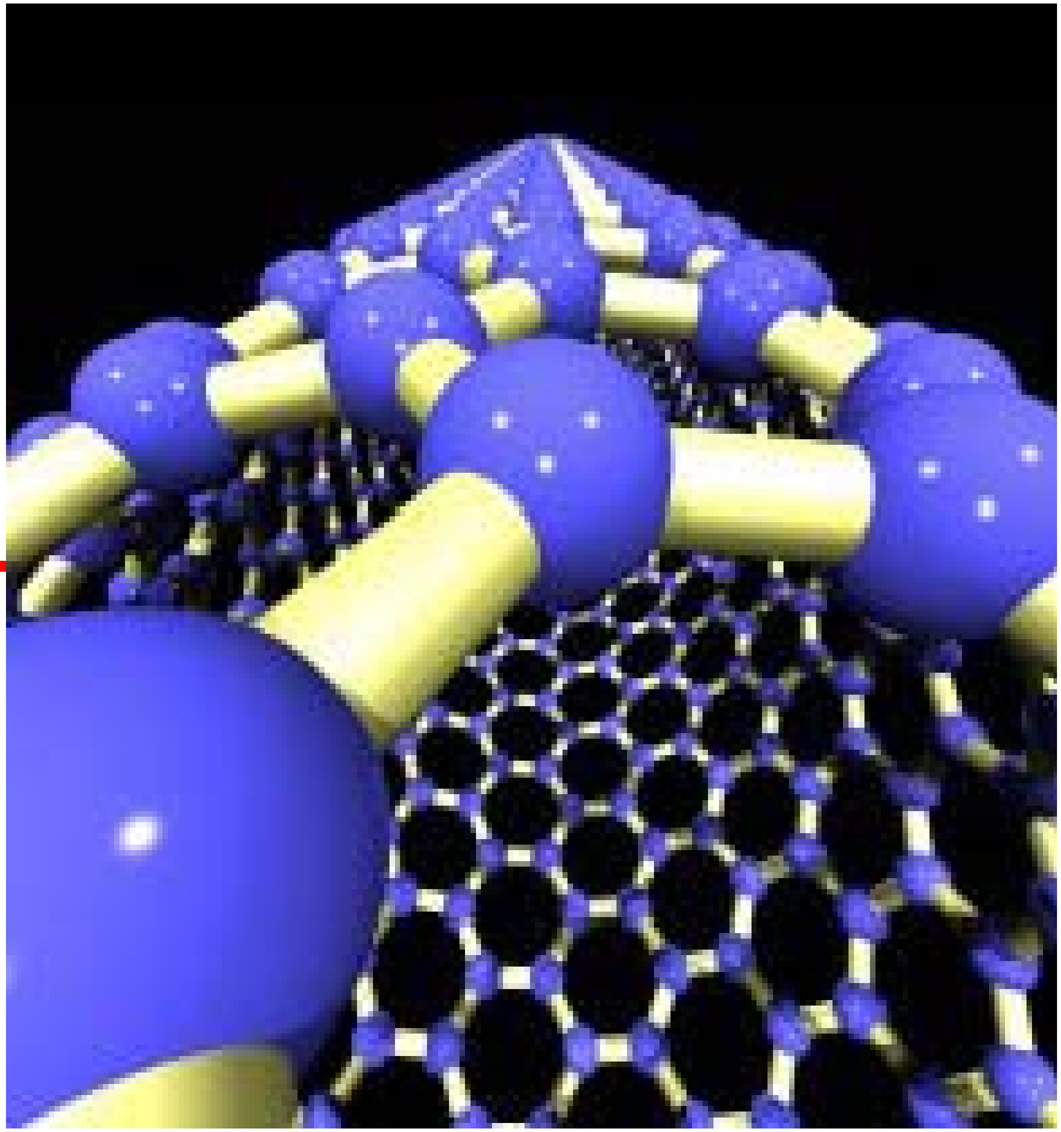
Nanomaterials with Antimicrobial Properties: Mechanisms, Implications and Applications

Synchrotron SOLEIL
Massy, 16 Sep 2009



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RICE   CBEN

Acknowledgements: NSF/CBEN, EPA

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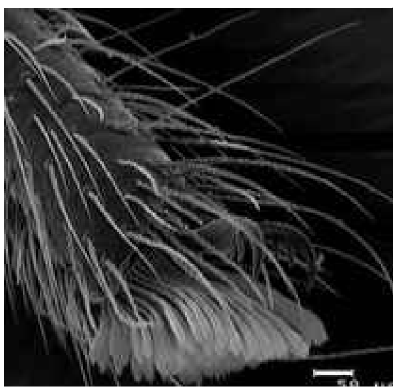
- Lon Wilson
- Mike Wong
- Joe Hughes

Responsible Nanotechnology

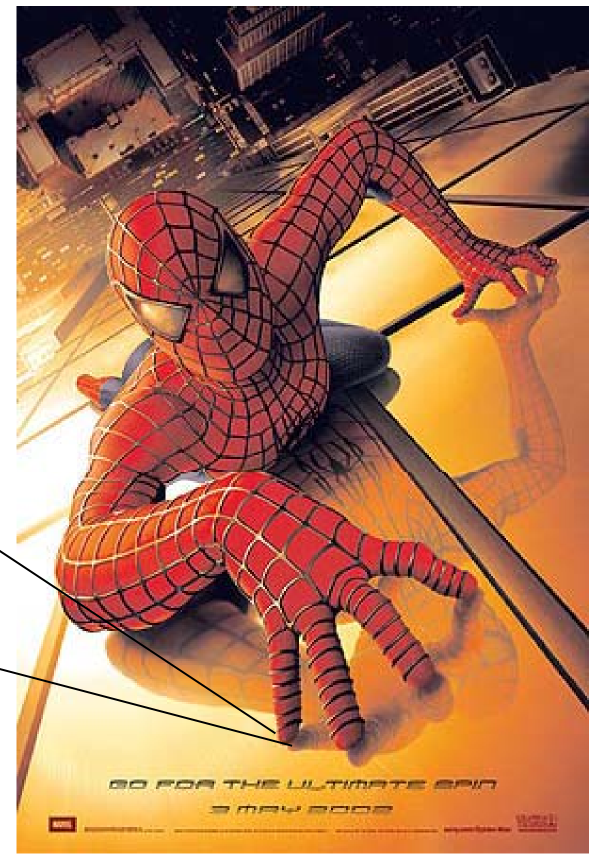
"With Great Power, Comes Great Responsibility"
Uncle Ben to Peter Parker in Spider Man



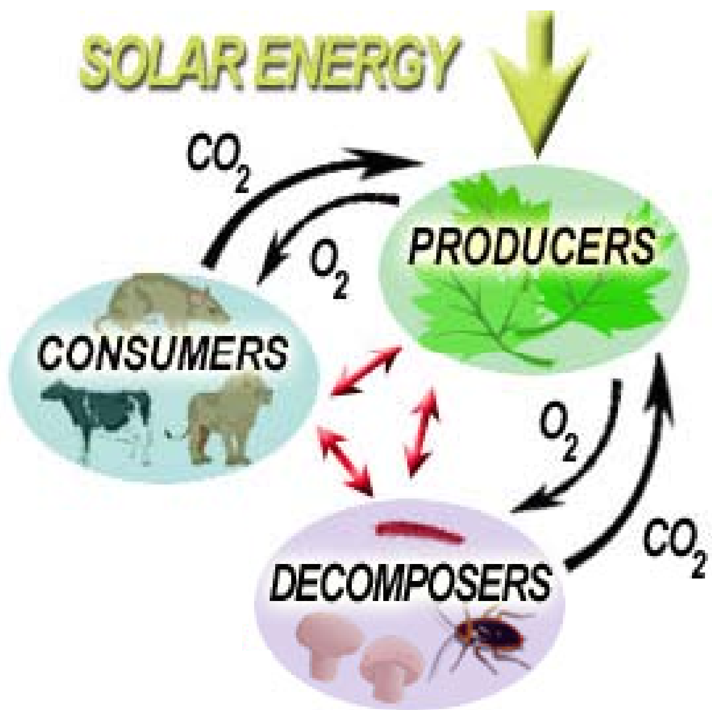
Nanoscale fibers on spider feet

(Dr. Nigel Walker, NIEHS NTP)

Paul Hermann Muller
Thomas Midgley

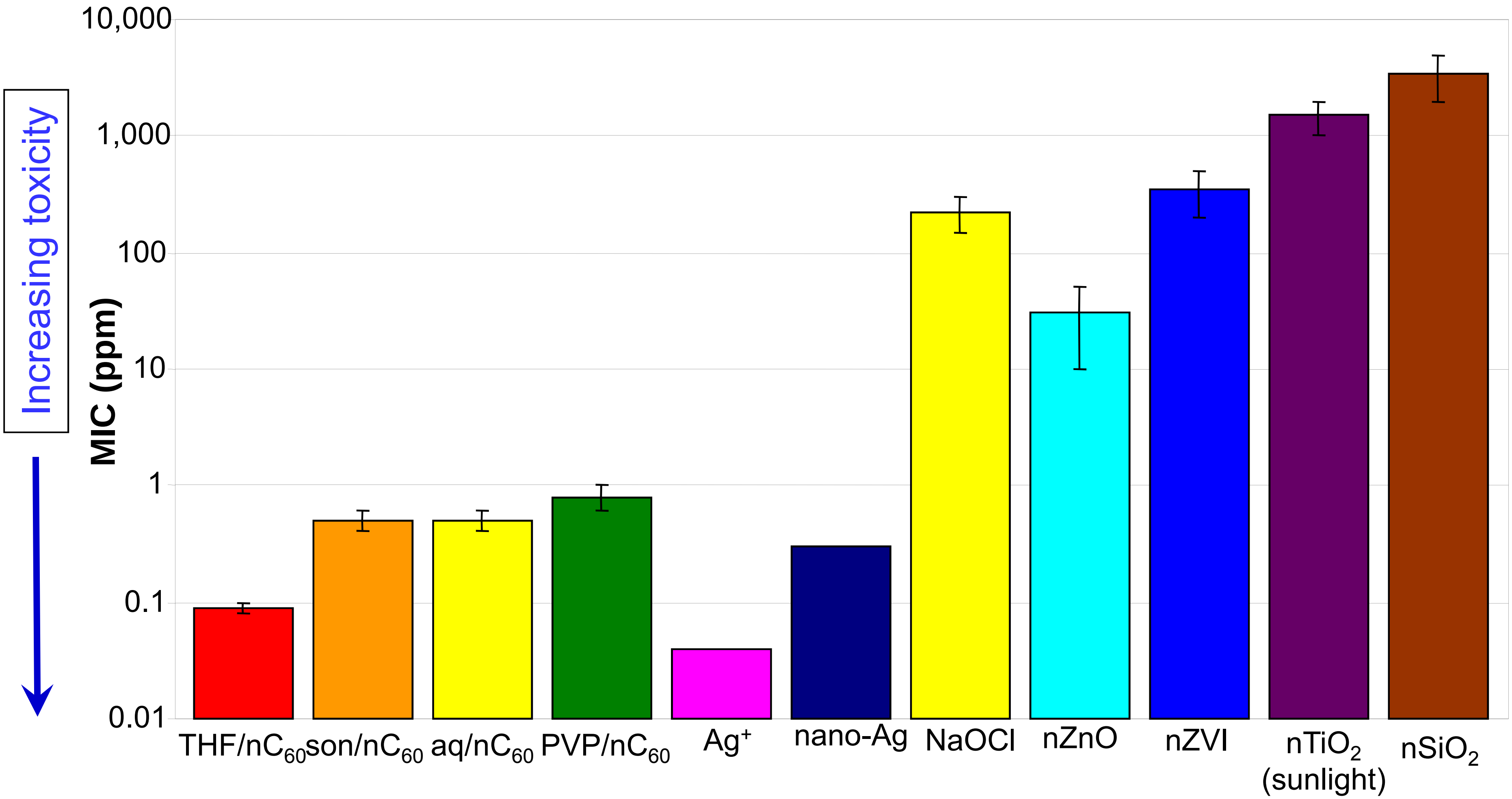


Microbial-nanoparticle Interactions to Inform Risk Assessment



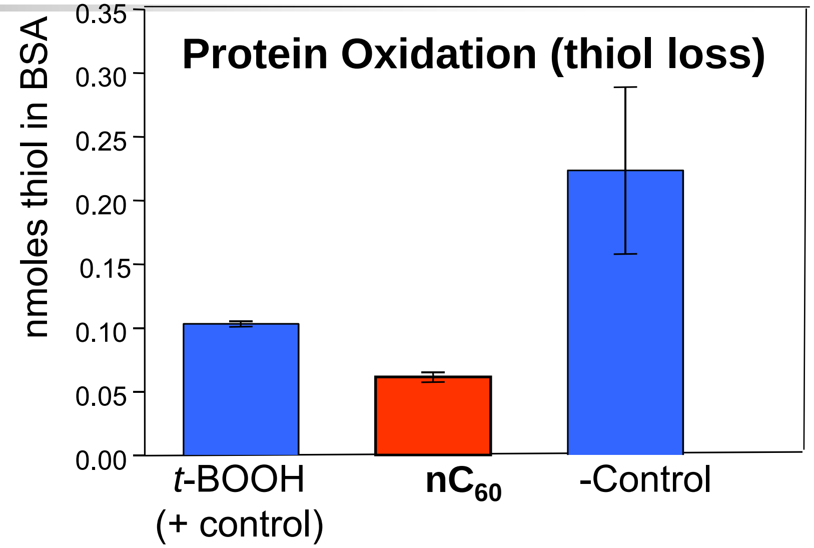
- Bacteria are at the foundation of all ecosystems, and carry out many ecosystem services
- Disposal/discharge can disrupt primary productivity, nutrient cycles, biodegradation, agriculture, etc.
- Antibacterial activity may be indicative of toxicity to higher level organisms

Toxicity of common nanomaterials to *B. subtilis*

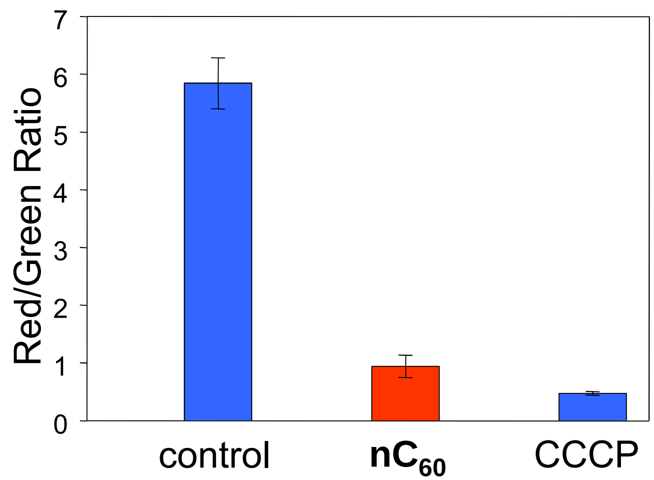


Antibacterial Mechanisms of nC_{60}

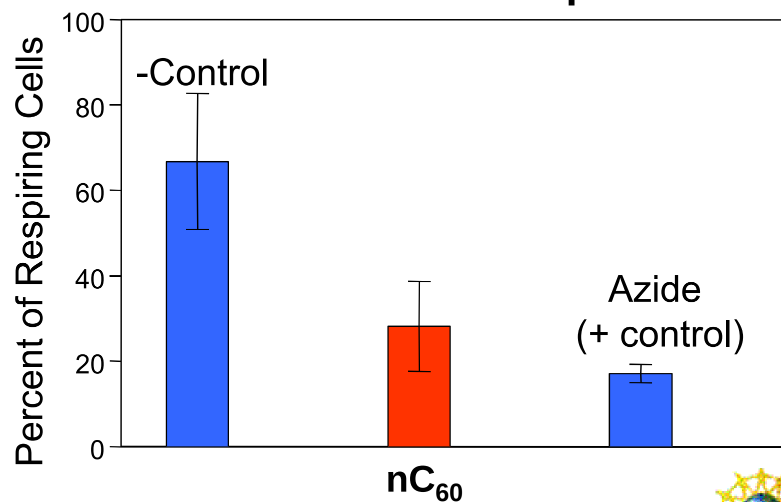
nC_{60} exerts ROS-independent oxidative stress, with evidence of protein oxidation, collapse of membrane potential, and *interruption of cellular respiration & energy transduction*



Decrease in *B. subtilis* membrane potential



Decrease in *E. coli* respiration



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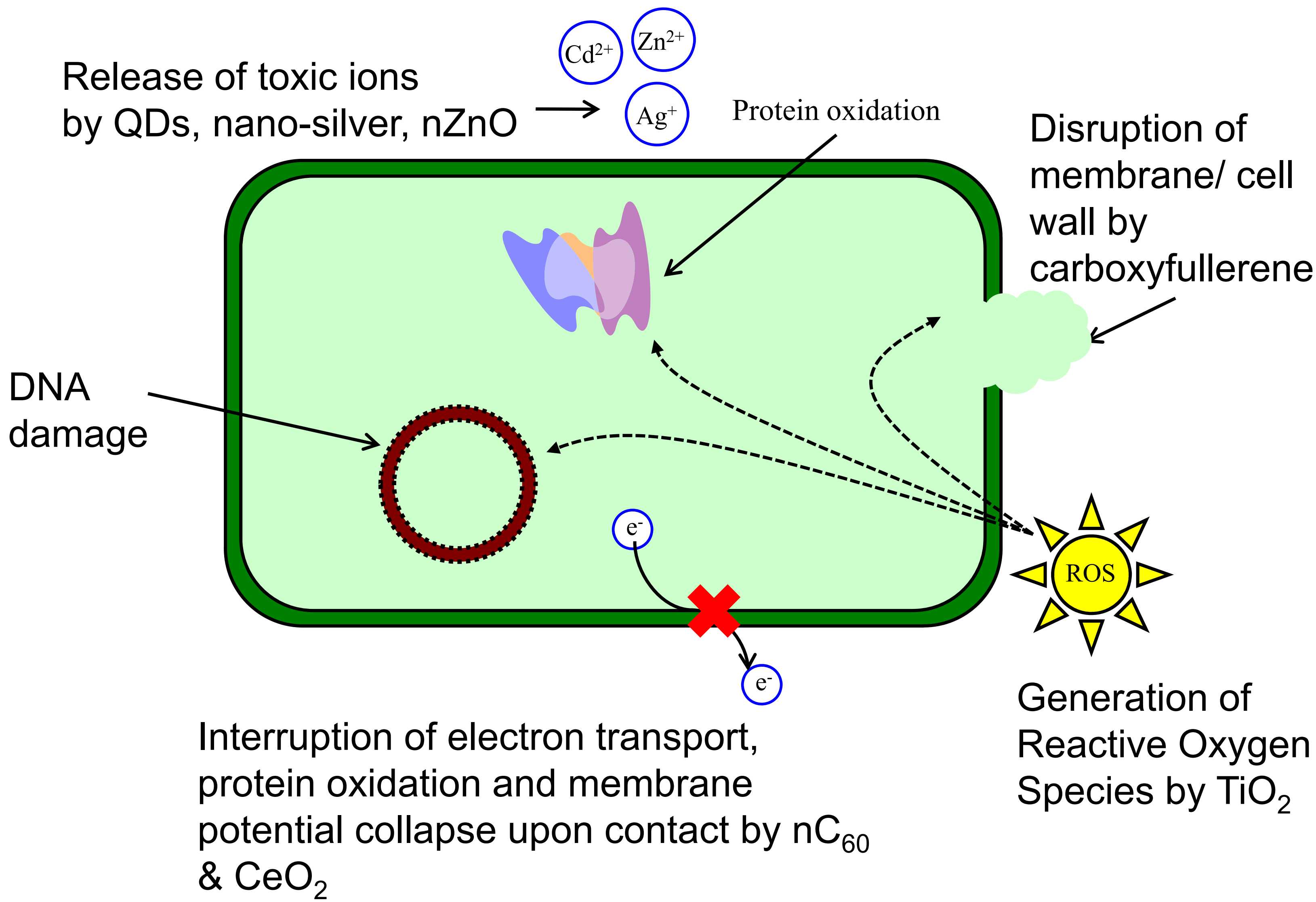
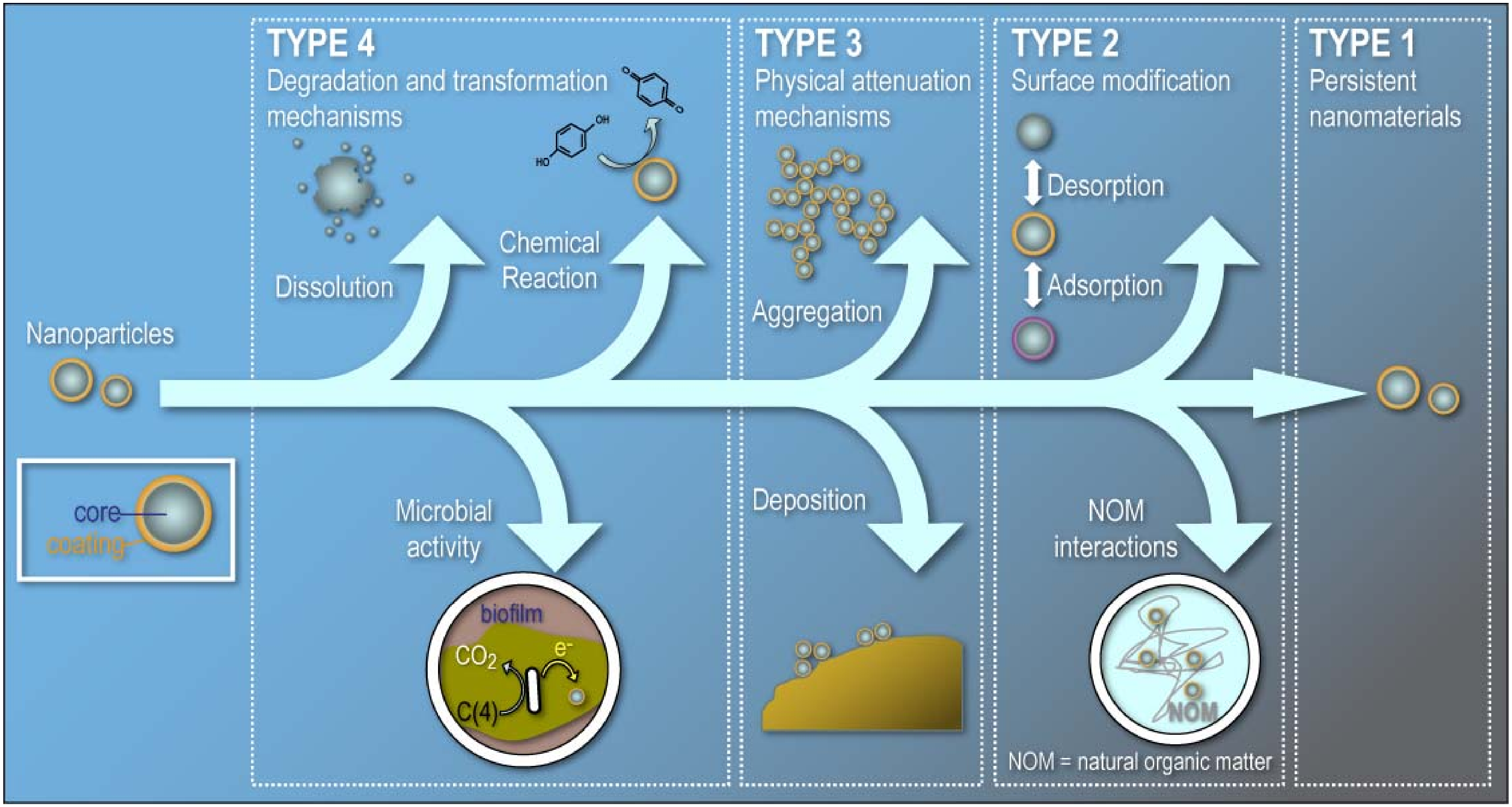
Lyon D.Y., L. Brunet, G.W. Hinkal, M.R. Wiesner, and P.J.J. Alvarez (2008). Nanoletters. 8(5): 1539-1543.
Lyon & Alvarez (2008). ES&T. 42:8127-8132

Bacterial Toxicity Mechanisms

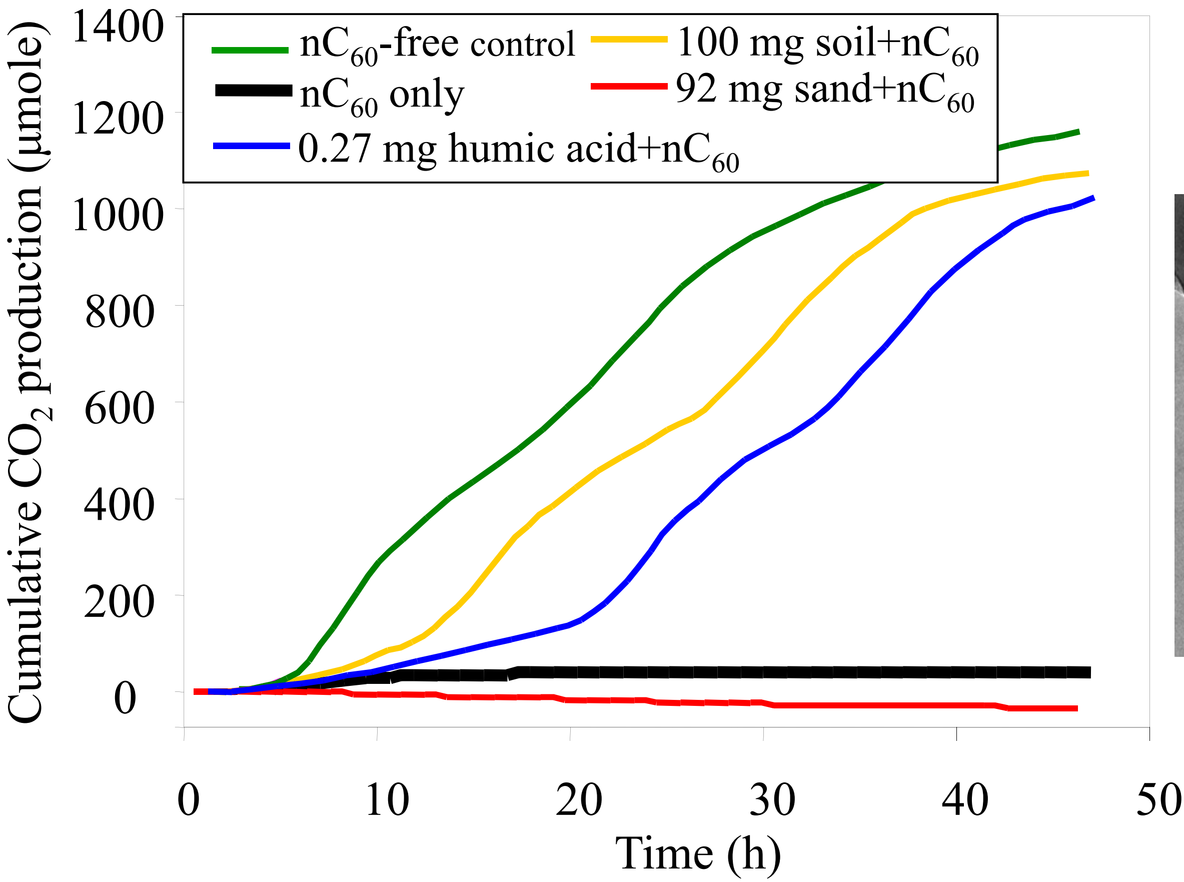


Nanoparticle Modifications in the Environment

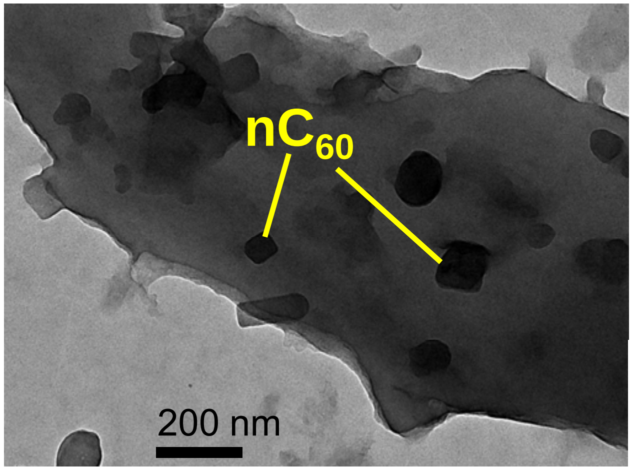


Alvarez P.J.J., V. Colvin, J. Lead and V. Stone (2009). Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano 3(7): 1616-1619.

NOM reduces bioavailability & toxicity of nC_{60}



nC_{60} trapped by humic colloids



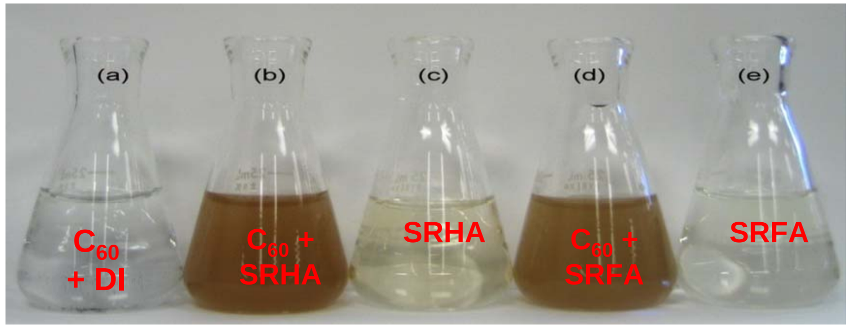
Humic acid concentrations as low as 0.1 mg/L eliminated toxicity

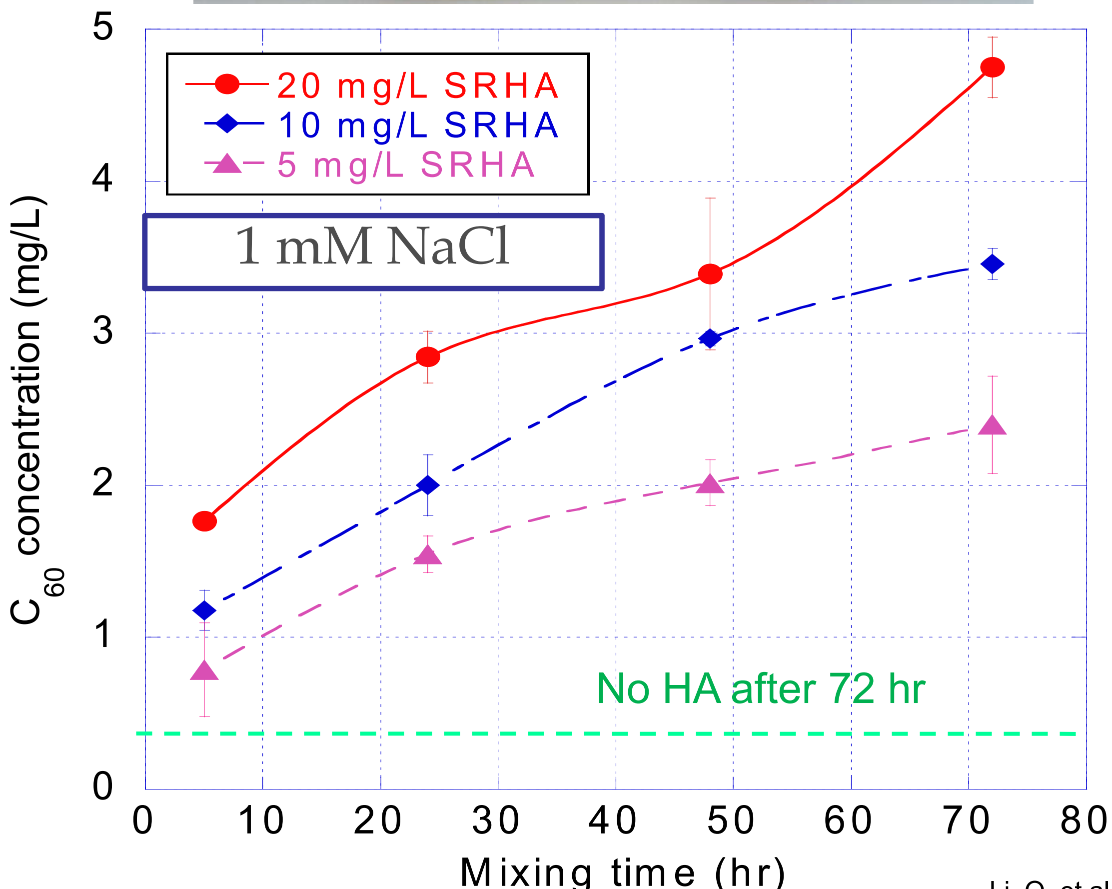
CENTER FOR BIOLOGICAL AND ENVIRONMENTAL NANOTECHNOLOGY CBEN

Li, D., Lyon D.Y., Q. Li, and P.J.J. Alvarez (2008). Environ. Toxicol. Chem. 27(9):1888-1894

Dissolved NOM Enhances C_{60} Dispersion

- *Dispersed C_{60} was measured as dissolved TOC*

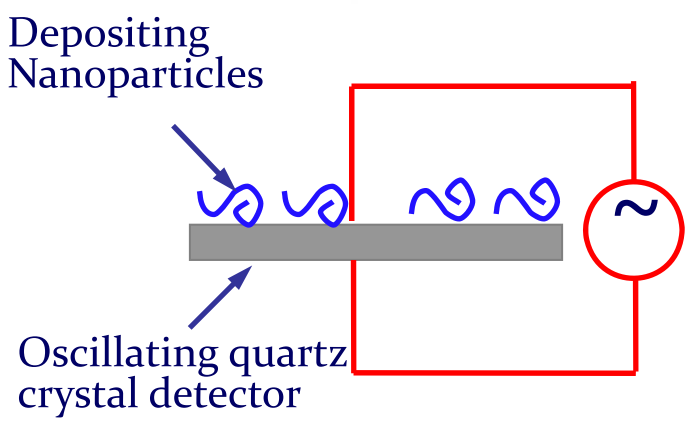


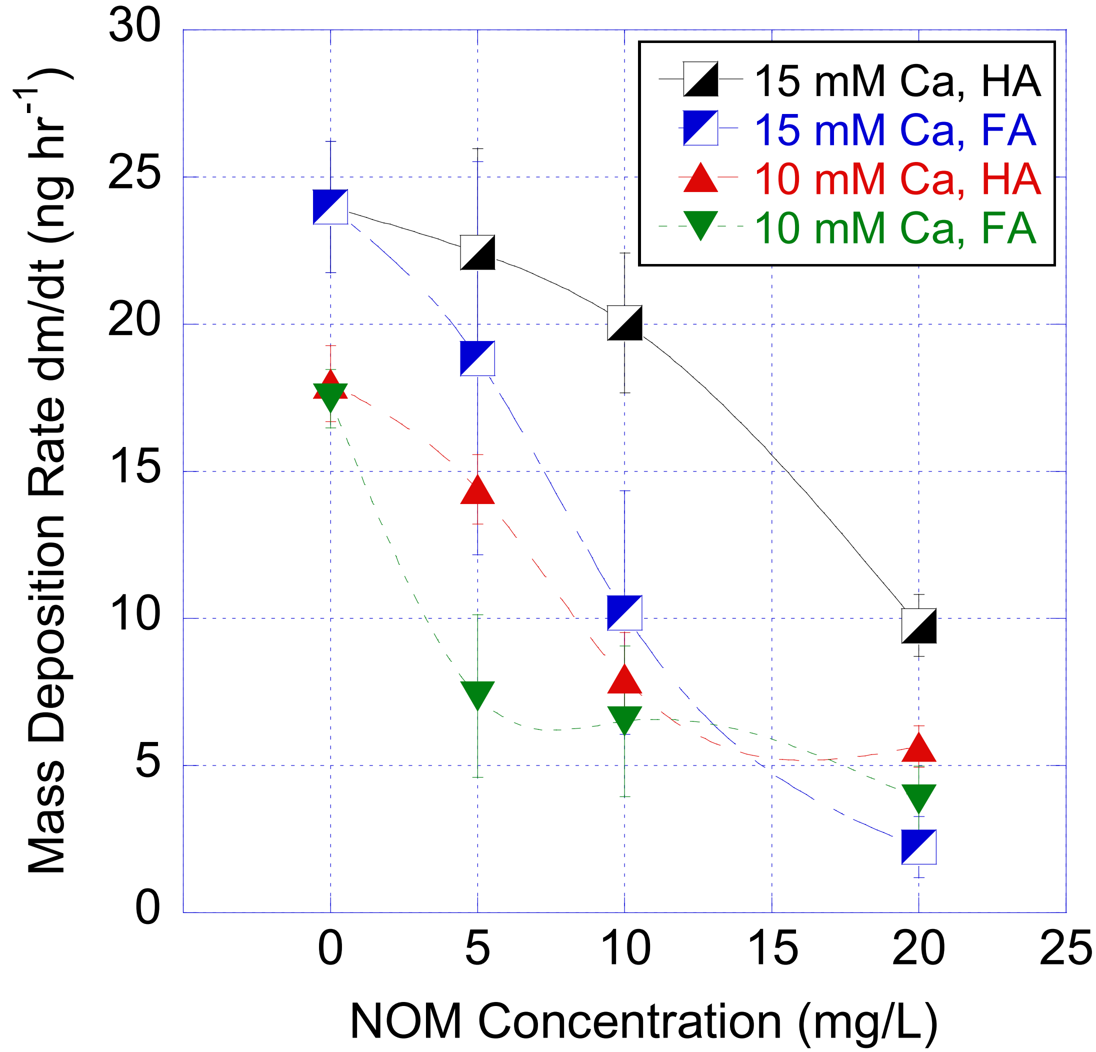


Li, Q. et al., ES&T, 2009, 43(10): 3574-3579.

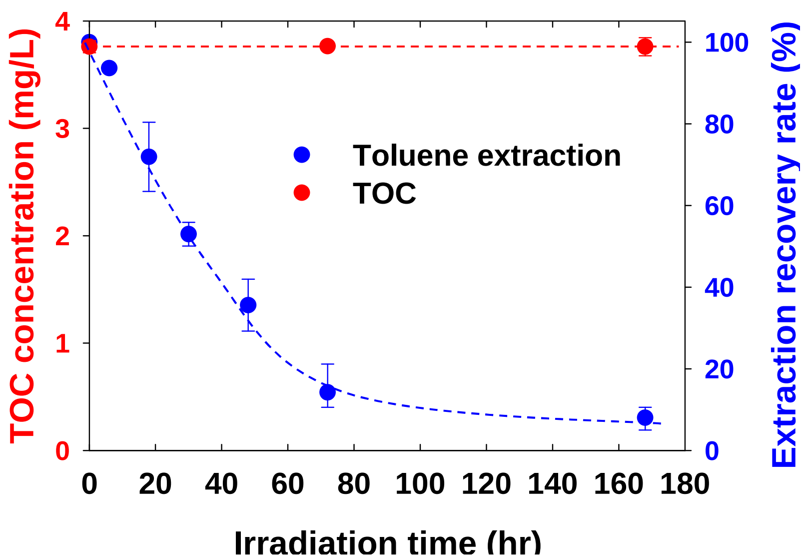
Dissolved NOM Decreases nC_{60} Deposition onto a Quartz Surface, Increases Mobility in Water

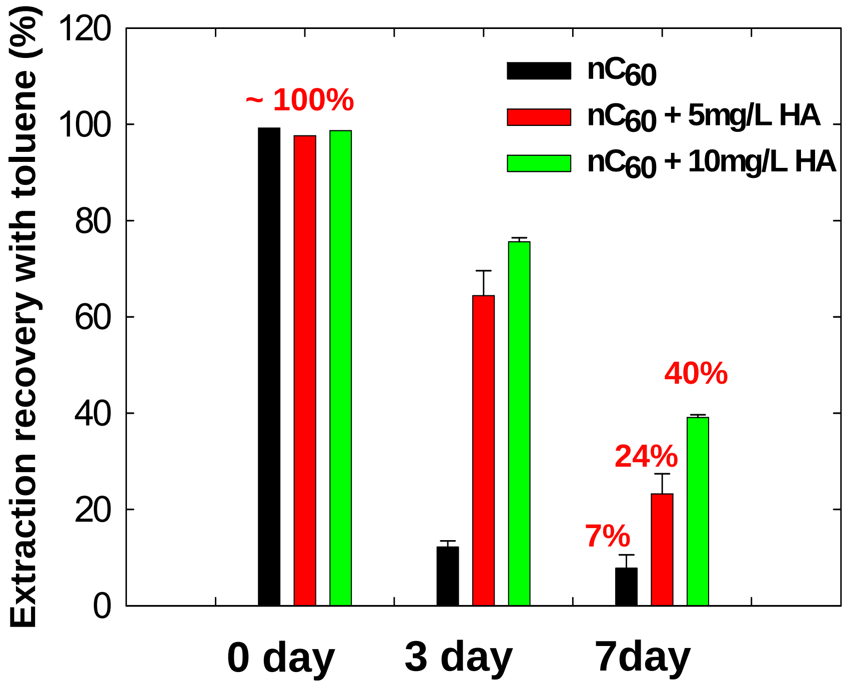
Quartz Crystal Micro Balance





NOM hinders photo-transformation of nC_{60}





In the presence of O_2 and UV light,
The surface of nC_{60} is transformed (C-OH, C-OH, C=O).
This hinders its extraction with toluene

Dissolved humic and fulvic acids hinder this transformation, enhance extraction with toluene

Risk = Hazard × Exposure

Hazard, but no exposure

Exposure but no hazard

Hazard as well as exposure

Cost & Environmental Impact
Therapeutic Measures
Restoration
Remediation
Preventive Measures
End-of-pipe treatment
Options to Control Pollution

The 12 Principles of Green Nanotechnology

1. Inherent rather than circumstantial (use raw materials and elements that are inherently non-hazardous if released)
2. Prevention rather than treatment (containment, minimize exposure, *design away hazardous functionalities or features without impacting useful functions*?)
3. Design for separation and purification of wastes (take advantage of magnetic properties for separation? Stabilizing coatings that can be intentionally removed?)
4. Maximize mass, energy, space and time efficiency (multi-functionality of NPs may be desirable)
5. “Out-pulled” rather than “input-pushed” through the use of energy and materials (quality > quantity, need > greed, enough > more, long-term > short-term)

The 12 Principles (Continued)

6. Find opportunities for recycle, reuse or beneficial disposition (non toxic NPs that enhance nutrient or water retention and soil fertility?)

7. Target durability rather than immortality (pick the "right" coatings, avoid indefinite persistence)

8. Need rather than excess - don't design for unnecessary capacity – avoid "one size fits all" (incorporate just what you need, avoid excess MNMs in commercial products)

9. Minimize material diversity to strive for material unification and promote disassembly + value retention (take advantage of economy of scales, minimize variability and sources of a given MNM?)

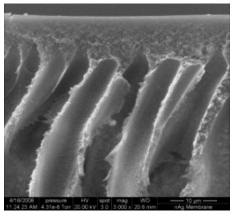
The 12 Principles (Continued)

10. Integrate local material and energy flows (holistic LCA perspective, look for interconnectivity, system of systems)
11. Design for commercial "afterlife" (enable recycling, remanufacturing and/or reuse opportunities? beneficial disposition?)
12. Use renewable & readily available inputs through life cycle (minimize carbon, land use and water footprint?)

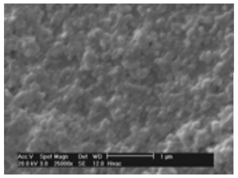
Potential Leapfrogging Opportunities for Microbial Control and Disinfection

Some Potential Applications

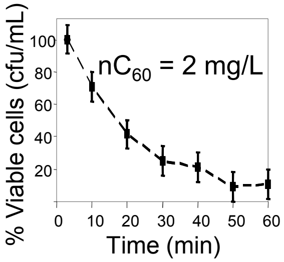
- Fouling-resistant membranes
  - Zodrow K., L. Brunet, S. Mahendra, Q. Li, and P.J.J. Álvarez (2009). Wat. Res. 43:715-723.



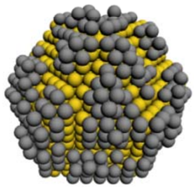
- Antimicrobial coatings
  - Lyon D.Y., D, Brown, E. Sundstrom, and P. J.J.Alvarez (2008). Int. Biodeterior. Biodegrad. 62:475-478.



- Chemical Disinfection without DBPs
  - Li Q., S. Mahendra, D. Y. Lyon, L. Brunet, M. V. Liga, D. Li and P. J.J. Alvarez (2008). Wat. Res. 42:4591-4602.



- Pd/Au Hypercatalysts for reductive dechlorination
  - Wong M.S., P.J.J. Alvarez, Y.L. Fang, N. Akçin, M.O. Nutt, and K.H. Heck (2008). J. Chem. Technol. Biotechnol. 84:158-166.



- **Photocatalytic Disinfection with fullerenes**

Potential Application: Enhancing UV Disinfection

- UV disinfection is increasingly used to inactivate cyst-forming protozoa such as *Giardia* and *Cryptosporidium*.
- However, UV is relatively ineffective to treat virus unless the contact time and energy output are significantly increa$ed

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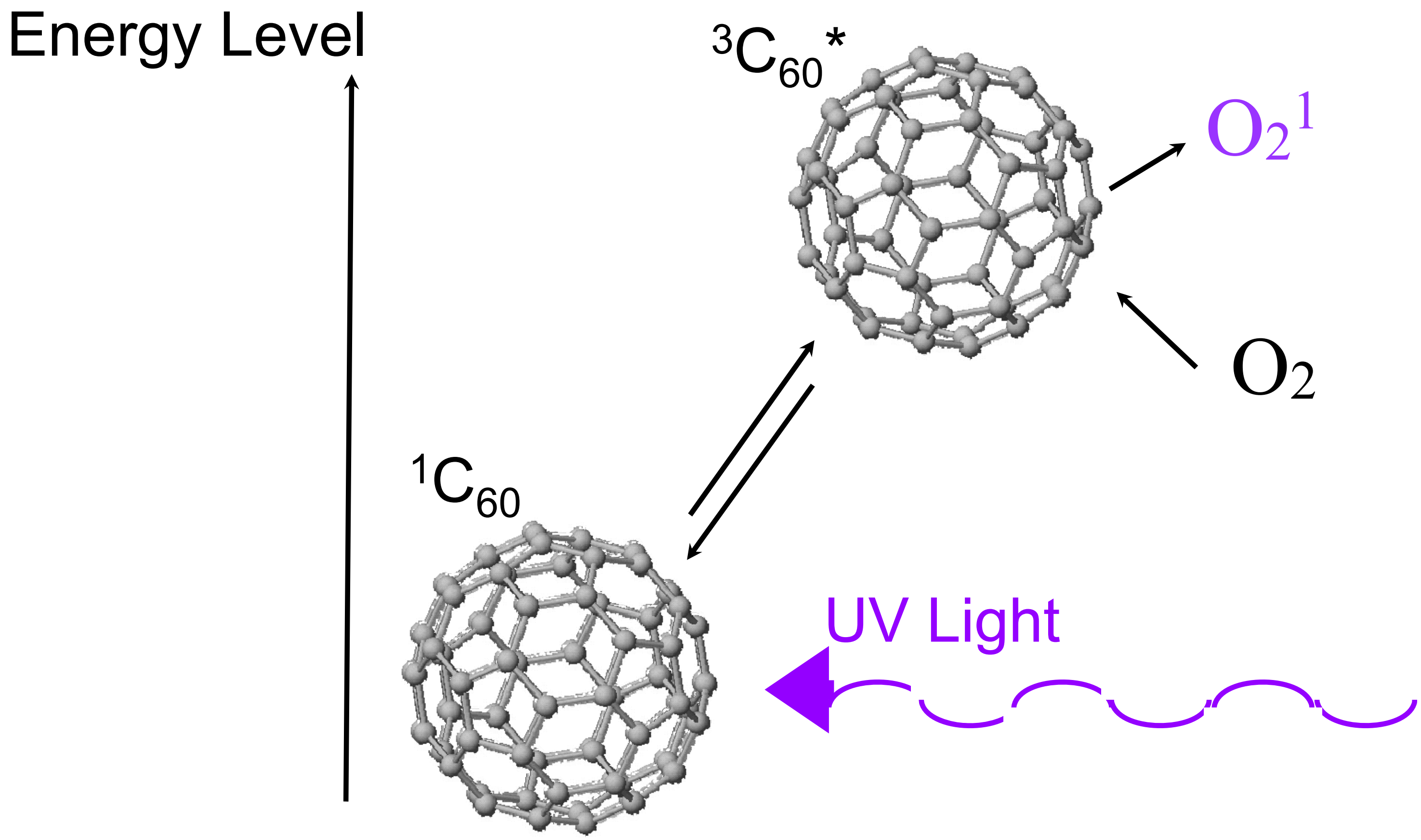
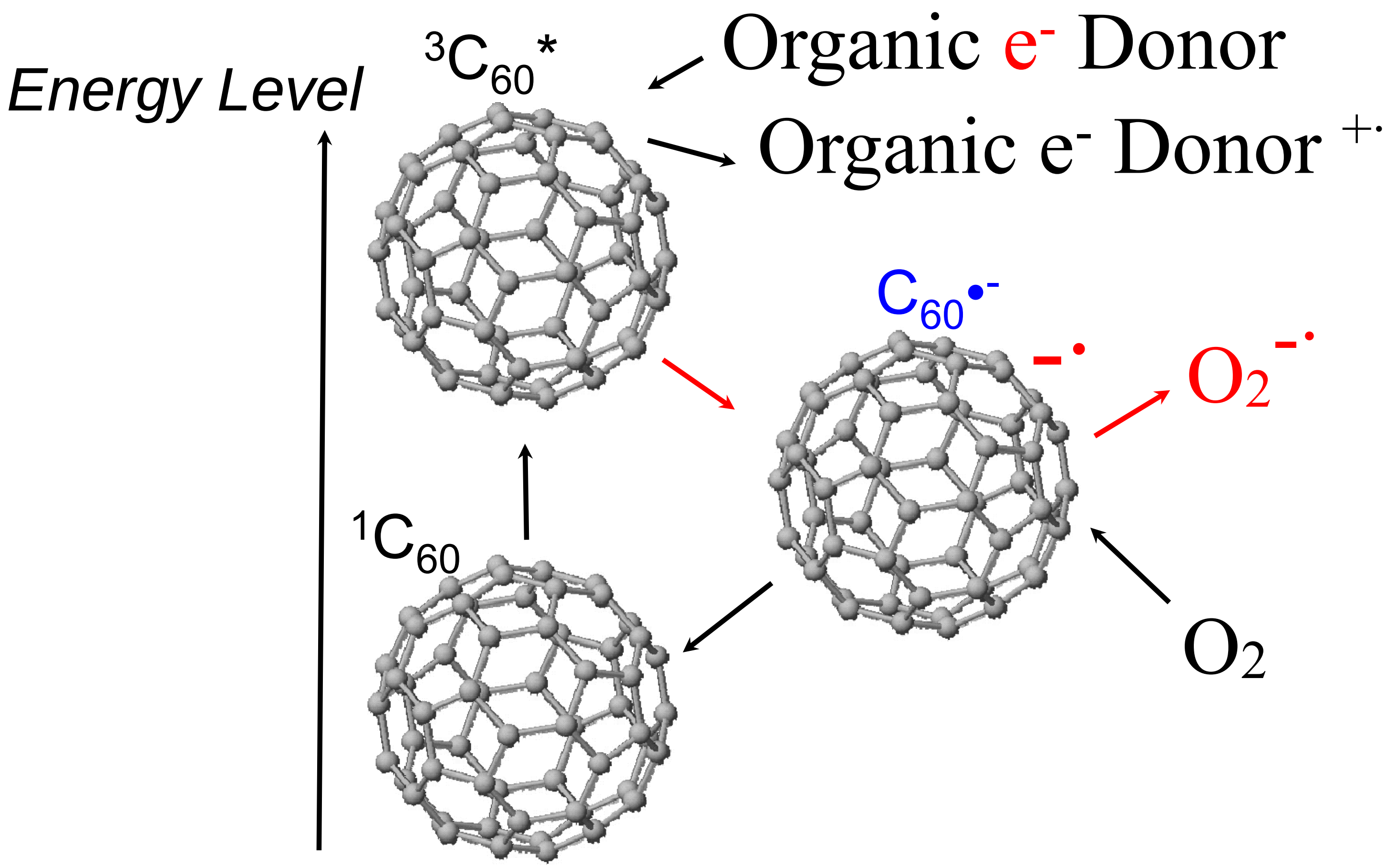


Light excites C_{60} to triplet state. Energy transfer between $^3C_{60}^*$ and molecular oxygen gives rise to singlet oxygen ($^1O_2$)

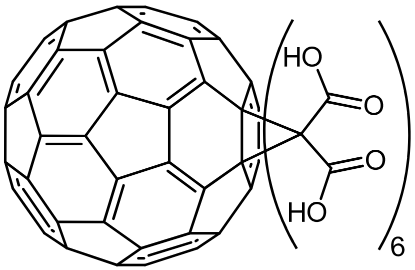
Hotze M., J. Labille, P.J.J. Alvarez and M. Wiesner (2008). Environ. Sci. Technol. 42, 4175–4180



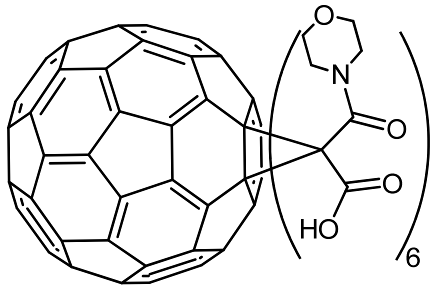
$^3C_{60}$* transforms to C_{60} radical anion (C_{60}•-) in the presence of some electron donors, which reduces O_2 to superoxide (O_2^{-}•)

Hotze M., J. Labille, P.J.J. Alvarez and M. Wiesner (2008). Environ. Sci. Technol. 42, 4175–4180

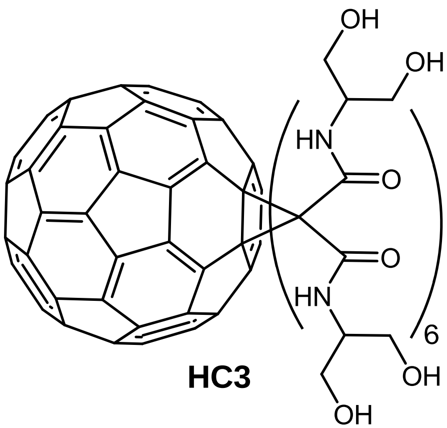
“Water Soluble” Derivatized Fullerenes



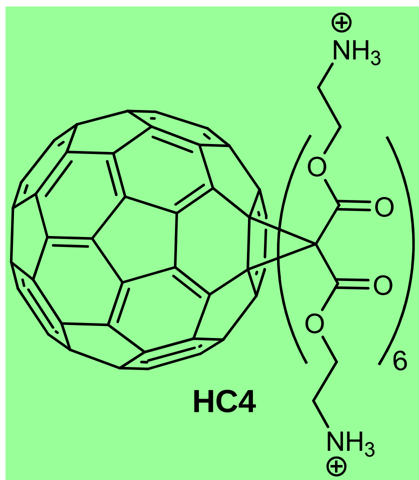
HC1



HC2

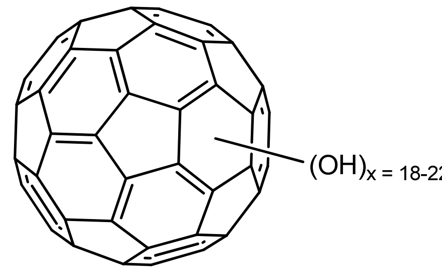


HC3



HC4

VS



Fullerol

* Commercially Available, MER Corp.

* Synthesized in Lon Wilson’s lab, Dept of Chemistry, Rice University (Bingel Reaction)

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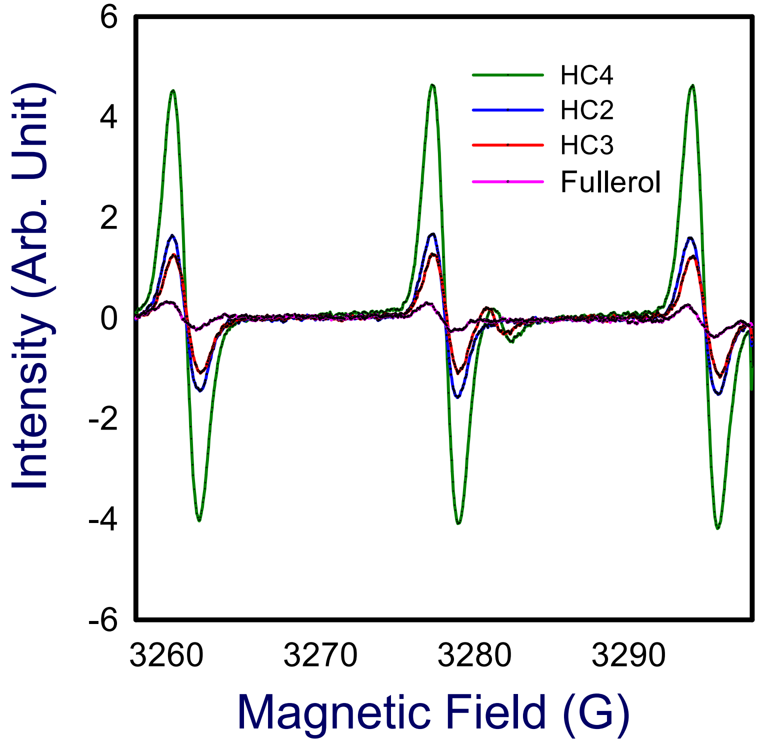
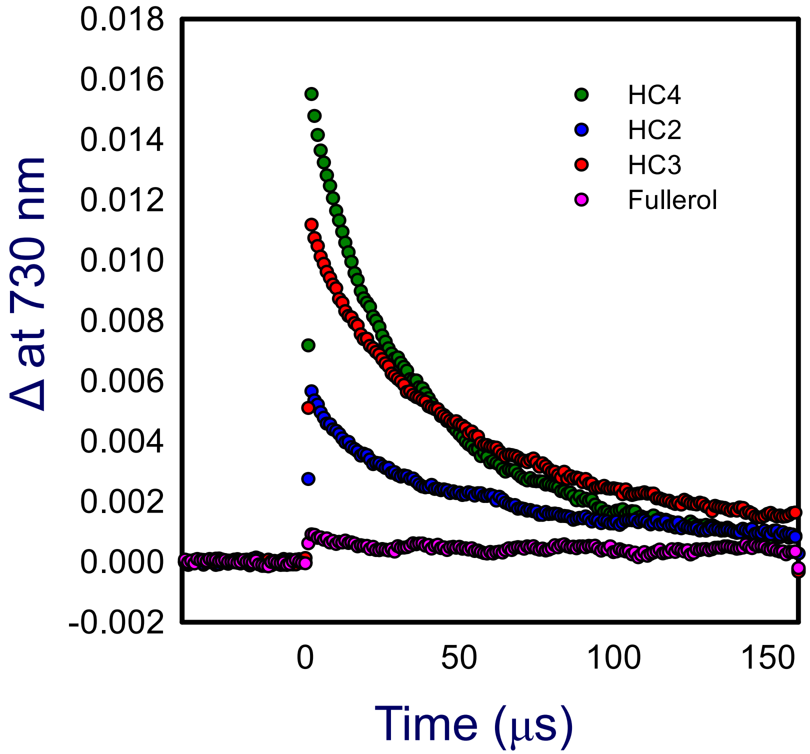
Superior Photosensitized $^1O_2$ Production

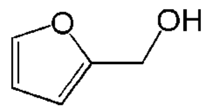
- Larger Electron Paramagnetic Resonance Spectra Peaks Correspond to Higher $^1O_2$ Generation (All Outperform Fullerol)
- Nanosecond Laser Flash Photolysis Confirms Long-lived Triplet State, Conducive to Efficient ROS Production (HC4 >> Fullerol)



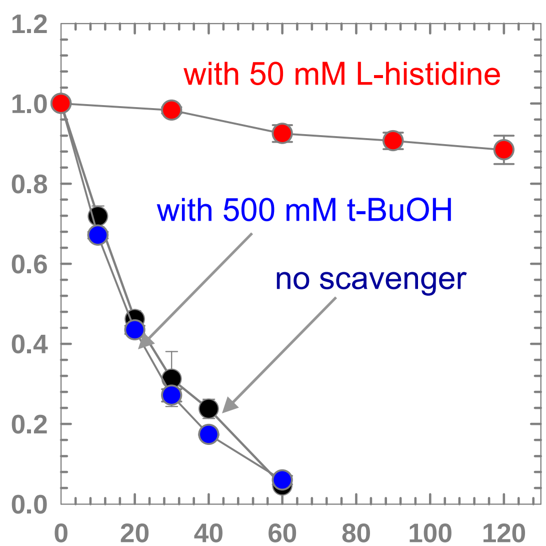


J.Lee, Y.Mackeyev, M.Cho, D.Li, J.-H. Kim, L.J. Wilson, and P.J.J. Alvarez, *Environ. Sci. Technol.* (2009) 43:6604-6610

Significant $^{1}O_2$ production despite clustering



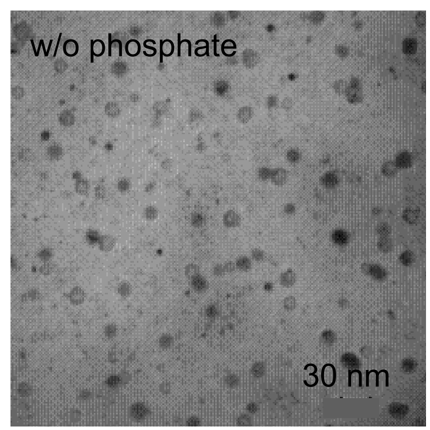
FURFURYL ALCOHOL
($^{1}O_2$ INDICATOR)

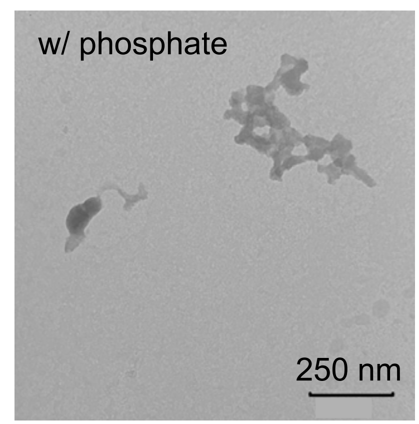


MIC test with *E. coli* shows minimum toxicity

DERIVATIVES	MIC (μM)	DIAMETER (nm)
HC1	> 400	1.32 / 1.12[a]
HC2	> 400	281.1 / 60.5
HC4	120	1.50 / 1114
Fullerol	> 400	2.43 / 6.10

[a]: *determined in the presence of 10 mM phosphate*

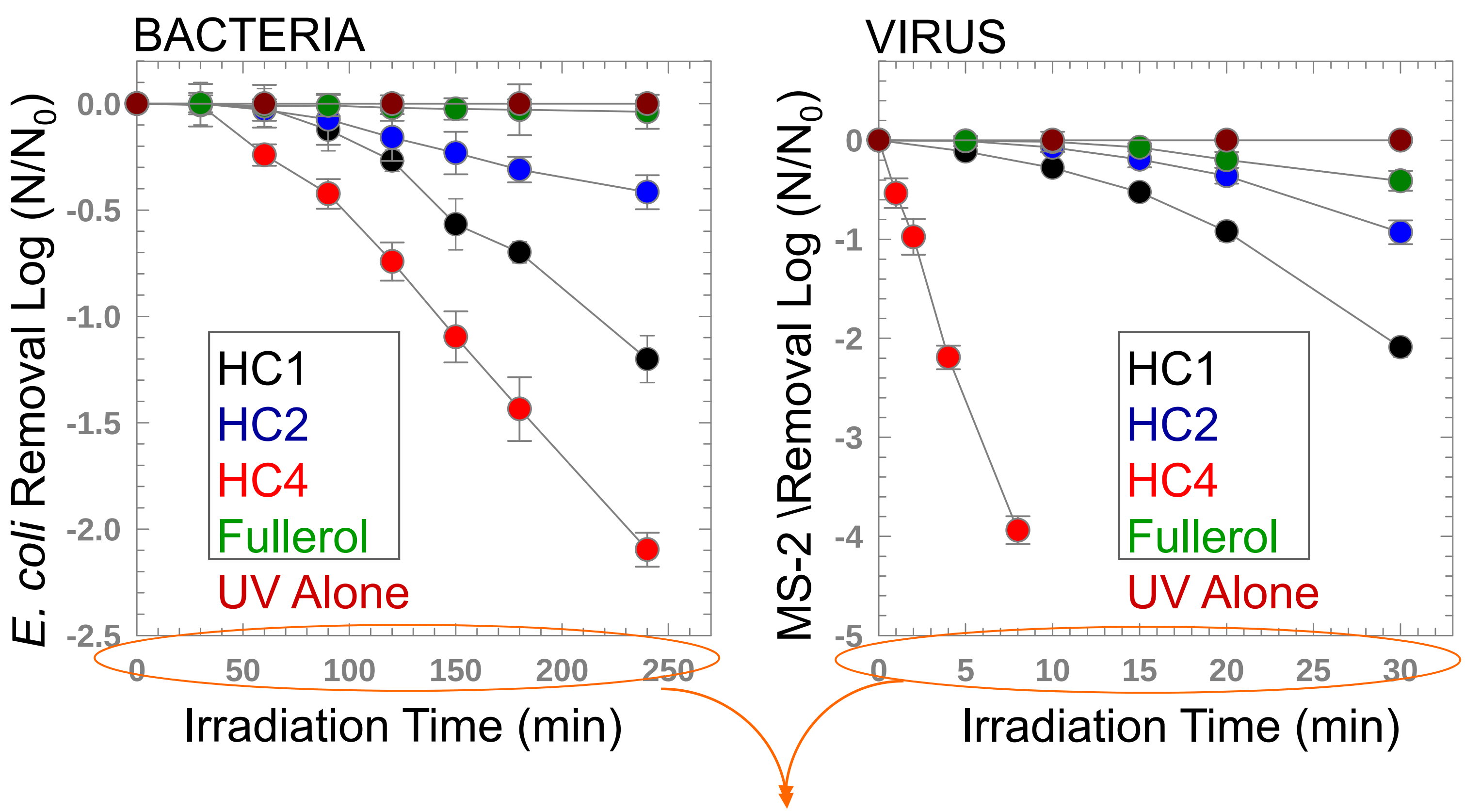




J.Lee, Y.Mackeyev, M.Cho, D.Li, J.-H. Kim, L.J. Wilson, and P.J.J. Alvarez, *Environ. Sci. Technol*. (2009) 43:6604-6610

Photocatalytic Disinfection

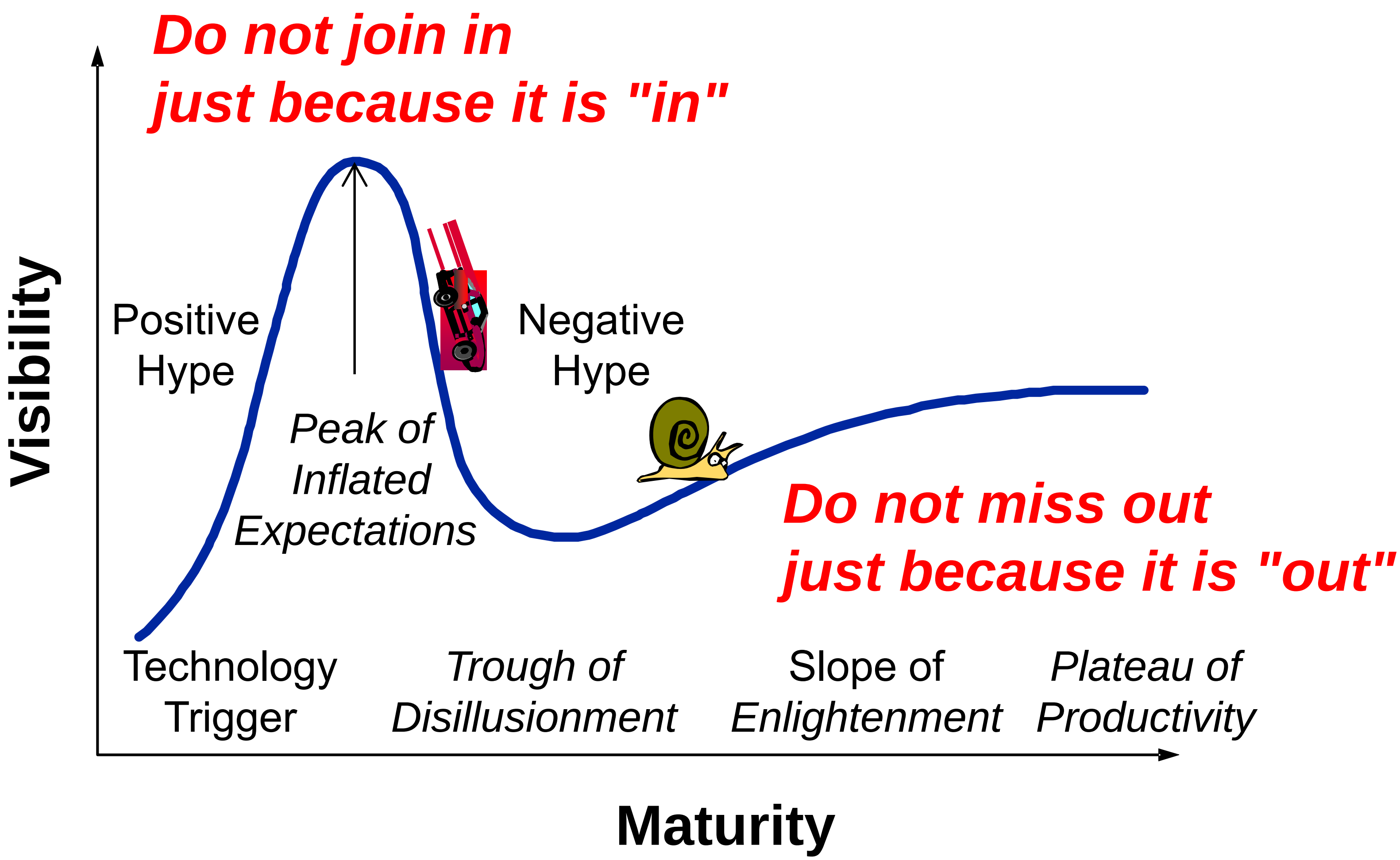
[C_{60} derivative] = 50 μM, BLB lamp 350 - 400 nm, *I* = 6 ×10^{-6} Einstein·$min^{-1}L^{-1}$



BETTER PERFORMANCE FOR VIRAL INACTIVATION
(unusual for traditional disinfection with UV, O_3, Cl_2 etc.)

J.Lee, Y.Mackeyev, M.Cho, D.Li, J.-H. Kim, L.J. Wilson, and P.J.J. Alvarez, *Environ. Sci. Technol*. (2009) 43:6604-6610

Quo Vadis, Nano?



“Nanohype” - Berube

So What?

- <u>Implications</u>:
  Ecotoxicology- Biodiversity and food webs?
  Biogeochemical cycling?
  Mitigated by NOM, salts

- <u>Applications</u>:
  DBP-free disinfection (sunlight-driven?), Advanced oxidation of micropollutants? Antifouling or anticorrosion coatings? Membranes?