs
Single-crystalline Si	24 %	Higher production yields, lowering of cost and energy content
Multi-crystalline Si	18 %	Lower manufacturing cost and complexity
Amorphous Si	13 %	Lower production costs, increase production volume and stability
Dye-sensitized solar cells	10 – 12 %	Improve overall efficiency and lifetime via system regeneration
Organic solar cells	6 – 7 %	Improve system stability and efficiency significantly

Lewis, *PNAS* (2006)  
Kamat, *JPC* (2007)  
Gratzel, *Nature* (2001)

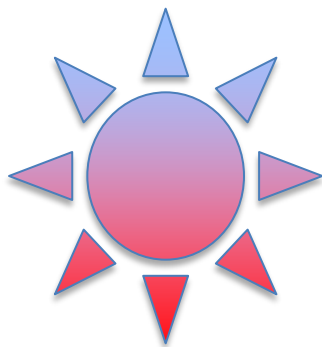
One of the key drawbacks of Dye-sensitized solar cells:

Decrease in the system performance over time due to photo-induced damage of dye

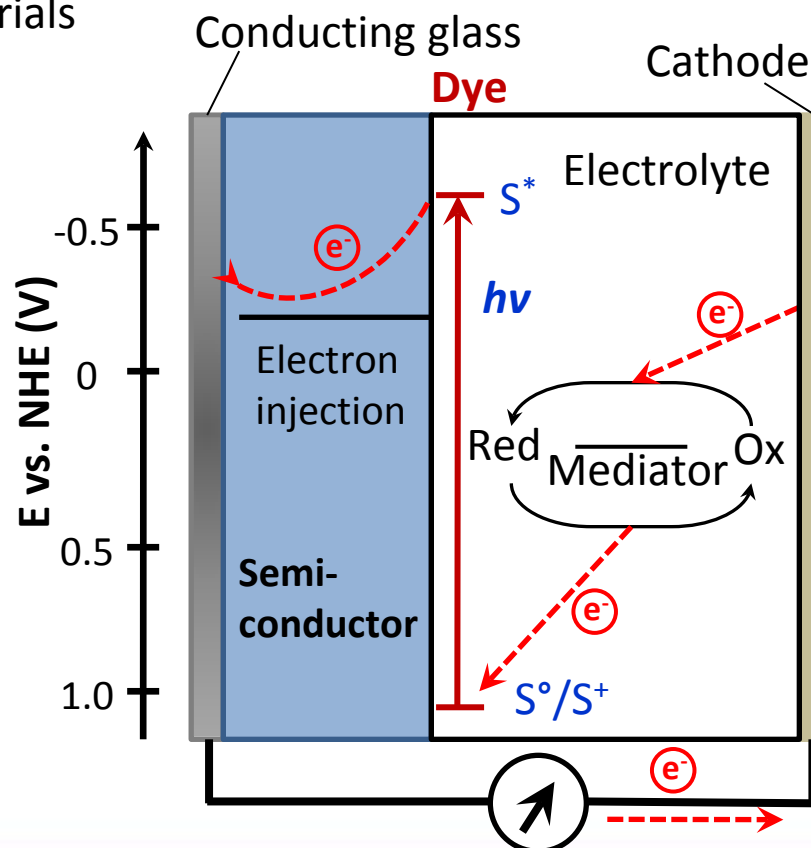


## Electrochemical Photovoltaic Cells

- Electrodes: ITO as WE and Pt as CE
- Electrolyte solutions
- Light absorbing dye: Ru compounds, porphyrin derivatives, etc
- Semiconductor nanomaterials



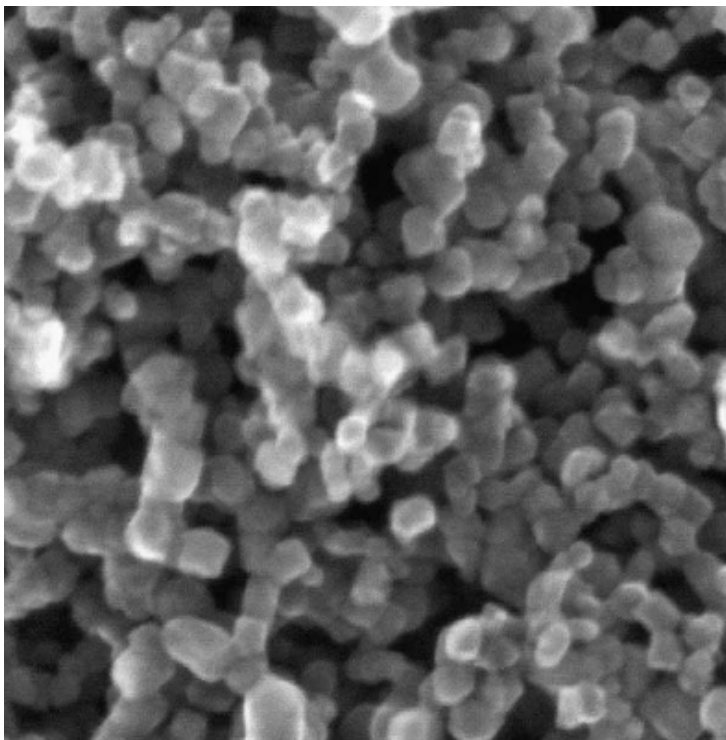
Gratzel, *JPPC PR* (2003)





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Currently:

Nanostructured materials provide high surface areas for energy conversion

Problems:

Invariably static structures are unable to cope with degradation of dye molecules over time

Solutions:

We draw inspiration from natural photosynthesis, where structurally flexible systems self regenerate to improve overall efficiency and lifetime

## Self-Repair in Natural Photosynthesis

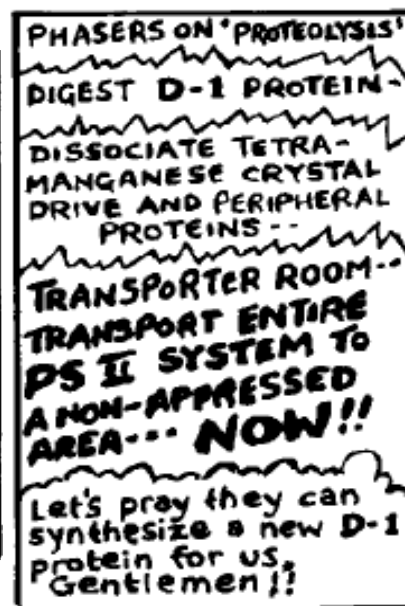
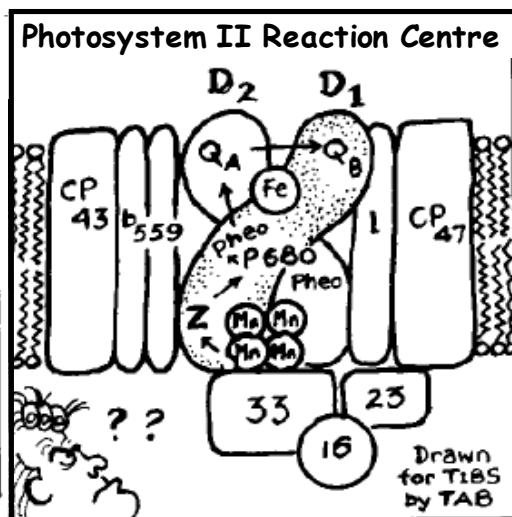
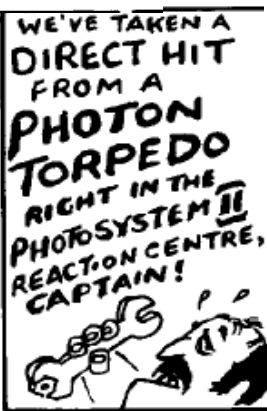
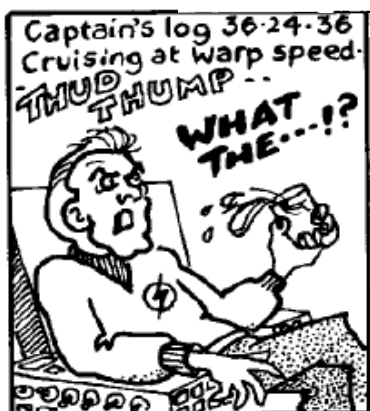


- Nature uses rapid and facile mechanisms of self repair that enable energy harvesting under conditions of photo-induced damage or degradation
- Photo-damaged components (i.e.  $D_1$  protein) in the reaction center are constantly replaced – every hour

**There is no such self generative analog in the synthetic realm !**

### PLANT TREK<sup>2</sup>

by Barber & Andersson.



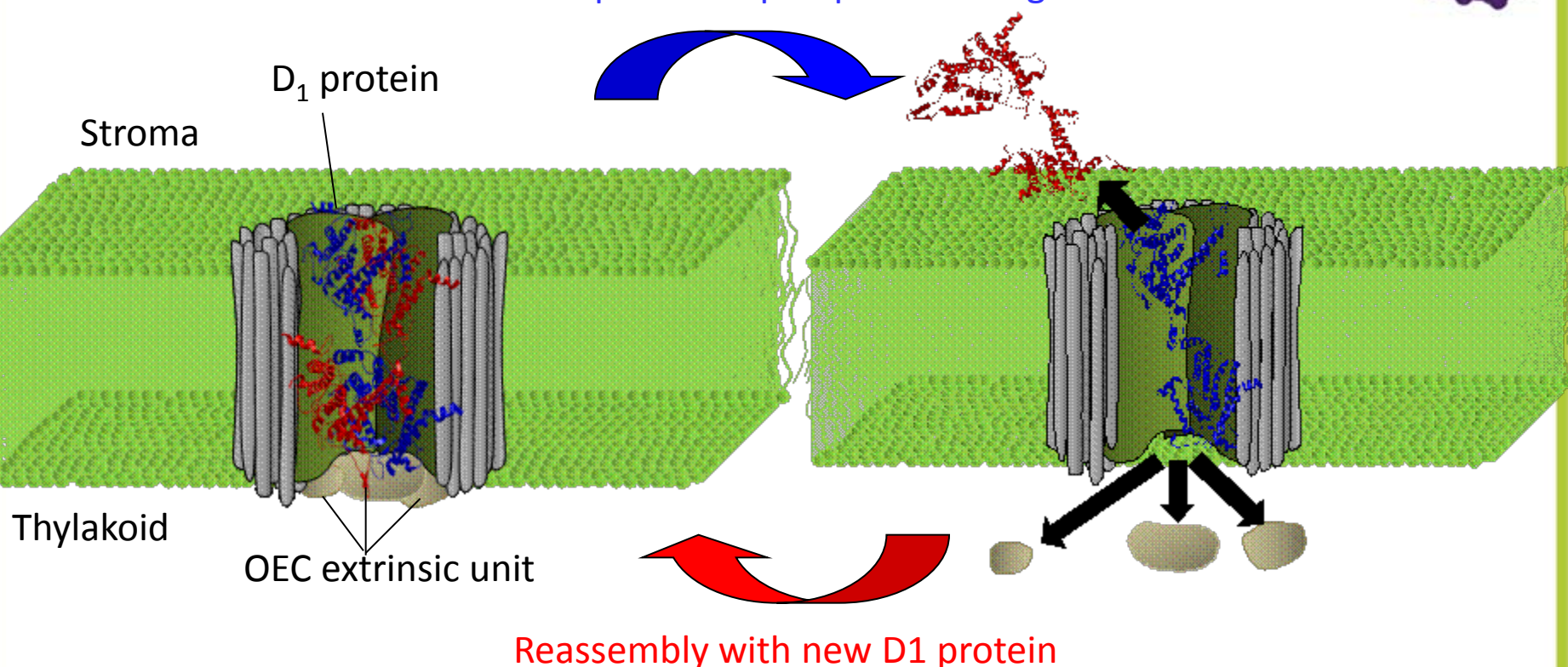
Barber and Andersson *Trends in Biochemical Sciences* (1992)



## Self-Repair in Plant Photosystem II



Decomposition upon photodamage



This natural self repair process relies on:

- Molecular recognition and Thermodynamic meta-stability
- Self assembly processes that can be reversed

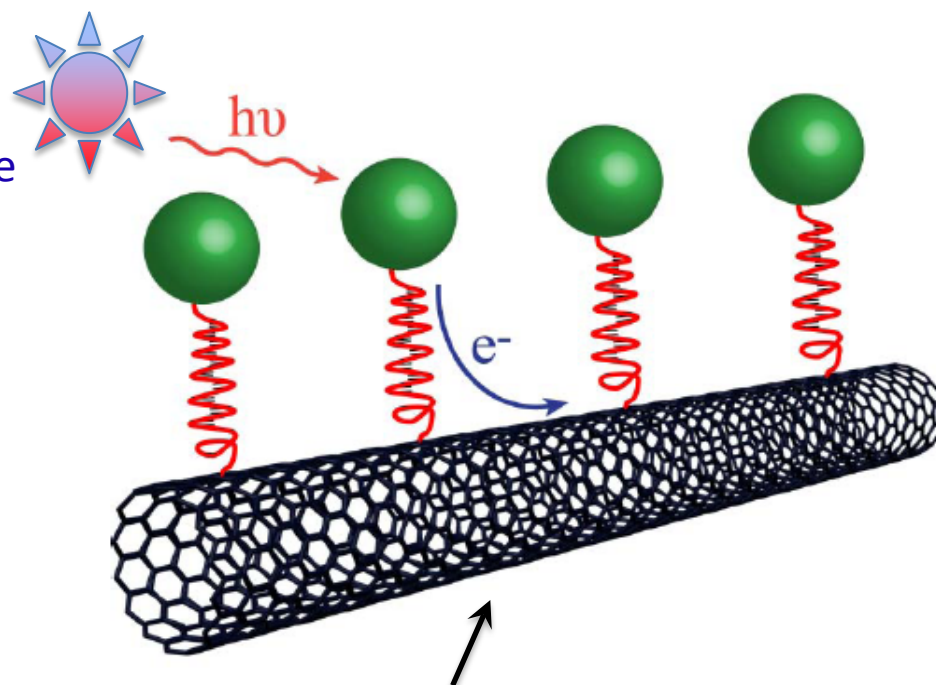
# Artificial Photosystems



We mimic photosynthesis processes by reversibly assembling carbon nanotubes and photosynthetic reaction centers that are capable of self-repair.

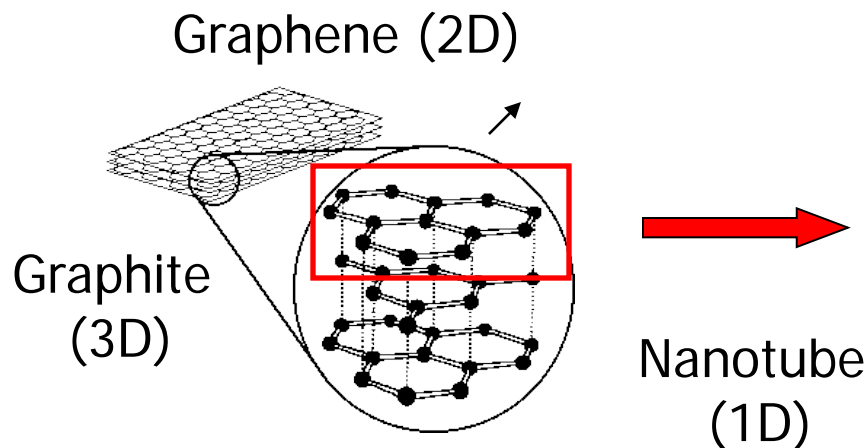
Photosynthetic proteins that generate electron from solar radiation  
- extracted from purple bacteria

Rhodobacter  
sphaeroids



Carbon nanotube as a molecular wire

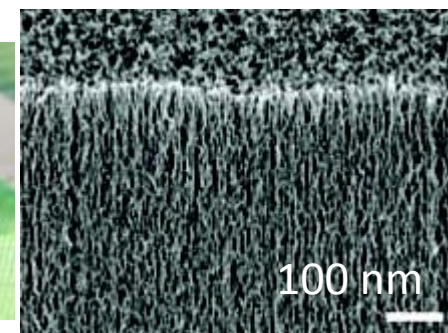
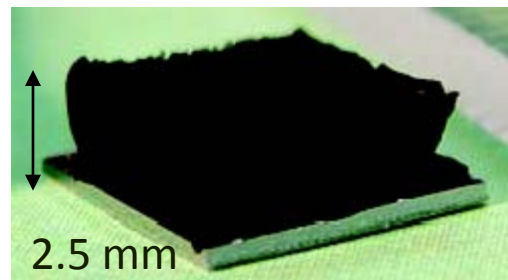
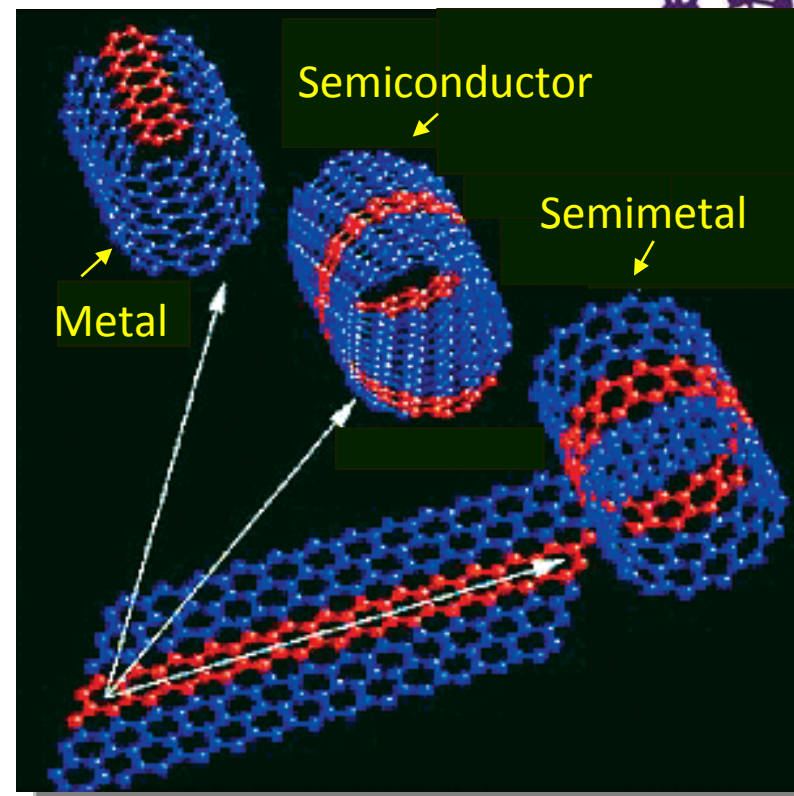
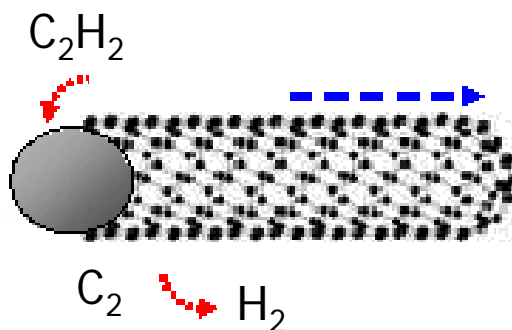
# What is a Carbon Nanotube?



Electrons restricted to single dimension  
Diameter  $\sim 1$  nm

## Synthesis

Chemical vapor deposition  
Over metal (Fe, Co, Mo) nanoparticle

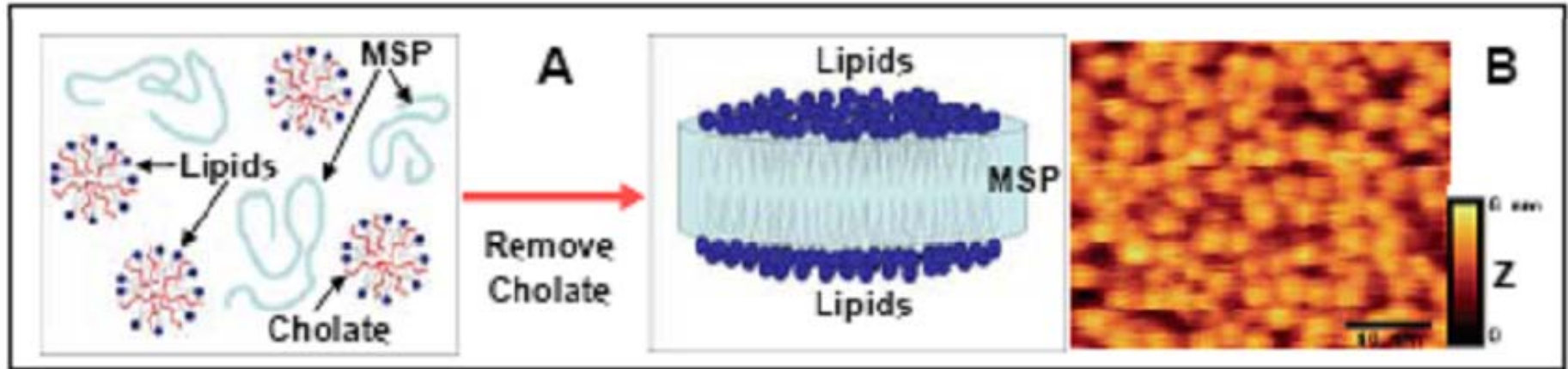


Length can range from 10 nm to 1 cm





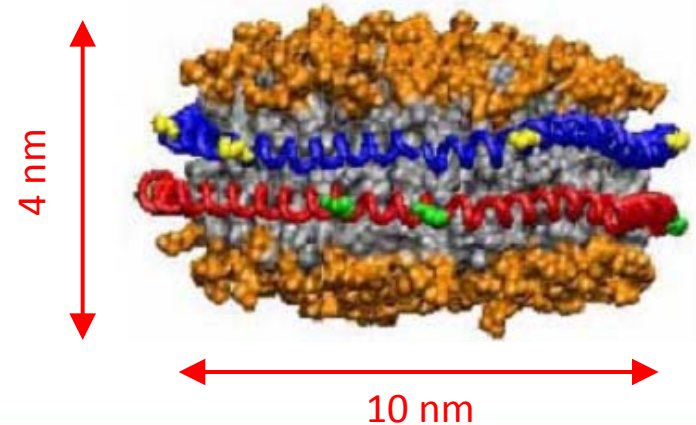
## Mimicking Plant Cell Membrane – Lipid Nanodisc Nanodisc formation for protein reconstitution



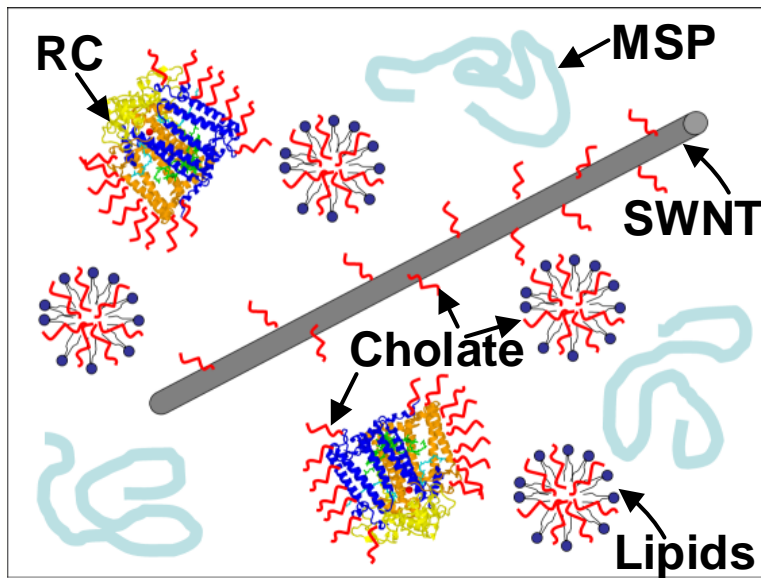
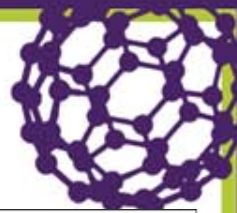
System initially stabilized with  
surfactant: sodium cholate

- Phospholipids and Membrane scaffold protein (MSP) → Nanometer-sized discs
- Spontaneous self-assembly upon surfactant removal (cholate)
- Platform for suspending membrane proteins (i.e., photosynthetic reaction center or RC)

Sligar et al. *Nano Lett.* (2006)



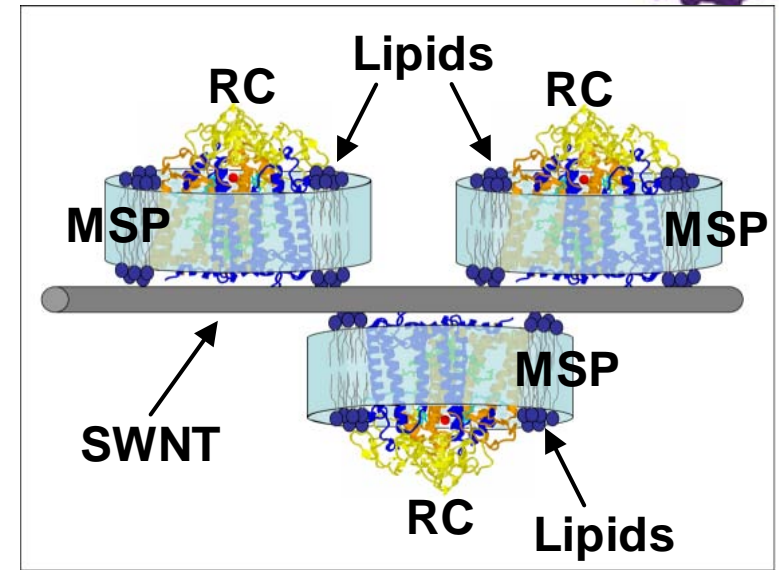
## Reversible Self Assembly



Surfactant  
removal



Surfactant  
addition

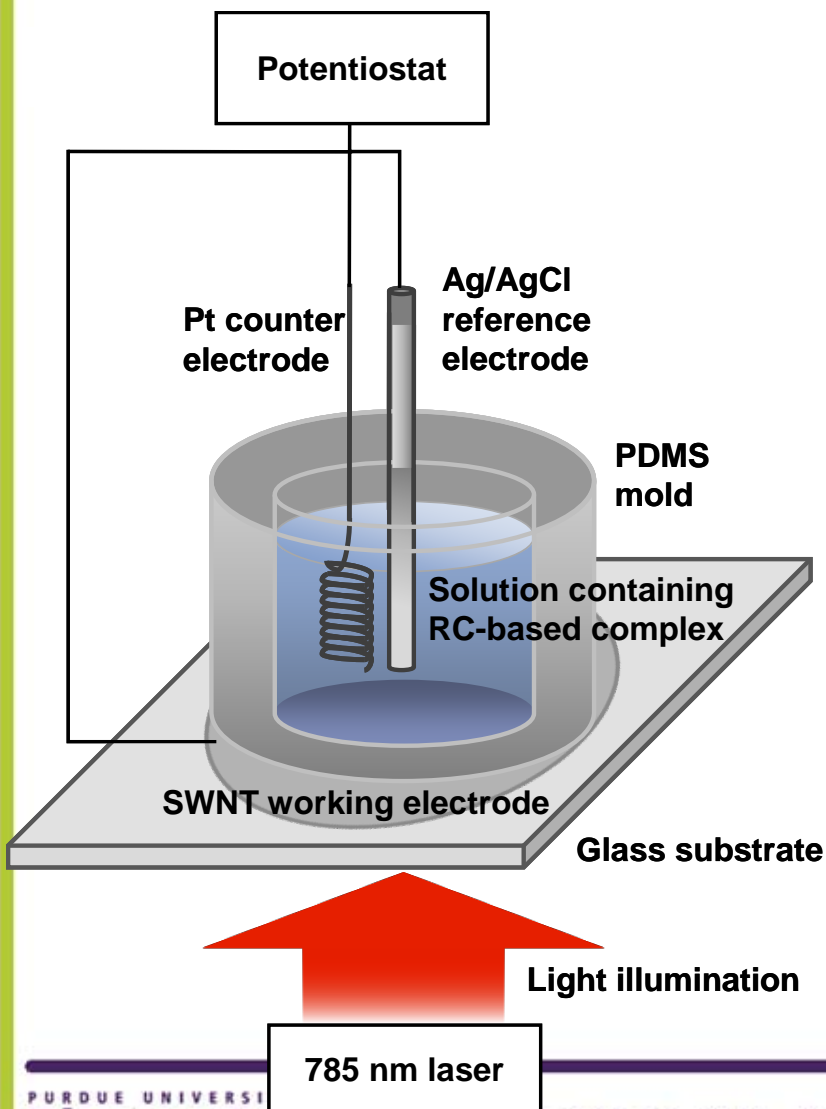


- Photosynthetic reaction centers (RC) isolated from purple bacterium, *Rhodobacter Sphaeroides*
- Nanodiscs reconstitutes RC, while suspending SWNT
- It could be the basis of light-harvesting devices with infinite lifetime
- Molecular recognition and thermodynamic meta-stability, just like molecular assembly in plants

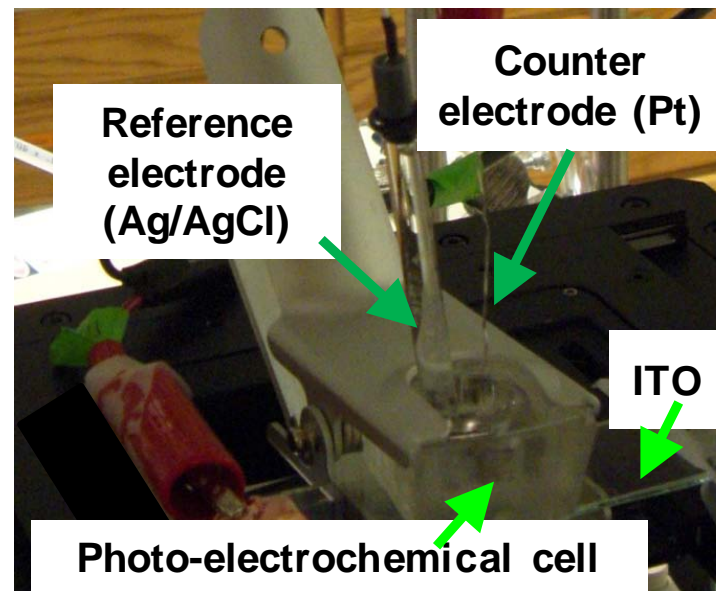
Ham, Choi et al. *Nature Chemistry* (2010)



## Photoelectrochemical measurement

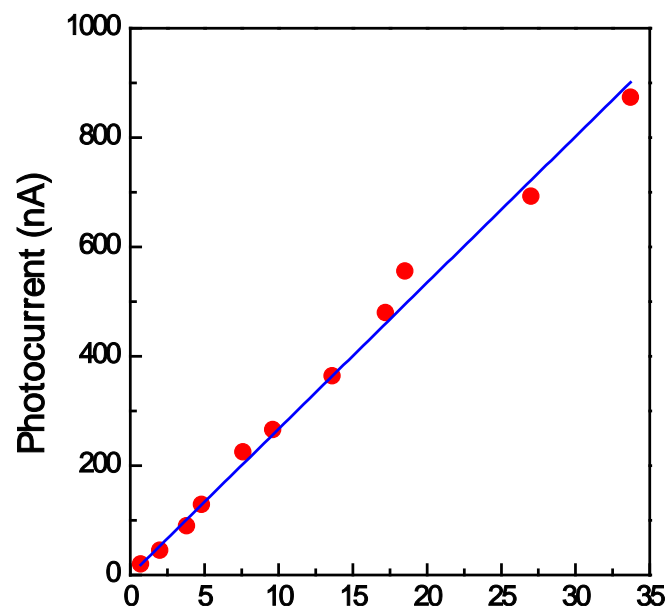
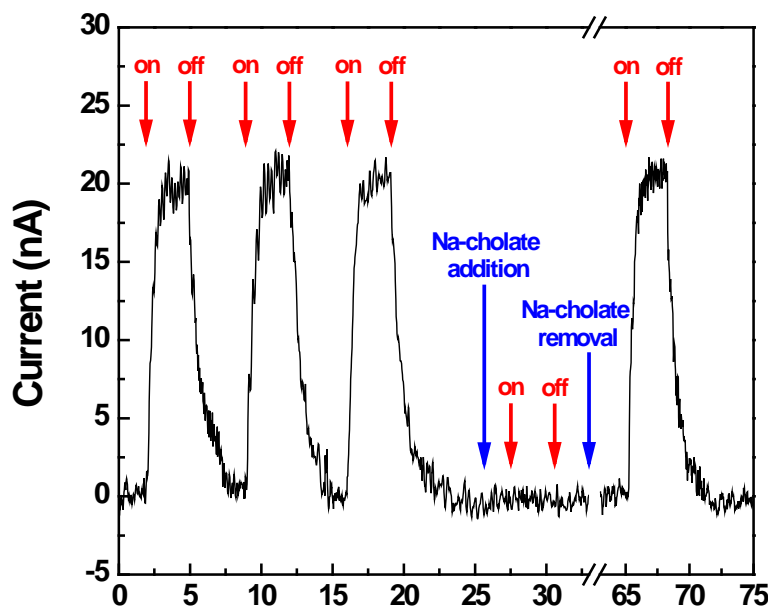


## Photocurrent generation

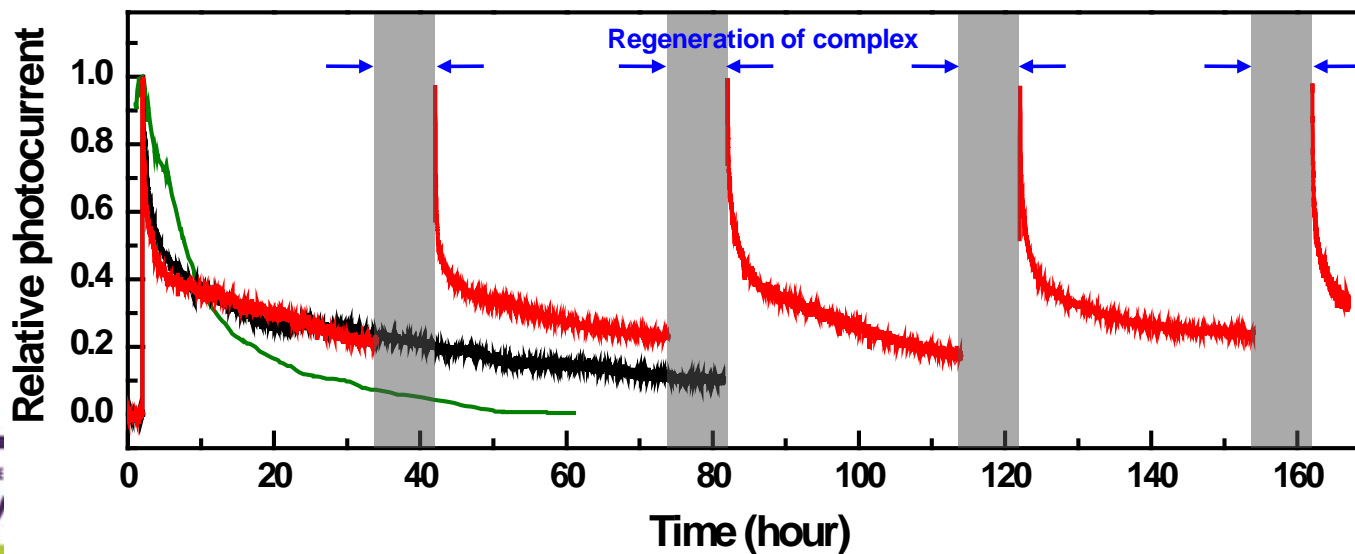


## Double redox mediator system:

- Ubiquinone / ubiquinol
- Ferri- & ferro-cyanide:  $\text{Fe}(\text{CN})_6^{-3/-4}$



Chemically-initiated self-regeneration during light harvesting



Ham, Choi et al.  
*Nature Chemistry*  
(2010)





## Acknowledgements

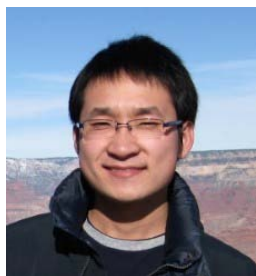
### Graduate students



Benjamin Baker



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### Undergraduate students



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Dane Sauffer



Janette Salgado



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