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Professor, Radiology and Biomedical Imaging, Chair, Chemistry and Environmental Safety Committee, University of California, San Francisco
ACS member for 36 years strong!

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ACS Industry Member Programs

**COMBATING CLIMATE CHANGE**

WITH NEW NANOBUGS

THIS ACS WEBINAR WILL BEGIN SHORTLY...
Combating Climate Change with New Nanobugs: Teaching Bacteria to Eat Carbon Dioxide and Light with Quantum Dots

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Combating Climate Change: Feasible?

CO₂ 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

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

---

**Solar Power**

$\text{CO}_2, \text{H}_2\text{O}, \text{N}_2$

**Inorganic Photocatalysts**

**Strong light absorption**

**High carrier mobility**

Mixed products

Limited to simple products

**Photosynthetic Organisms**

**Highly specific**

**Complex chemicals**

Limited Absorption

Lengthy processes

**QDs-microbes Nanobiohybrid**

**Strong light absorption**

**High carrier mobility**

Highly specific

Complex chemicals

**Fermentation**

Valuable Chemicals: $\text{H}_2, \text{C}_x\text{H}_y, \text{C}_x\text{H}_y\text{O}_z, \text{NH}_3$

---

**Low Selectivity**


Alivov, Singh, Ding, Cerkovnik, *Nanopai*, Nanoscale, 6, 18039 (2014)


**Low Efficiency**

Ding, *Nanopai*, Nanoscale, 8, 17496 (2016)


**High Efficiency, Selectivity?**

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, Nagpal*, Nanoscale, 8, 17496 (2016)
Living QD-A. vinelandii Nanobugs

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

Choosing QDs: Material and Size

QDs + Purified MFN (1:1, 1 μM)
Argon Atmosphere
100 mM L-ASC, HEPES (pH 7.4)
400 nm LED Irradiation
TON ~ 10,000 (30 min)
Choosing QDs: Material and Size

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


Choosing QDs: Material and Size

Choosing QDs: Material and Size

![Graph showing H₂ TON (mol/mol MFN) for CdS1, CdS2, CdS3, CdSe1, CdSe2, and CdSe3 with tuning band-edge with CdX1, CdX2, and CdX3.]

Tunable Band-edge


Selective QDs-Enzyme Coupling: Zn-Histidine

 ![Diagram showing CdS to CdS@ZnS (CZS) and MFN to His-MFN with Zn-NTA in IMAC.]

A. vinelandii DJ995
(7x Histidine at N-terminal)
Selective QDs-Enzyme Coupling: Zn-Histidine

CdSe@ZnS (CZSe)

QDs + Lysate
QDs + MFN

QDs + Cell Lysate
Argon Atmosphere
Light Irradiation

Yield increase significantly after ZnS coating
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

![Graph showing photoluminescence spectra for different shell thicknesses.](image)

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

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

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**Light-driven QD-Enzyme Biocatalysis**

**Imidazole:**
Competitively binds to zinc

**Higher acidity:**
Protonates histidine

![Graph showing net H₂ generation.](image)

\[2H^+ + 2e^- + nhv \rightarrow H_2\]
Light-driven Air-Water Reduction

\[
\text{N}_2 + 8\text{H}^+ + 8\text{e}^- + \text{nu} \rightarrow 2\text{NH}_3 + \text{H}_2
\]


Intracellular Uptake of QDs

Maintaining Cell Viability

**MPA (-):** Some toxicity

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

**CA (+):** Highly toxic

---

**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**

---

[Graphs showing extinction and photoluminescence spectra for different compounds]
Expand the Absorption Spectrum

A. vinelandii

NH₃ TON (mol / mol cells)

CZS1, CZS2, CZSe1, CZSe2, CZSe3, IPZS, CZTS

Nanobug Factories

NH₃ or H₂ TON (mol / mol cell)

TOF (s⁻¹) in 1 h:

8730 for NH₃
4350 for H₂

Total QY: ~ 13%

Nanobug Factories

Like Solar Cells

Nanobug Factories

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

Total QY: ~ 13%

Range of fuels, fertilizers, preservatives, bioplastics
Nanobugs utilize CO₂, air, and sunlight
Process can be scaled up efficiently
Tandem Cells for optimal utilization of sunlight

Nanobug Factories

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

If we convert all emitted CO2/year (37.1 bn tonnes) using nanobugs, how much volume of nanobugs would it require?

Nanobugs TON (7.3×1010 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 bn tonnes = $37.1 \times 10^{12}$ kg = $37.1 \times 10^{15}/44$ mol CO$_2$

= $8.43 \times 10^{14}$ mol CO$_2$

Using PHB = $5 \times 10^8 \times 365$ days/2.5 day run/mol cells

TON (5×10$^8$ mol PHB/mol cells/run) = $7.3 \times 10^{10}$ mol PHB/year

= $7.3 \times 10^{10} \times 4$ mol CO$_2$/year/mol cells (C$_4$H$_6$O$_2$)

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

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

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

= $1.74 \times 10^9 m^3$ = 1.74 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, *Nagpal*, Nanoscale, 8, 17496 (2016)


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Nagpal Group members

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**Fan of the Week**

Henry VanBroeklin, PhD  
Professor, Radiology and Biomedical Imaging, Chair, Chemistry and Environmental Safety Committee, University of California, San Francisco  
ACS member for 36 years strong!


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