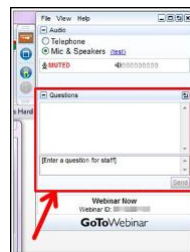
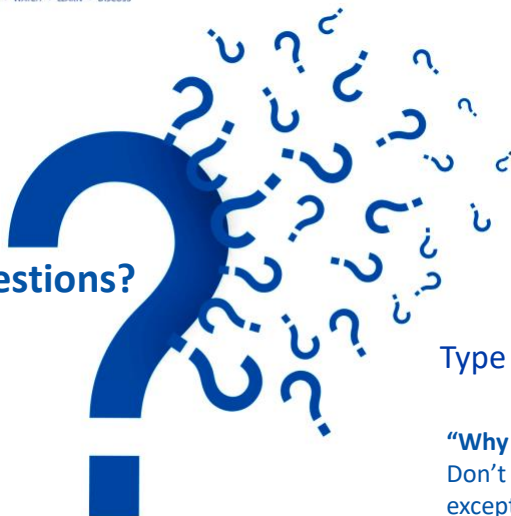




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Inspiring Hero Stories



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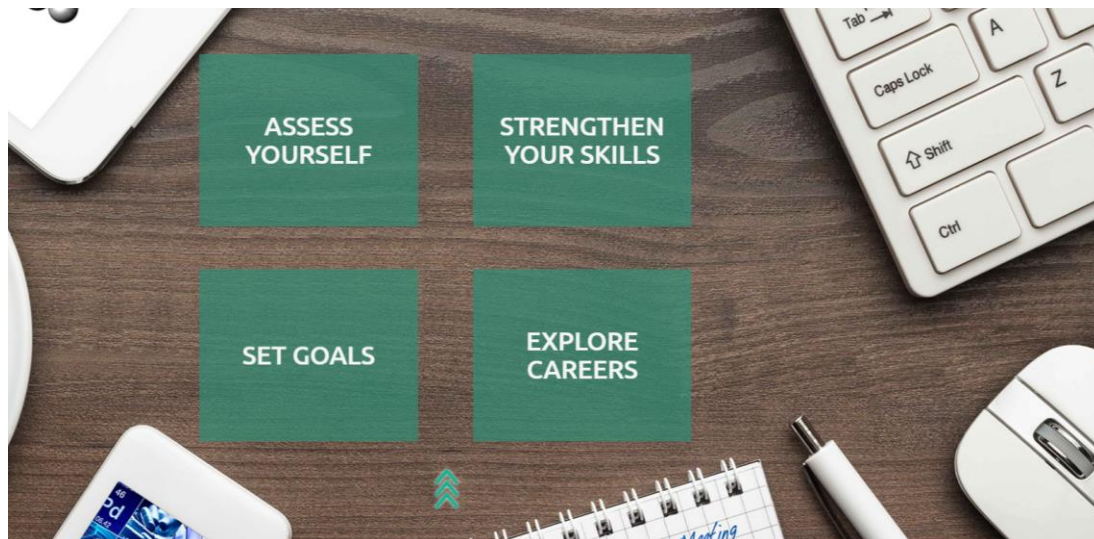
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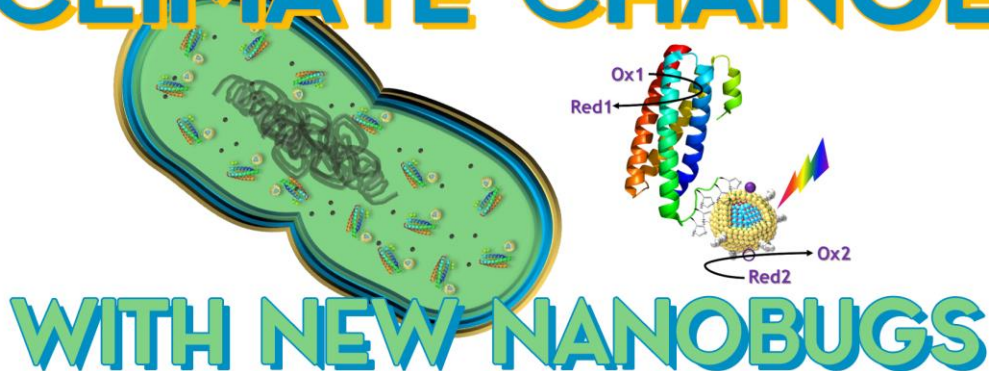
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11

ACS Industry Member Programs

# COMBATING CLIMATE CHANGE



# WITH NEW NANOBUGS

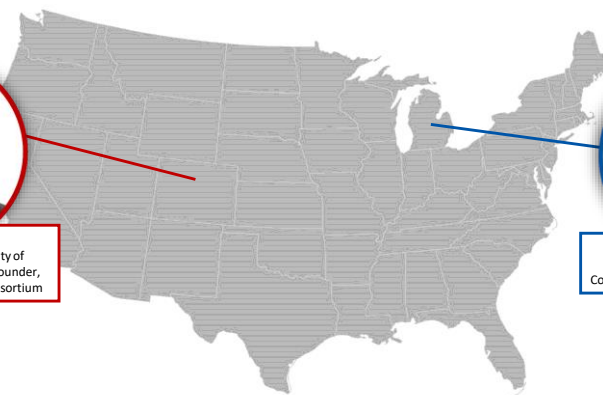
THIS ACS WEBINAR WILL BEGIN SHORTLY...

12

## Combating Climate Change with New Nanobugs: Teaching Bacteria to Eat Carbon Dioxide and Light with Quantum Dots



**Prashant Nagpal**  
 Assistant Professor, University of Colorado Boulder and the Co-Founder, Antimicrobial Regeneration Consortium



**Mark Jones**  
 Executive External Strategy and Communications Fellow, Dow Chemical

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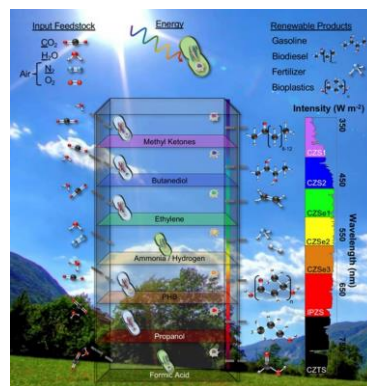
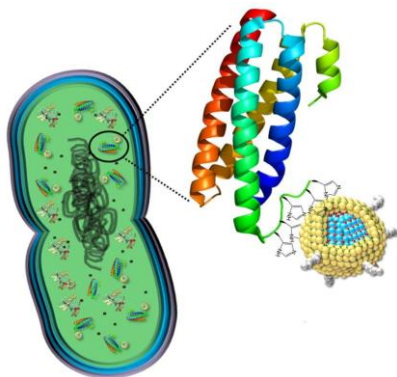
13

## Combating Climate Change with New Nanobugs: Teaching Bacteria to Eat Carbon Dioxide and Light with Quantum Dots



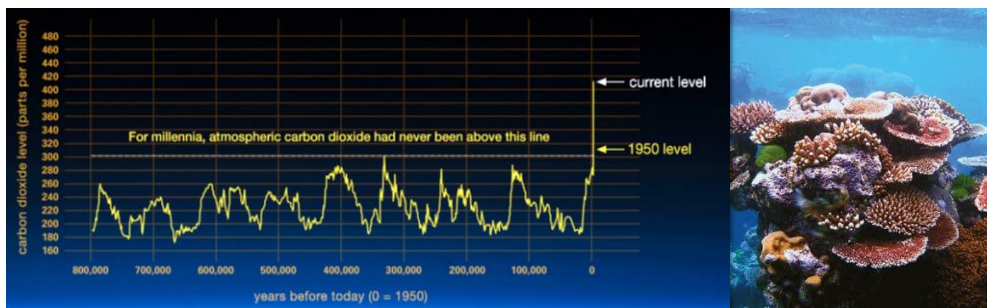
**Prashant Nagpal**

Department of Chemical and Biological Engineering  
 Renewable and Sustainable Energy Institute (RASEI)  
 Materials Science and Engineering  
 University of Colorado Boulder  
[www.colorado.edu/lab/nagpal](http://www.colorado.edu/lab/nagpal)



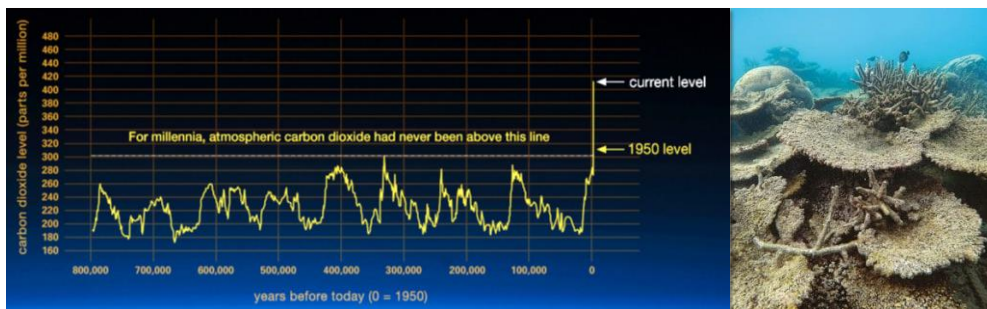
Antimicrobial Regeneration Consortium, ARC  
[www.amrconsortium.org](http://www.amrconsortium.org)

## Combating Climate Change: Feasible?



<https://climate.nasa.gov/evidence>

## Combating Climate Change: Feasible?



**CO<sub>2</sub> at 408 ppm:** Highest in 3 million years  
17/18 warmest years since 2000

**800 million people:** 11% of the world's population vulnerable to climate change

**Global carbon emissions 2018:**  
All-time high of **37.1bn tonnes**

<https://climate.nasa.gov/evidence>



## Combating Climate Change: Feasible?



70% of Earth's oxygen comes from oceans...

By 2050, plastic > fish in oceans by weight

We produce ~**381 million tonnes** of plastic each year

<https://www.unenvironment.org/interactive/beat-plastic-pollution>

### Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



**The amount of plastic waste each year (381 million tonnes) is equivalent to the weight of how many people?**

- Few thousand people
- Population of a large city
- Population of a large country
- Almost entire human population

*\* If your answer differs greatly from the choices above tell us in the chat!*

# Combating Climate Change: Feasible?

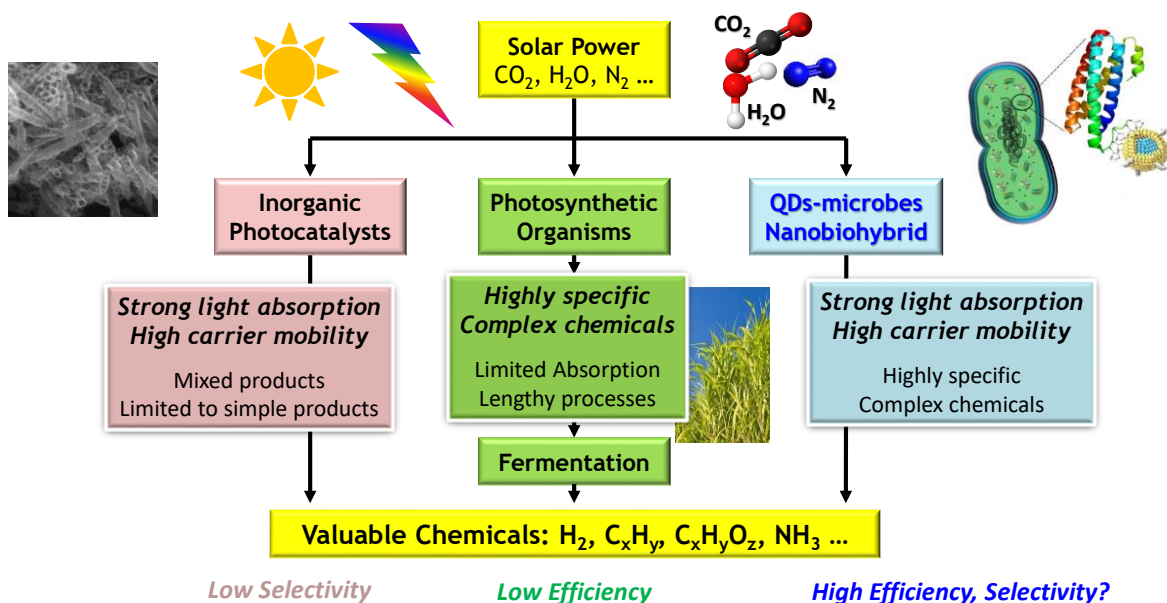


**Answer: Almost entire human population**

381 million tonnes =  $381 \times 10^9$  kg

Assuming an average human weight of 75 kg

381 million tonnes =  $381 \times 10^9 / 75 = 5.08$  billion people  
or ~2/3 of entire human population

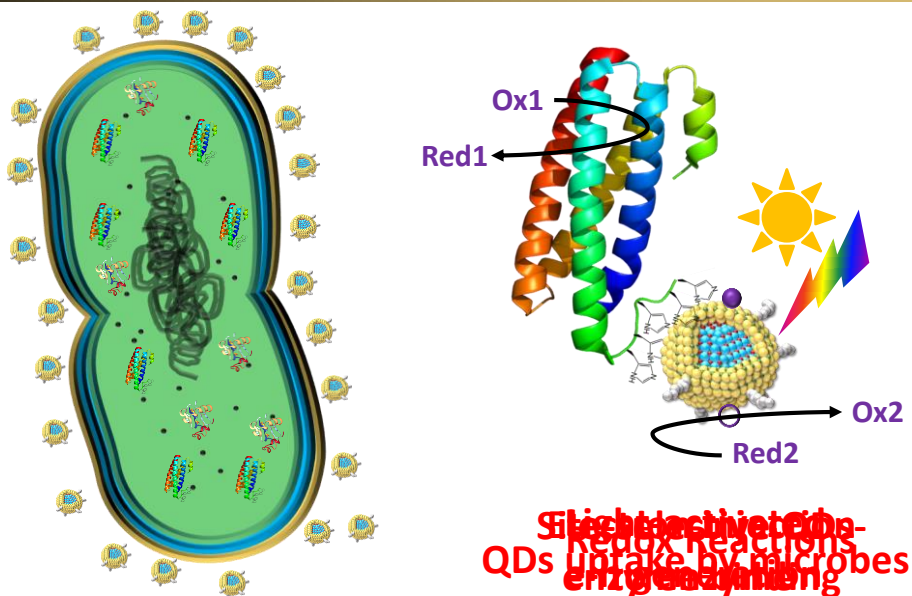


Singh, Beltran, Ribot, Nagpal\*, *Nano Lett.*, 14, 597 (2014)  
Alivov, Singh, Ding, Cerkovnik, Nagpal\*, *Nanoscale*, 6, 18039 (2014)  
Sun, Ding, Goodman, Funke, Nagpal\*, *Nanoscale*, 6, 12450 (2014)

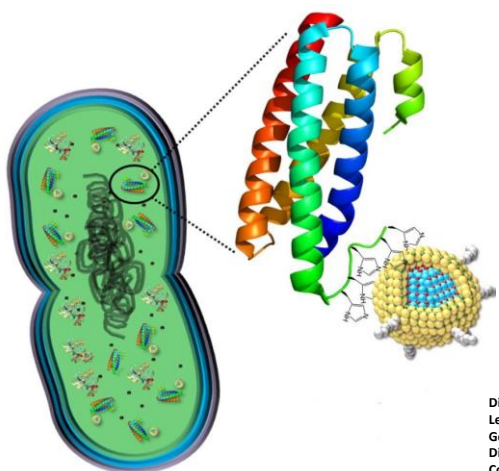
Ding, Nagpal\*, *Nanoscale*, 8, 17496 (2016)  
Ding, Nagpal\*, *Phys. Chem. Chem. Phys.*, 19, 10042 (2017)

Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## How can we make Nanobugs



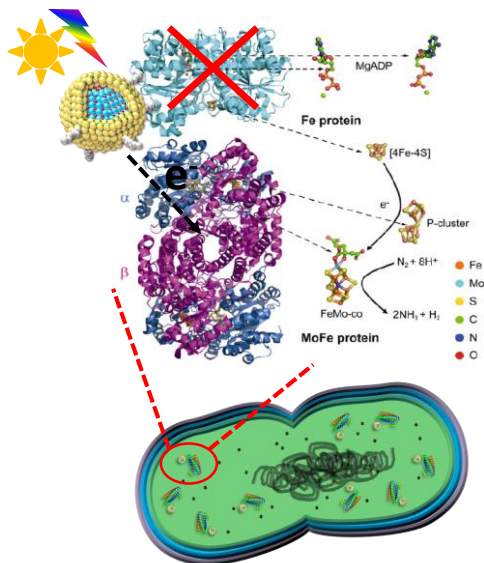
## Challenges



- Quantum Dot (QD) uptake
- Site-specific QDs-enzyme binding
- Efficient electron transfer
- QDs Stability
- Low QDs Toxicity
- Balanced Electron Flux...

Ding, Bertram, Eckert, Bommareddy, Patel, Conrady, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)  
 Levy, Chowdhury, Nagpal\*, *J. Biol. Eng.*, 13:48 (2019)  
 Goodman, Levy, Li, Ding, Courtney, Chowdhury, Erbse, Chatterjee, Nagpal\*, *Front. Chem.*, 6:46,1 (2018)  
 Ding, Nagpal\*, *Phys. Chem. Chem. Phys.*, 19, 10042 (2017)  
 Courtney, Goodman, Nagy, Levy, Bhusal, Madinger, Detweiler, Nagpal\*, Chatterjee\*, *Science Adv.*, 3, e1701776 (2017)  
 Courtney, Goodman, McDaniel, Madinger, Chatterjee\*, Nagpal\*, *Nature Materials*, 15, 529 (2016)  
 Ding, Nagpal\*, *Nanoscale*, 8, 17496 (2016)  
 Goodman, Noh, Singh, Cha, Nagpal\*, *Appl. Phys. Lett.*, 106, 083109 (2015)  
 Goodman, Siu, Singh, Nagpal\*, *Nanoscale*, 7, 18435 (2015)  
 Goodman, Singh, Ribot, Chatterjee, Nagpal\*, *J. Phys. Chem. Lett.*, 5, 3909 (2014)  
 Singh, Beltran, Ribot, Nagpal\*, *Nano Lett.*, 14, 597 (2014)

## Living QD-A. *vinelandii* Nanobugs



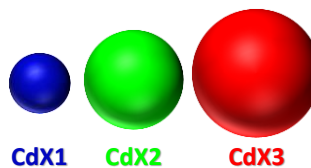
- *Gram-negative diazotroph*
- *Utilizes dinitrogen from air*
- *Can fix nitrogen aerobically*

*Nitrogen Fixation: Methods and Protocols*, Springer, 2011

## Choosing QDs: Material and Size

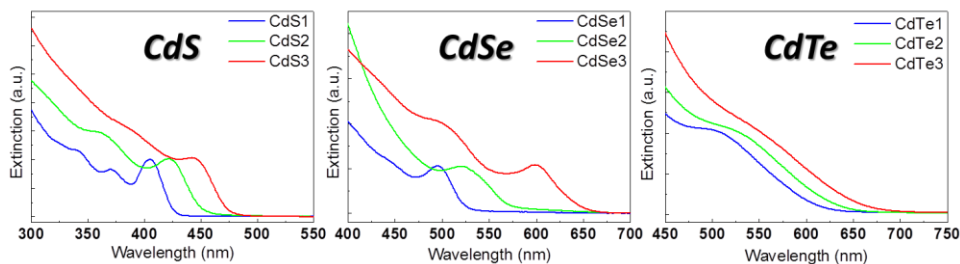


QDs + Purified MFN (1:1, 1  $\mu$ M)  
 Argon Atmosphere  
 100 mM L-ASC, HEPES (pH 7.4)  
 400 nm LED Irradiation  
 TON ~ 10,000 (30 min)



Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Choosing QDs: Material and Size



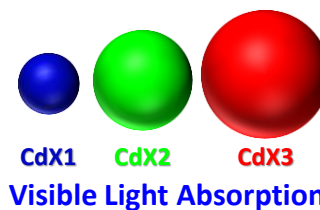
QDs + Purified MFN (1:1, 1  $\mu$ M)

Argon Atmosphere

100 mM L-ASC, HEPES (pH 7.4)

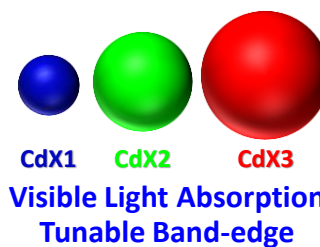
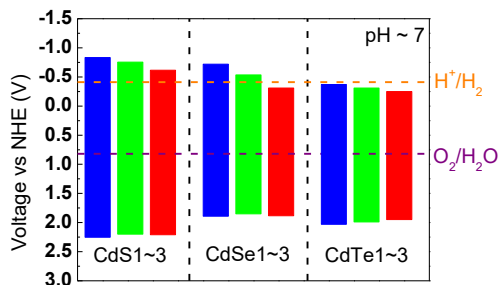
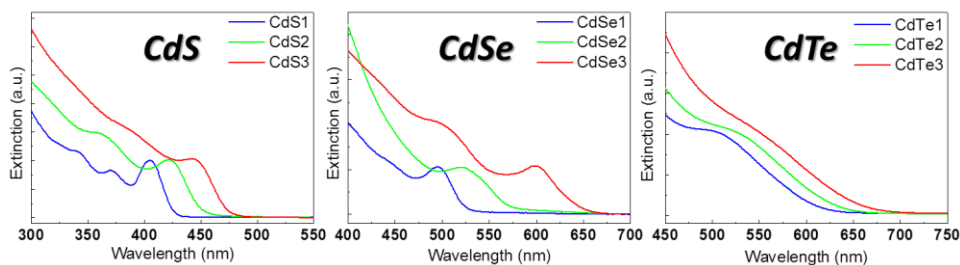
400 nm LED Irradiation

TON  $\sim$  10,000 (30 min)



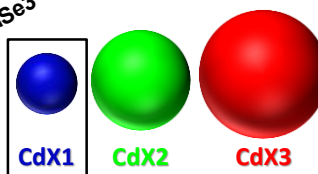
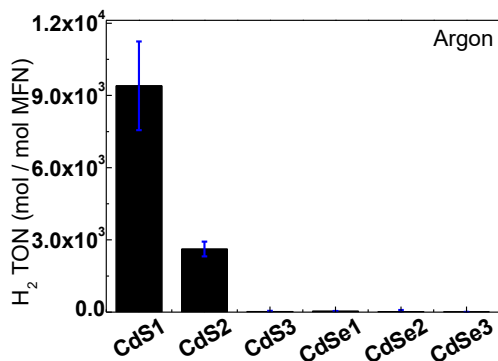
Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Choosing QDs: Material and Size



Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Choosing QDs: Material and Size



Tunable Band-edge

Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

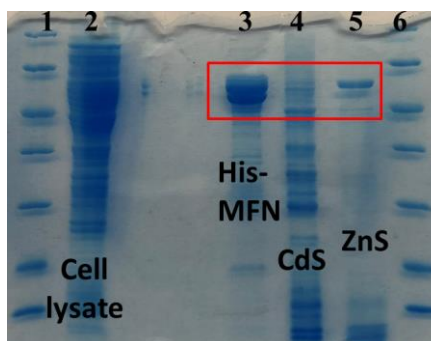
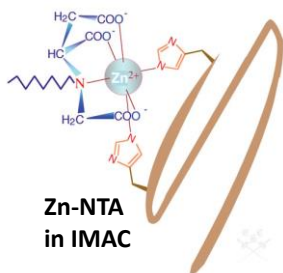
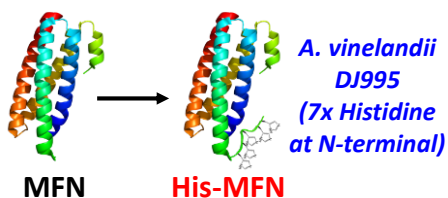
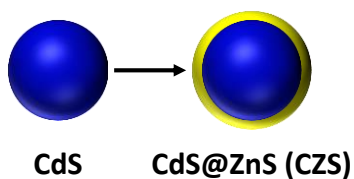
University of Colorado Boulder

Chemical and Biological Engineering

Renewable and Sustainable Energy Institute

27

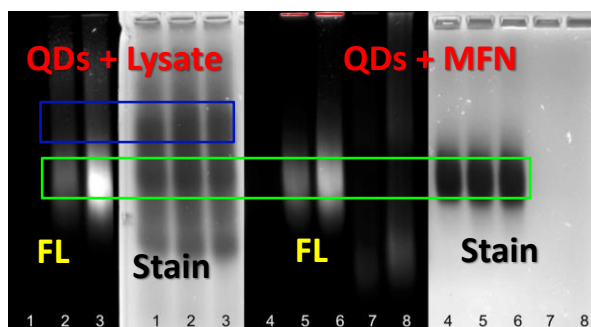
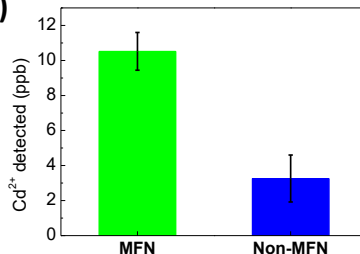
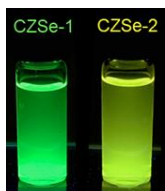
## Selective QDs-Enzyme Coupling: Zn-Histidine



## Selective QDs-Enzyme Coupling: Zn-Histidine



### CdSe@ZnS (CZSe)

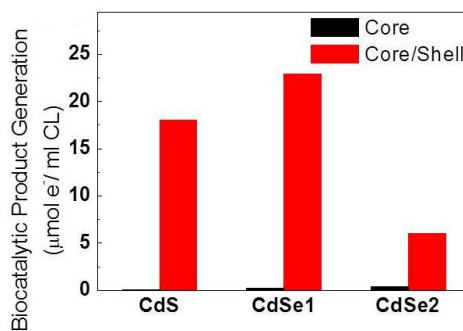


## Selective QDs-Enzyme Coupling: Zn-Histidine



QDs + Cell Lysate  
Argon Atmosphere  
Light Irradiation

*Yield increase significantly  
after ZnS coating*



## Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



If a nanobug has ~10,000 copies of an enzyme of interest, and chosen QD has molecular weight of 120 g/mol, **how much QDs are required to make 1 mol of nanobugs?**

- 1200 kg of QDs
- $6.023 \times 10^{24}$  kgs
- 120 kg
- Need more information

*\* If your answer differs greatly from the choices above tell us in the chat!*

## How much QDs are required to make a nanobug?



**Answer: 1200 kgs**

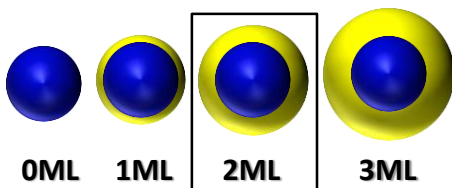
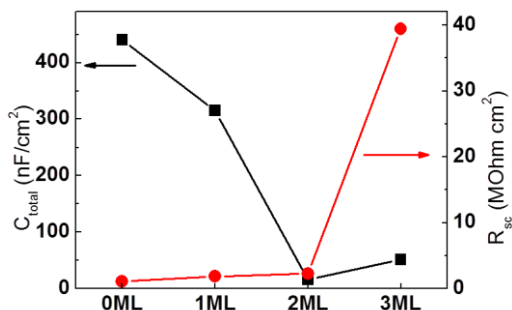
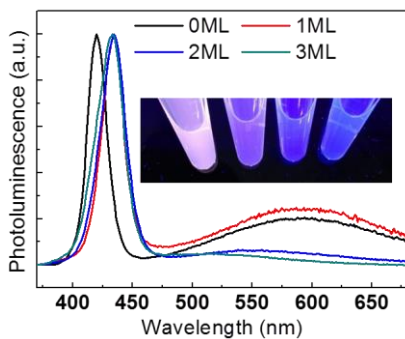
1 mol of nanobugs requires 10,000 mols of QDs (to saturate every enzyme)

Using QD molecular weight (120 g/mol)

To make 1 mol of nanobugs =  $10,000 \times 120\text{g} = 1200 \text{ kgs}$



## Tuning the Shell Thickness

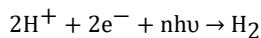
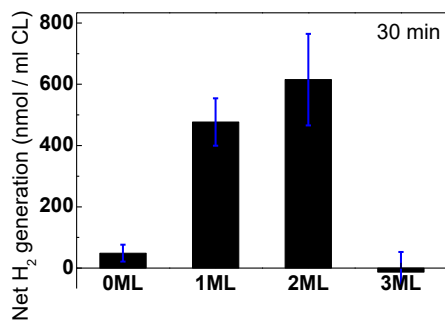


**Effective Surface Passivation**  
**Small Electron Transport Barrier**

Ding, Nagpal\*, *Nanoscale*, 8, 17496 (2016)

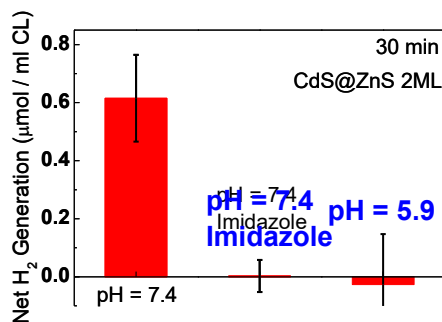
Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Light-driven QD-Enzyme Biocatalysis

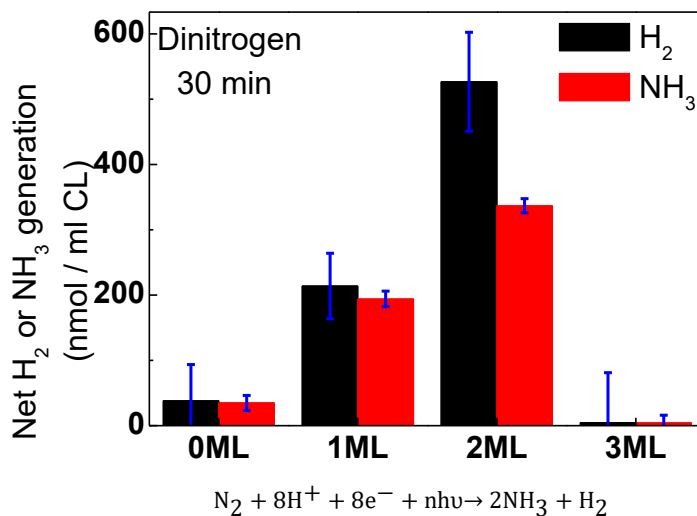


**Imidazole:**  
Competitively binds to zinc

**Higher acidity:**  
Protonates histidine

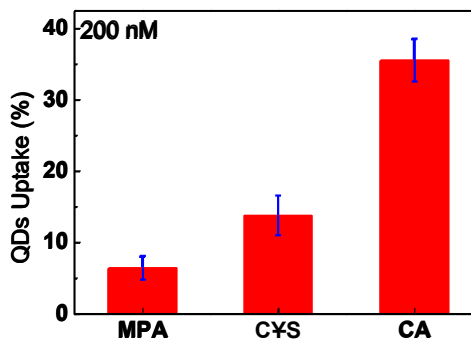
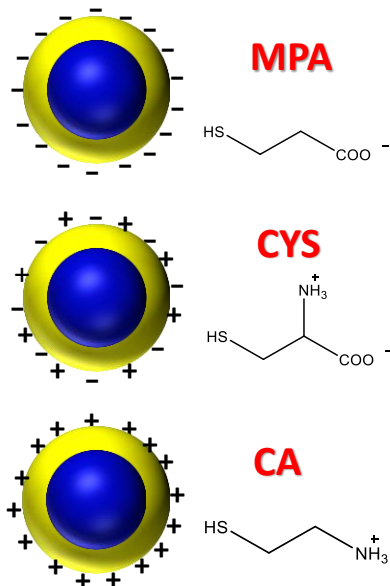


## Light-driven Air-Water Reduction



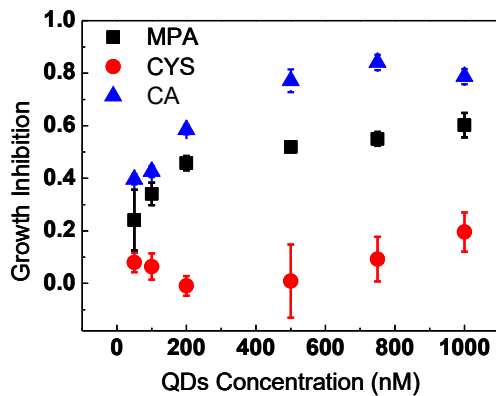
Ding, Bertram, Eckert, Bommareddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Intracellular Uptake of QDs



Courtney, Goodman, McDaniel, Madinger, Chatterjee\*, Nagpal\*, *Nature Materials*, 15, 529 (2016)  
 Courtney, Goodman, Nagy, Levy, Bhusal, Madinger, Detweiler, Nagpal\*, Chatterjee\*, *Science Adv.*, 3, e1701776 (2017)  
 Goodman, Levy, Li, Ding, Courtney, Chowdhury, Erbse, Chatterjee, Nagpal\*, *Front. Chem.*, 6, 46 (2018)  
 Levy, Chowdhury, Nagpal\*, *J. Biol. Eng.*, 13:48 (2019)  
 Ding, Bertram, Eckert, Bommareddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

## Maintaining Cell Viability

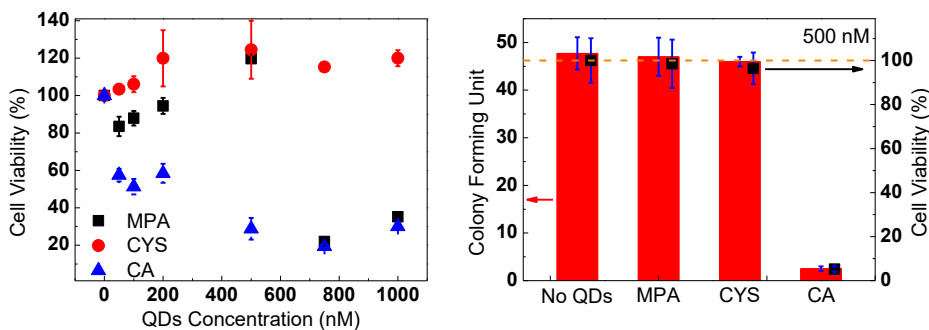


**MPA (-):** Some toxicity

**CYS (+-):** Non-toxic

**CA (+):** Highly toxic

## Maintaining Cell Viability

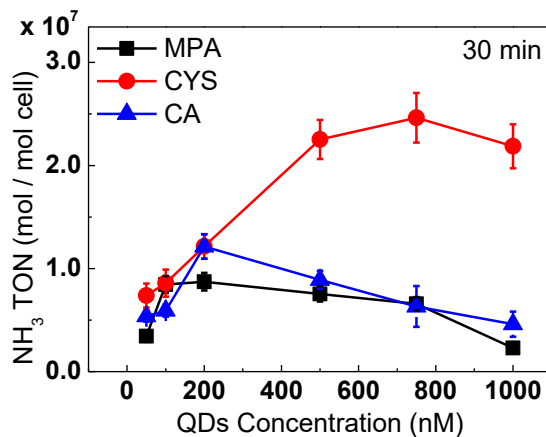


**MPA (-):** Toxic at high concentration

**CYS (+-):** Non-toxic

**CA (+):** Toxic even at low concentration

## Light-driven Selective Catalysis by Nanobugs

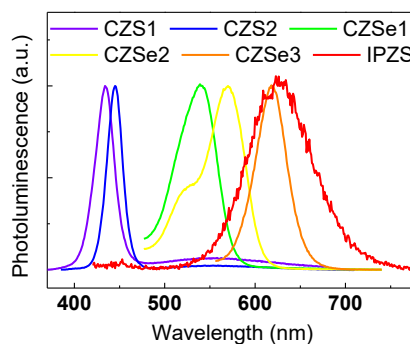
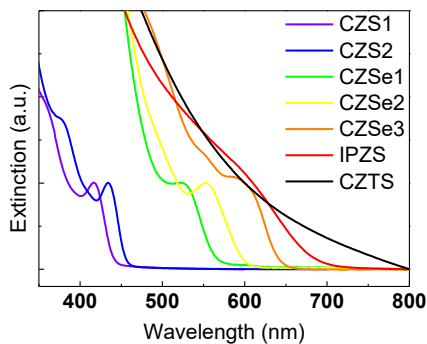


**MPA (-):**  
*Low uptake*  
*Toxicity at high conc.*

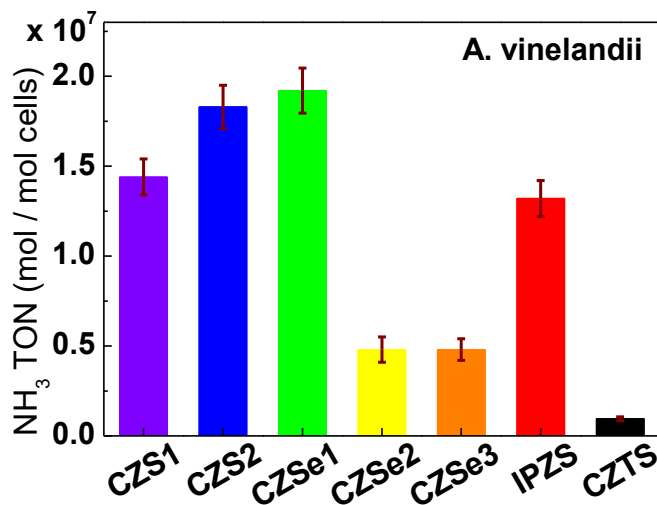
**CA (+):**  
*High uptake*  
*Highly Toxic*

**CYS (+-):**  
*Moderate uptake*  
*Non-toxic*

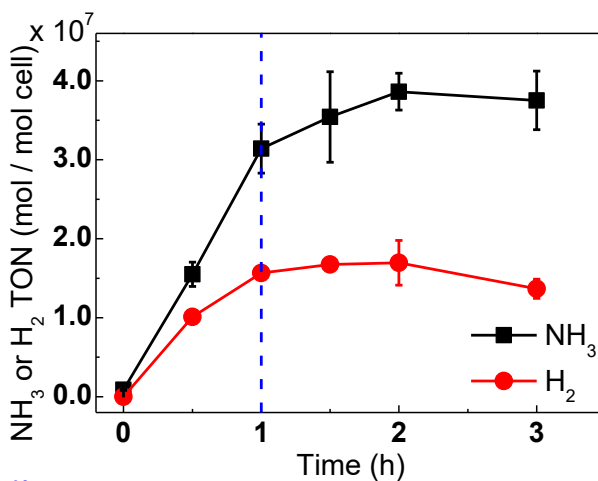
## Expand the Absorption Spectrum



## Expand the Absorption Spectrum



## Nanobug Factories



Like Solar Cells

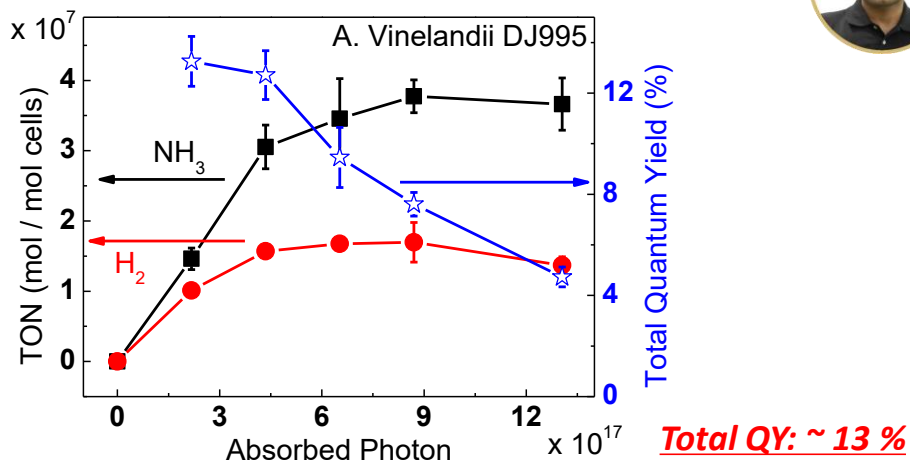
**TOF ( $s^{-1}$ )  
in 1 h:**

**8730 for  $\text{NH}_3$   
4350 for  $\text{H}_2$**

**Total QY: ~ 13 %**

Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal<sup>\*</sup>, *J. Am. Chem. Soc.*, 141, 10272 (2019)

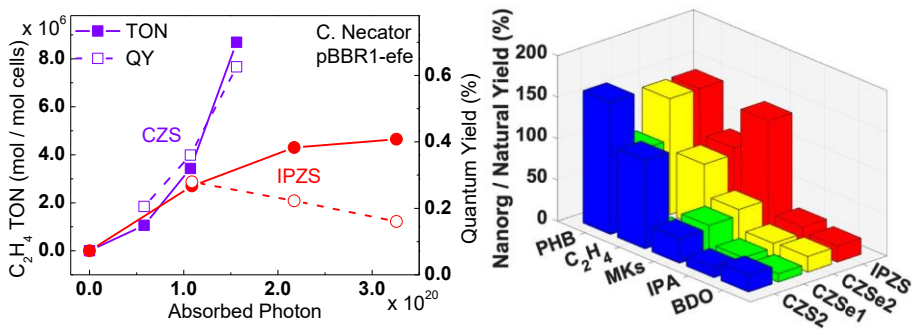
## Nanobug Factories



Conversion Limited by Enzyme turnover Max theoretical QY: 16-20%

Ding, Bertram, Eckert, Bommarreddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)

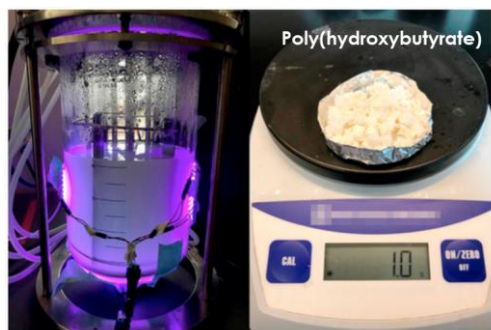
## Nanobug Factories



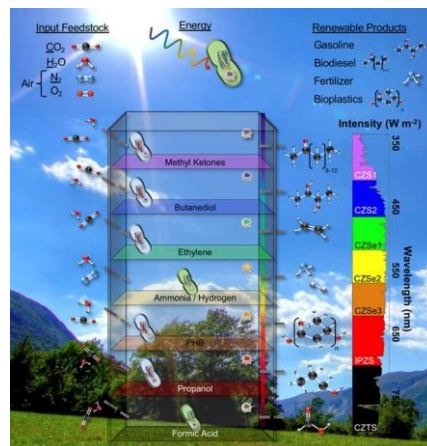
- Range of fuels, fertilizers, preservatives, bioplastics
- Nanobugs utilize  $\text{CO}_2$ , air, and sunlight
- Process can be scaled up efficiently
- Tandem Cells for optimal utilization of sunlight

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## Nanobug Factories

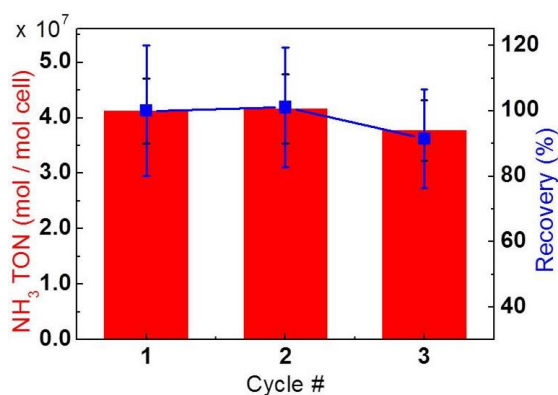


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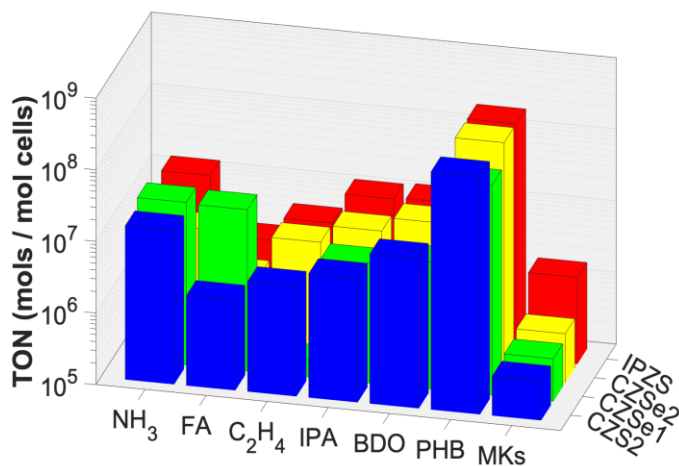
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## Nanobug Factories



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# Nanobug Factories



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47

48

## Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT



**If we convert all emitted CO<sub>2</sub>/year (37.1 bn tonnes) using nanobugs, how much volume of nanobugs would it require?**

Nanobugs TON (7.3 × 10<sup>10</sup> mol PHB/mol cells/year)

- A small reservoir or pond
- A large lake
- A whole sea
- An entire ocean

*\* If your answer differs greatly from the choices above tell us in the chat!*



## Combating Climate Change with Nanobugs?



**Answer: A large lake**

$$37.1 \text{ bn tonnes} = 37.1 \times 10^{12} \text{ kg} = 37.1 \times 10^{15} / 44 \text{ mol CO}_2 \\ = 8.43 \times 10^{14} \text{ mol CO}_2$$

$$\text{Using PHB} = 5 \times 10^8 \times 365 \text{ days} / 2.5 \text{ day run/mol cells} \\ \text{TON} (5 \times 10^8 \text{ mol PHB/mol cells/run}) = 7.3 \times 10^{10} \text{ mol PHB/year} \\ = 7.3 \times 10^{10} \times 4 \text{ mol CO}_2/\text{year/mol cells (C}_4\text{H}_6\text{O}_2)$$

$$\text{Total mol cells required} = 8.43 \times 10^{14} / 7.3 \times 10^{10} \times 4 = 2887 \text{ mol}$$

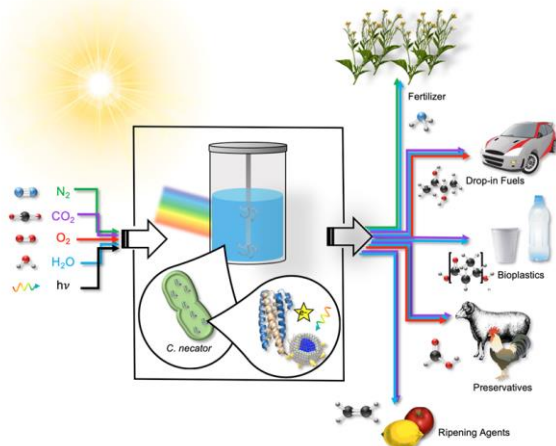
Volume of 1 cell  $\sim 1 \mu\text{m}^3$  or  $10^{-15} \text{ L}$

$$\text{Total volume of cells reqd.} = 1 \times 10^{-18} \text{ m}^3 \times 2887 \times 6.023 \times 10^{23} \\ = 1.74 \times 10^9 \text{ m}^3 = 1.74 \text{ km}^3$$



Approximately a large lake  
(e.g. Navajo Reservoir, Colorado, Lake Minnetonka or Calhoun, Minneapolis)

## Combating Climate Change with Nanobugs



- Efficiency like solar-cells
- Scalable, low-cost fuel and chemical generation
- Easy to implement technology
- Sustainable Nanobug factories

Ding, Bertram, Eckert, Bommareddy, Patel, Conradie, Bryan, Nagpal\*, *J. Am. Chem. Soc.*, 141, 10272 (2019)  
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## Nagpal Group members

### Graduate Students:

- Sam Goodman (PhD., 2016)
- Yuchen Ding (Ph.D., 2017)
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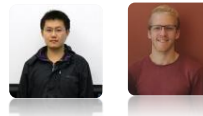
- Dr. Yuchen Ding

### Alumni :

- Dr. Gary Abel
- Dr. Yahya Alivov
- Dr. D.M. Sagar
- Dr. FeiFei Li

### Alumni :

- Dr. Vivek Singh
- Dr. Qi Charles Sun
- Dr. Sajida A. Khan
- Dr. Sepideh Afsari



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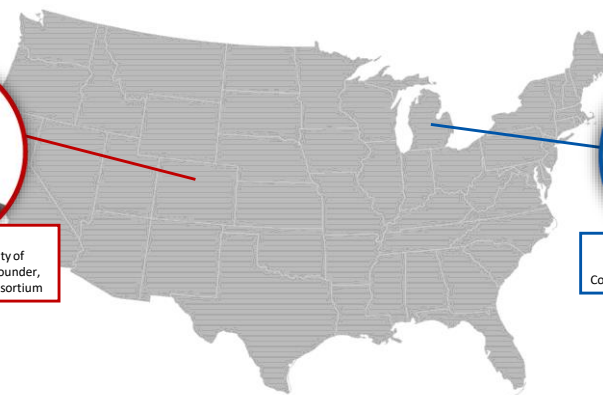
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## Combating Climate Change with New Nanobugs: Teaching Bacteria to Eat Carbon Dioxide and Light with Quantum Dots



**Prashant Nagpal**  
Assistant Professor, University of Colorado Boulder and the Co-Founder, Antimicrobial Regeneration Consortium



**Mark Jones**  
Executive External Strategy and Communications Fellow, Dow Chemical

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