Increasing the net environmental benefit of nanomaterials: Lessons from the design and production of ligand-stabilized gold nanoparticles

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Net environmental benefits: Importance of performance
Greener syntheses of precision nanoparticles
Design for net benefit

The promise of nanotechnology for society often relies on maximizing the net environmental benefit

Abundant clean energy

Efficient energy storage and use

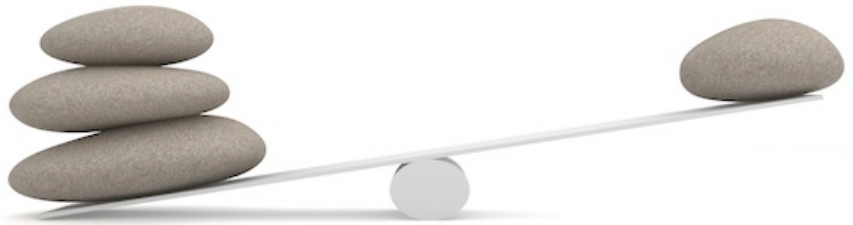
Access to drinkable water for all

Advanced diagnostics and therapies

Sustainable chemical production

Health hazards
Waste
Pollution
Resource depletion
Climate change

Description of net environmental benefit



Nano-Enabled Products

$$\text{Impact-Benefit Ratio (IBR)} = \frac{\text{Upstream Impacts}}{\text{Downstream Benefits}}$$

< 1 ✓ Pursue Development and Implementation
Realization of downstream benefits outweigh production impacts

= 1 Net Neutral Impact

> 1 ✗ No Added Value, Redesign
Production impacts outweigh realization of downstream benefits

$$\text{Impact-benefit ratio} = \frac{\text{Life cycle impacts}}{\text{Functional performance benefits}}$$

L.M. Gilbertson, et al. *Environ. Sci. Technol.* **2014**, *48*, 11360–11368.

L.M. Gilbertson, et al. *Chem. Soc. Rev.* **2015**, *44*, 5758-5777.

Performance matters! The impacts of what?

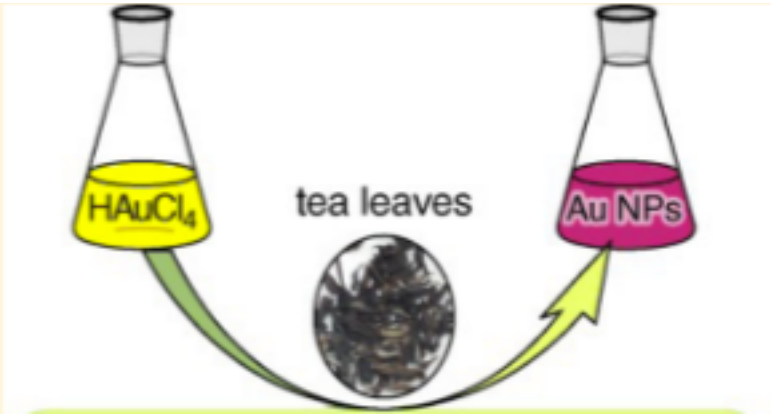
BOTH benefits and impacts need to be compared to alternatives

Example: Gold nanoparticles from green tea?

A simple, economic, and environmentally benign experimental route…

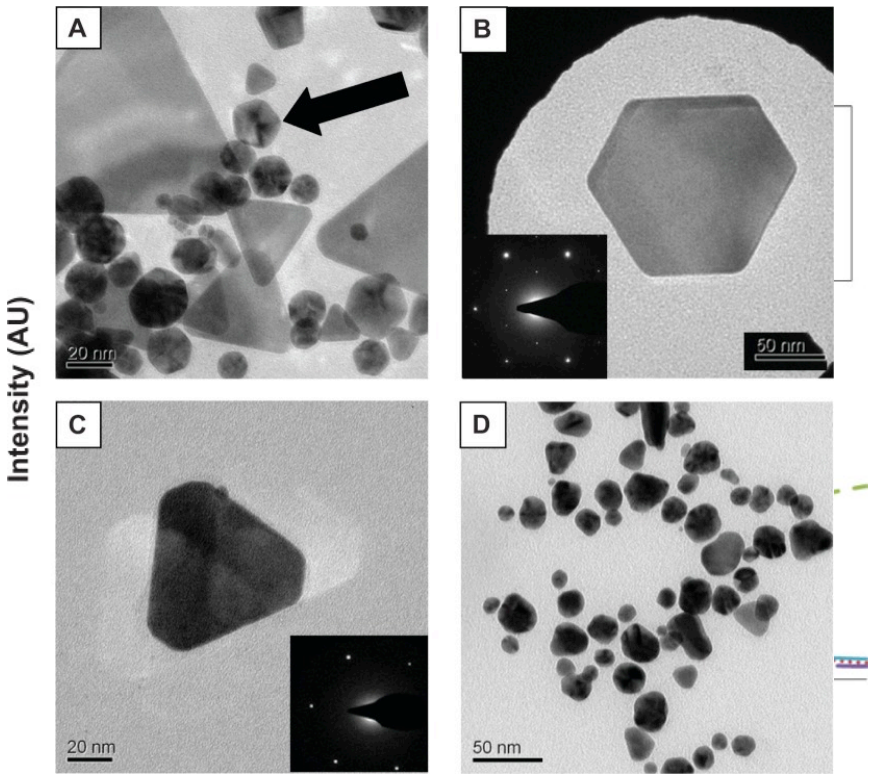
…to synthesize gold nanoparticles using tea leaves in an aqueous media at room temperature…

… single-step method circumvents the use of surfactant, capping agent, or template and follows several principles of green chemistry.



J. Chem. Educ. **2012**, *89*, 1316 – 1318.

Nanoparticle synthesis, structure and performance



Int J Nanomedicine **2014**, 9, 4007–4021

Do these features influence the desired performance?

Size, shape, dispersity

Dispersibility

Targeting groups

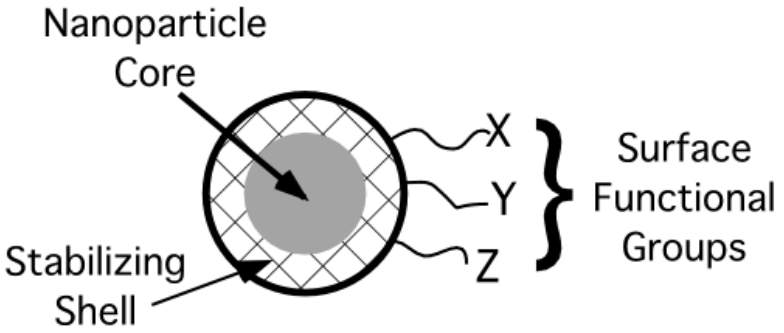
Different syntheses, different structures, different (?) performance

Many studies and applications require specific properties/performance

Where is precision synthesis needed?

Size-dependent or surface properties

- Next-generation applications
- NanoEHS studies
- Commercialization



Size, shape and dispersity: optical, electronic, catalytic, biologic

Stabilizing shell: biocompatibility, dispersibility, processing

Surface functional groups: targeting, self-assembly, linking

Define performance needed – Design to maximize net benefit

Greener nano, safer nano, sustainable nano…

Lux Research, 2007

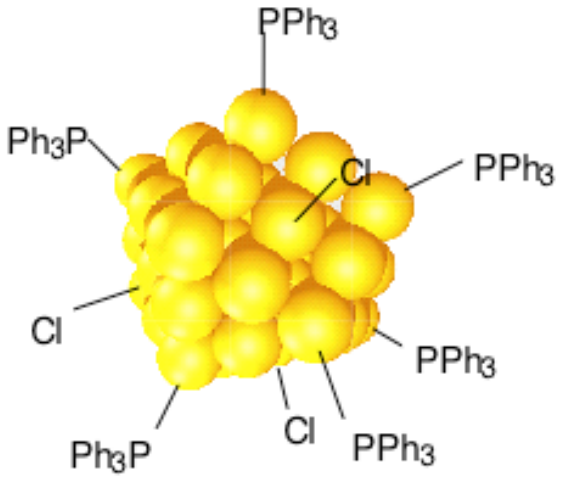
Apply 12 principles of green chemistry to
reduce hazards and
minimize impacts of production
across the value chain and lifecycle of nanomaterials

Molecular-level design to maximize net environmental benefits (in the context of alternatives)

McKenzie and Hutchison "Green nanoscience," *Chemistry Today,* **2004**, 30
Dahl, J.A.; Maddux, B. L. S.; Hutchison, J. E. *Chem. Rev.* **2007**, *107,* 2228
Hutchison, J.E. *ACS Nano* **2008**, *2*, 395-402

Early precision synthesis of gold nanoparticles…effective, but not so safe/green

$(PPh_3)AuCl \xrightarrow[\text{benzene}]{B_2H_6}$

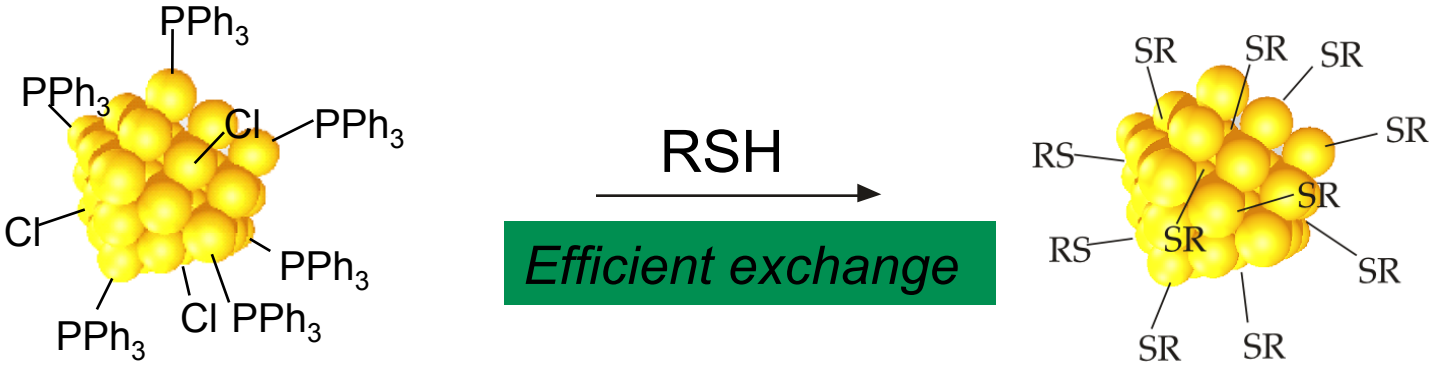


Schmid, G. *Inorg. Synth.* ***1990****,* 27*,* 214.

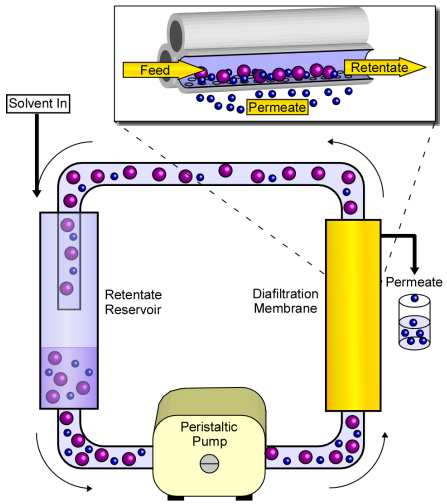
Hazardous, wasteful, low yields, batch-to-batch variation, impure samples (or unknown purity), little mechanistic knowledge to guide synthesis, expensive…

Tipping the balance: Precision nanoparticles can be prepared using greener approaches

Greener reagents, solvent



J. Am. Chem. Soc. **2000**, *122*, 12890; *Inorg. Syn*. **2004**, *34*, 228; *J. Am. Chem. Soc.* **1997**, *119*, 12384; *J. Phys. Chem. B* **2002**, *106*, 9979



Rapid, effective purification

J. Am. Chem. Soc. **2006**, *128*, 3190.

Greener,
cheaper,
faster,
better

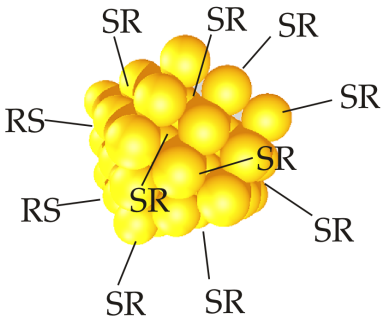
Precise core sizes and surface coatings can be prepared and characterized

R =

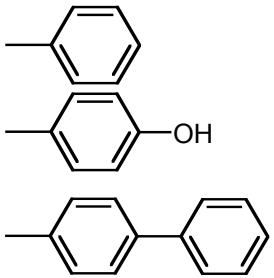
$-(CH_2)_{17}CH_3$
$-(CH_2)_{15}CH_3$
$-(CH_2)_{11}CH_3$
$-(CH_2)_9CH_3$
$-(CH_2)_8CH_3$
$-(CH_2)_7CH_3$
$-(CH_2)_5CH_3$
$-(CH_2)_2CH_3$
$-(CH_2)_2Si(OMe)_3$

$-(CH_2)_2SO_3^-Na^+$
$-(CH_2)_3SO_3^-Na^+$
$-(CH_2)_2N^+HMe_2Cl^-$
$-(CH_2)_2N^+Me_3Cl^-$
$-(CH_2)_2O(CH_2)_2N^+Me_3^-OTs$
$-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Me_3^-OTs$
$-(CH_2)_2O(CH_2)_2O(CH_2)_2N^+Et_3^-OTs$

$-CH_2COO^-Na^+$
$-(CH_2)_2COOH$
$-(CH_2)_{11}COOH$
$-(CH_2)_2OH$
$-(CH_2)_2PO(OH)_2$
$-[(CH_2)_2O]_2(CH_2)_2OH$
$-(CH_2)_2O(CH_2)_2OH$
$-[(CH_2)_2O]_2CH_2COOH$
$-(CH2)_2COGlyGlyOH$
$-(CH_2)_2CONH(CH_2)_{14}CH_3$



Core *d* = 0.8 and 1.5 nm (and a few other sizes)



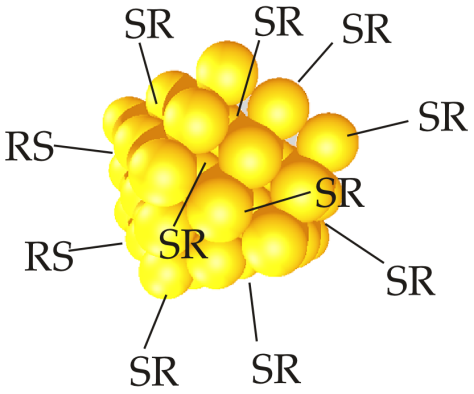
TEM/SAXS - size and dispersity
UV/vis - crude size, aggregation
NMR - small molecule contamination
TGA - ligand/core ratio
XPS or EA - elemental composition

J. Am. Chem. Soc. **2005**, *127*, 2172 and *Inorg. Chem.* **2005**, *44*, 6149

Direct synthesis should be greener – eliminates waste and purification steps

Target attributes for a versatile direct synthesis of AuNPs

- Precise control of core size, adjustable over 1-15 nm
- Precise control of coatings, including mixtures
- Reproducible
- Scalable
- High yield



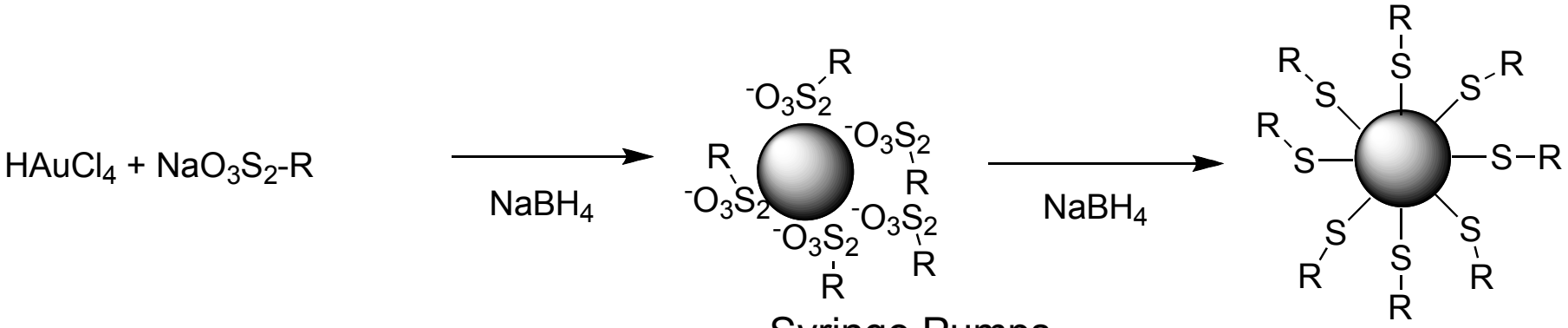
Ligand exchange

???

Brust direct synthesis

Ligand exchange: Citrate-stabilized AuNPs

Flow production of precision thiol-stabilized AuNPs

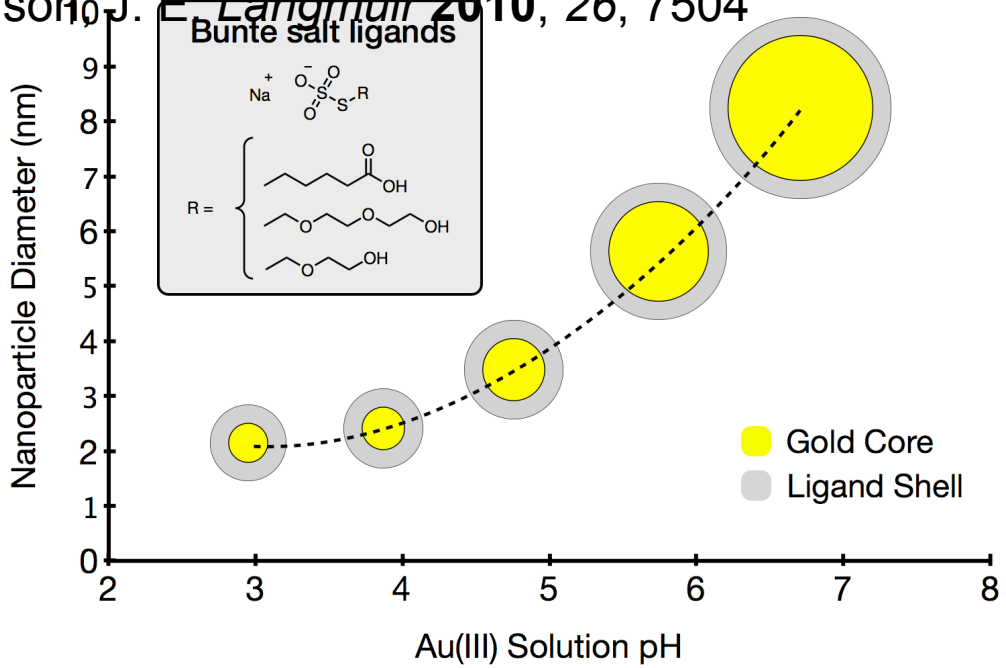


Syringe Pumps

Lohse, S. E.; Dahl, J. A.; Hutchison, J. E. *Langmuir* **2010**, *26*, 7504

pH	gold speciation
2.91	$[AuCl_{2.91}(OH)_{1.09}]$
4.01	$[AuCl_{2.46}(OH)_{1.54}]$
6.16	$[AuCl_{1.09}(OH)_{2.91}]$
8.01	$[AuCl_{0.67}(OH)_{3.33}]$
10.35	$[AuCl_{0.10}(OH)_{3.90}]$

Huang, W.; et al. *J. Phys. Chem. C.* **2009**. *113*. 6505.

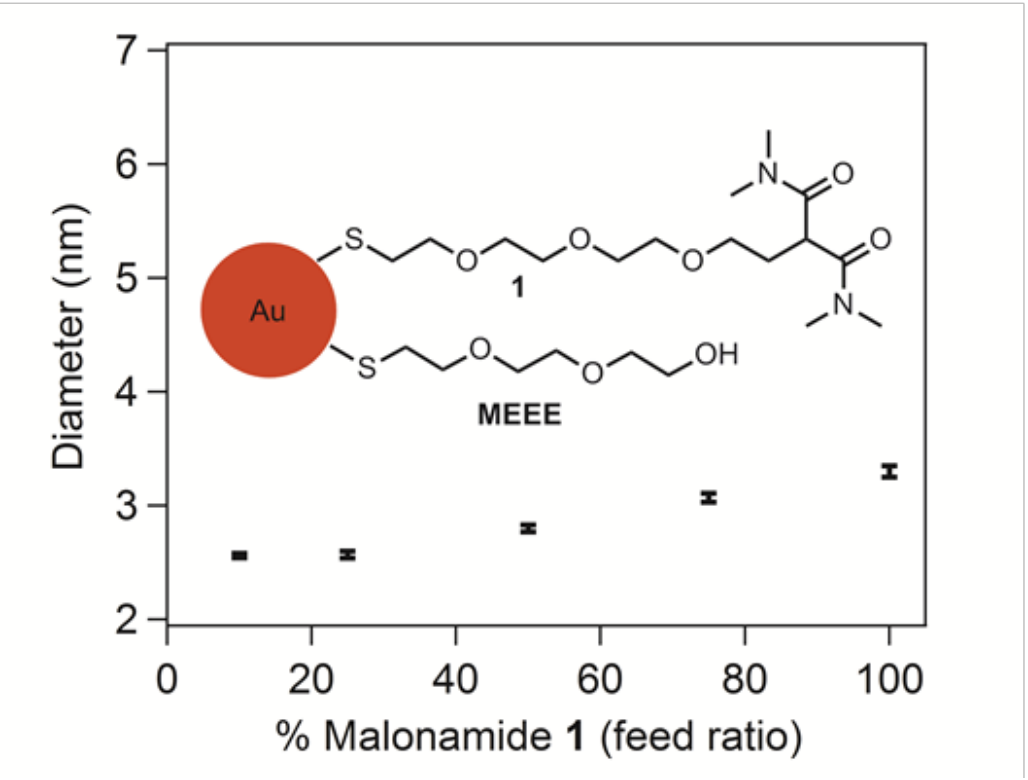


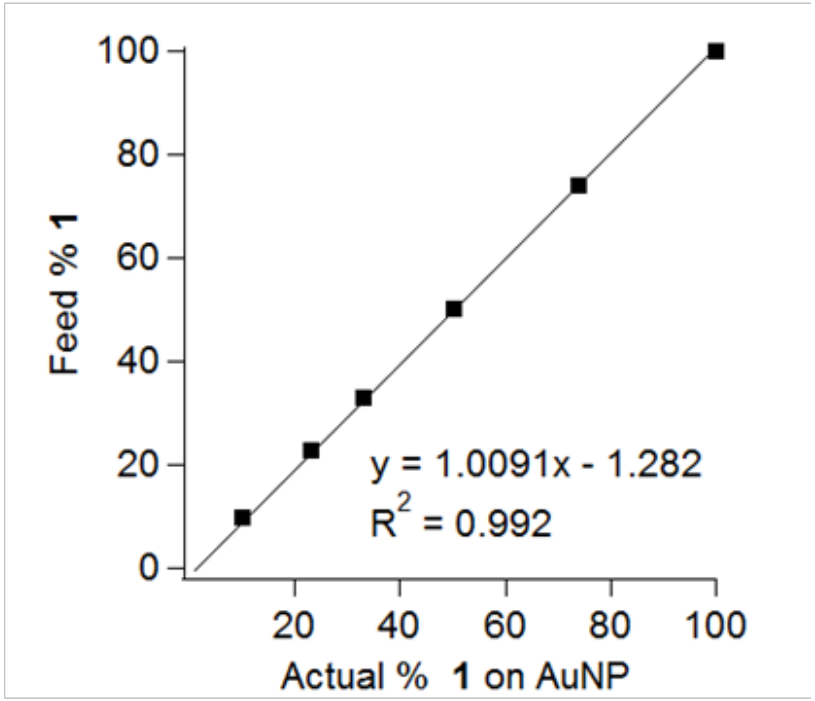
[1:5:2] ratio of
Ligand : $HAuCl_4$: $NaBH_4$

AuNPs

Haben, P.M.; Elliott, E.W.; Hutchison, J.E. *Langmuir*, **2015**, ASAP.

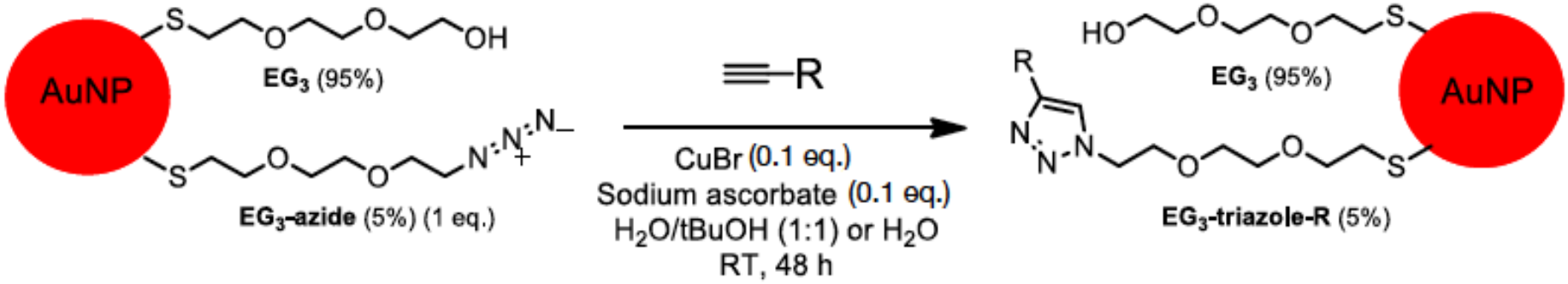
With the right linker, it is possible to precisely control ligand shell composition





Kennedy, Z.C.; Mitaru-Berceanu, D.S.; Hutchison, *Langmuir,* **2015**, ASAP.

Nanoparticle “reagents” can be used to couple diverse, precise building blocks



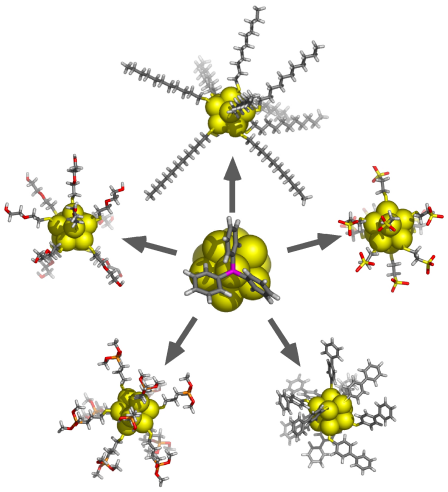
Core Diameter = 3.4 ± 0.4 nm

Ligand Shell Composition
EG3-azide / EG3 (5:95) AuNPs

Average Chemical Formula
$Au_{1580}(EG_3)_{171}(EG_3\text{-azide})_9$

Average Molecular Weight
3.41×10^5 g/mole

An iterative approach to developing design guidelines for inorganic nanoparticles

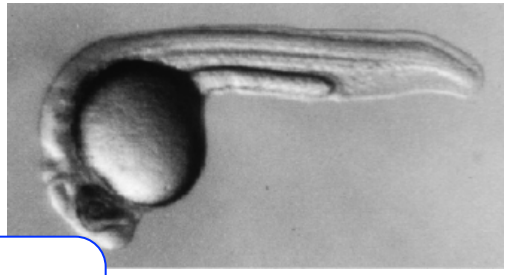


Precision nanomaterial libraries

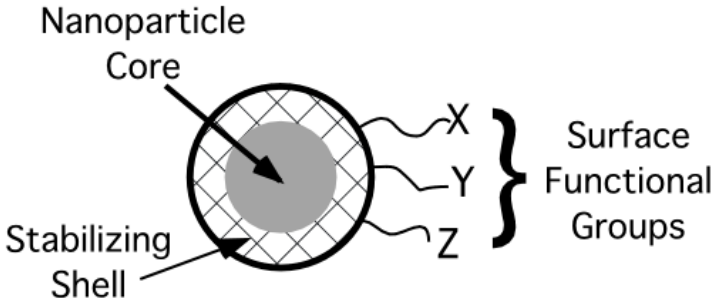
Characterization

Precise synthesis and purification

Rapid in vivo evaluation

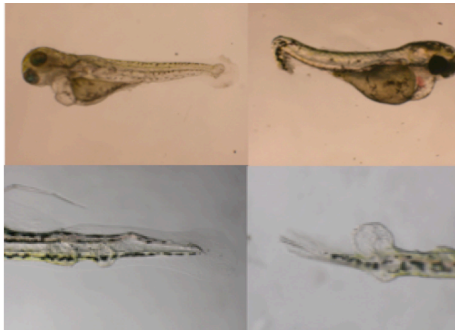


Guidelines for Sustainable Molecular Design of Nanoparticles



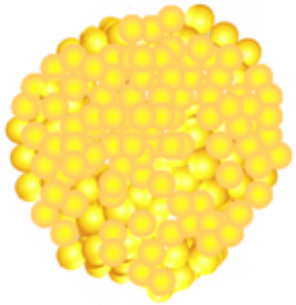
Feedback to design – early intervention

Example: Design principles from a systematic study of biological impacts of nanoparticles

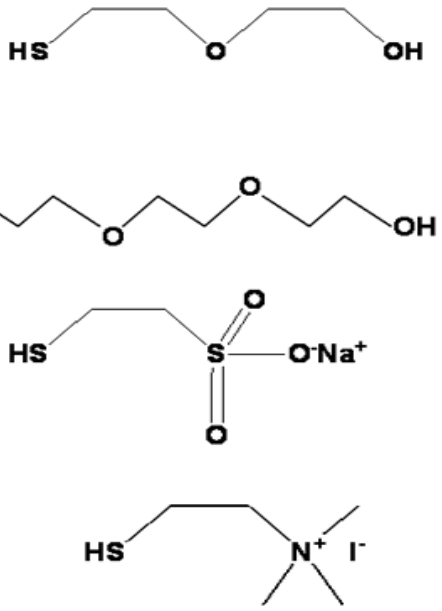


0.8 nm
11 Au Atoms
10 ligands

1.5 nm
101 Au Atoms
30-35 ligands



10 nm
37,000 Au Atoms
1400 ligands



malformations	malformations	NA
toxic	toxic	?

ACS Nano **2011**, 4688-97

Summary

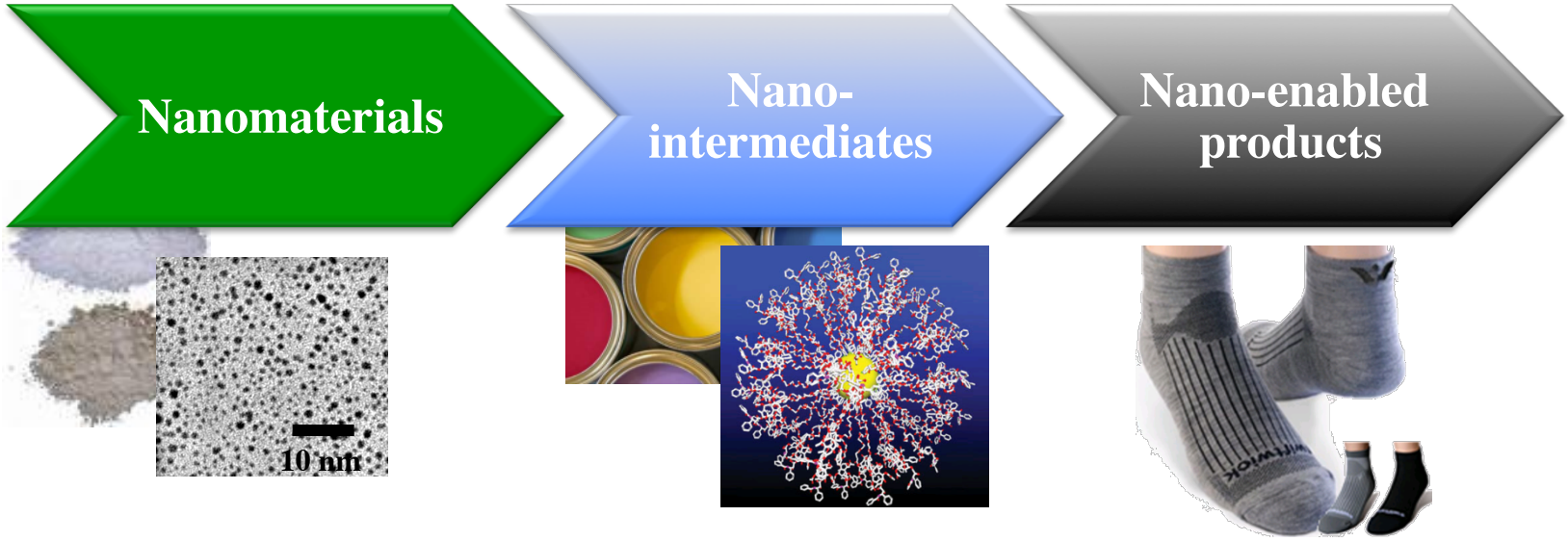
Greener syntheses of precision nanoparticles

- Precise control over core and surface coating for AuNPs – greener, scalable, cheaper
  - New reagents and solvents
  - New purification methods
  - New reaction chemistries
  - New (flow) reactors

Design to enhance net environmental benefit

- Design for maximum performance
- Design for reduced impacts
- Consideration of lifecycle impacts
- Compare to nano and non-nano alternatives

What about nano-enabled products?

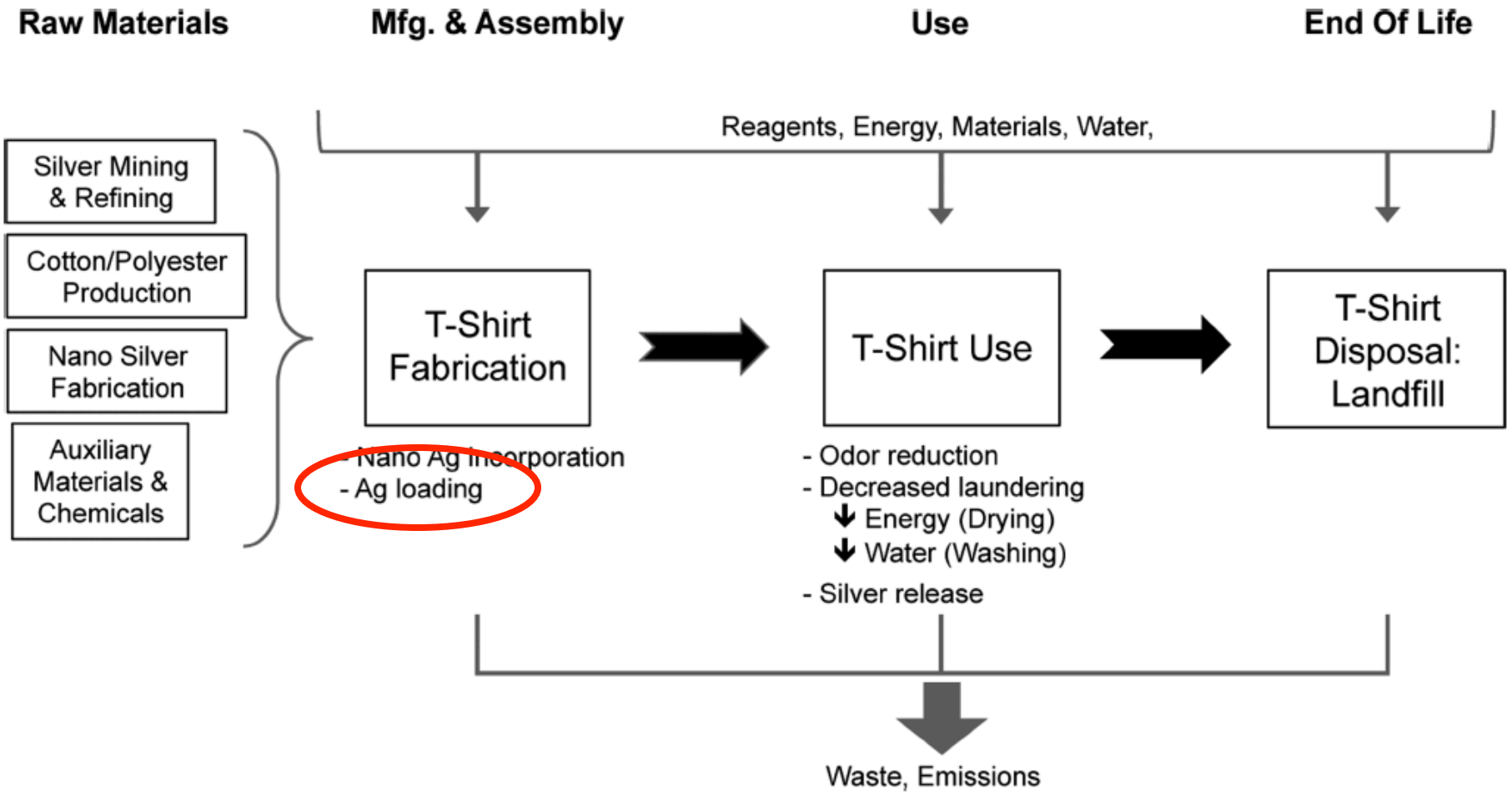


Lux Research, 2007

Typically NPs will be used in (or on) consumer products

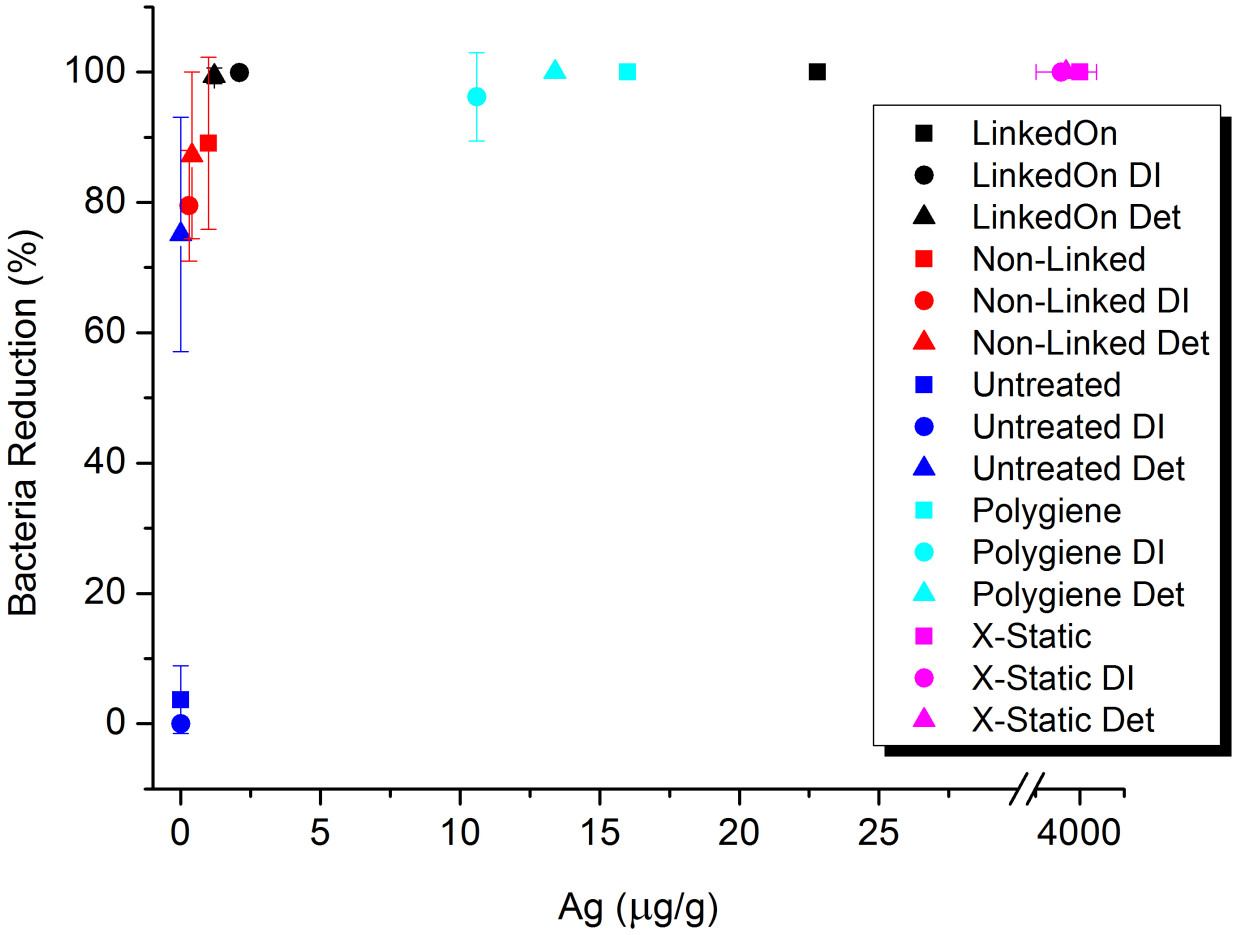
- What are the impacts of nano-enabled products?
- What is the reactivity of NPs bound to surfaces?
- Can the answers to these questions provide feedback for better (greener) designs?

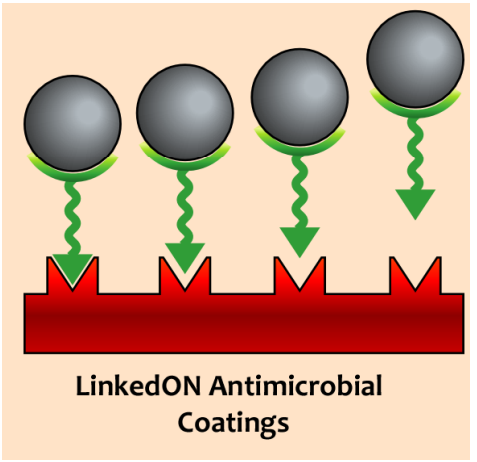
Lifecycle thinking - use minimum effective silver to maximize the net environmental benefit



"Life Cycle Payback Estimates of Nanosilver Enabled Textiles under Different Silver Loading, Release, and Laundering Scenarios Informed by Literature Review," A. L. Hicks et al. *Environ. Sci. Technol.* **2015**, 7529–7542.

Lower Ag loadings decrease impacts while maintaining high performance





In preparation, LCnano team

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