Using Nanotechnology to Clean Contaminated Water - A Catalytic Approach

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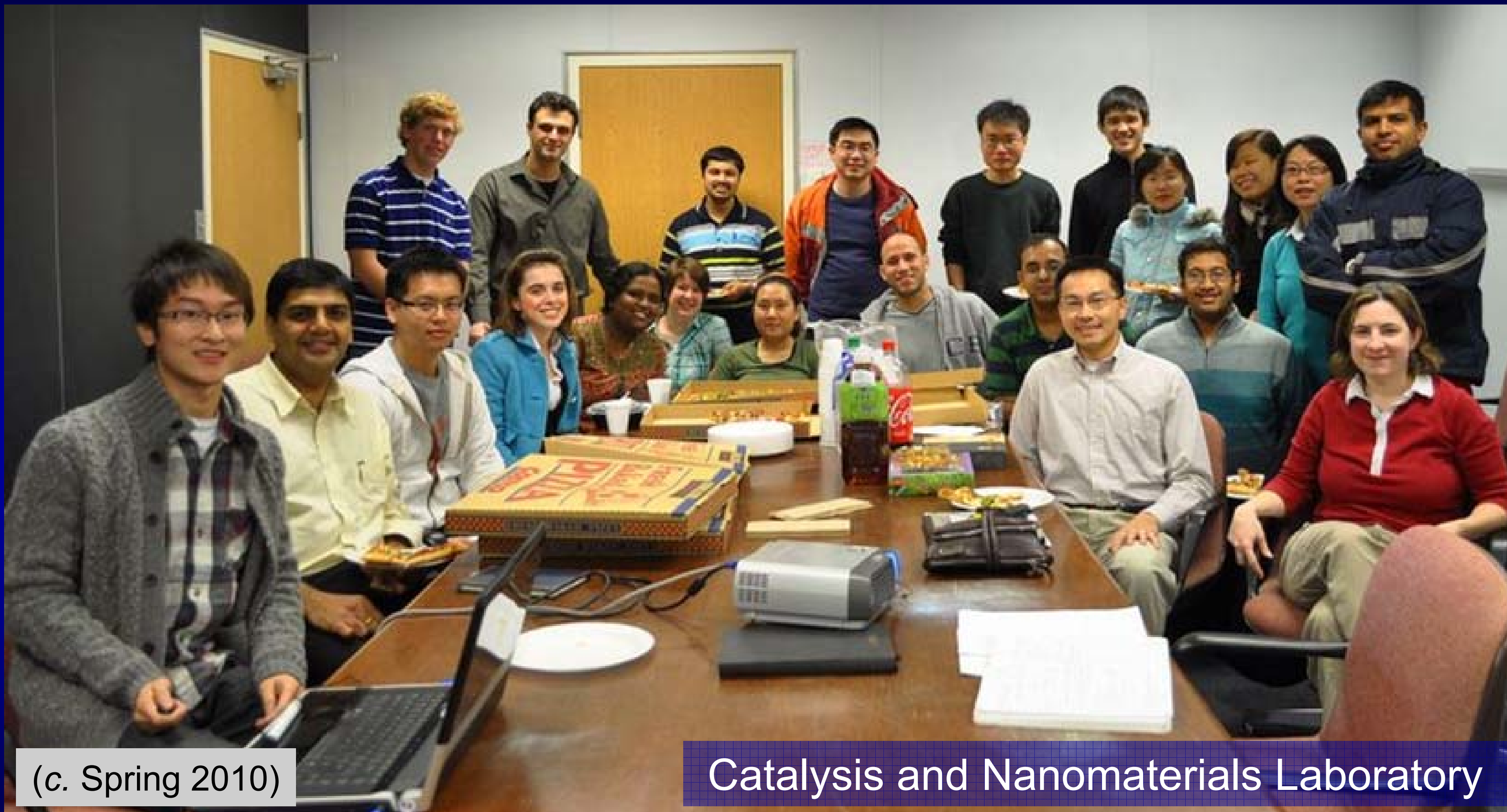
May 6, 2010

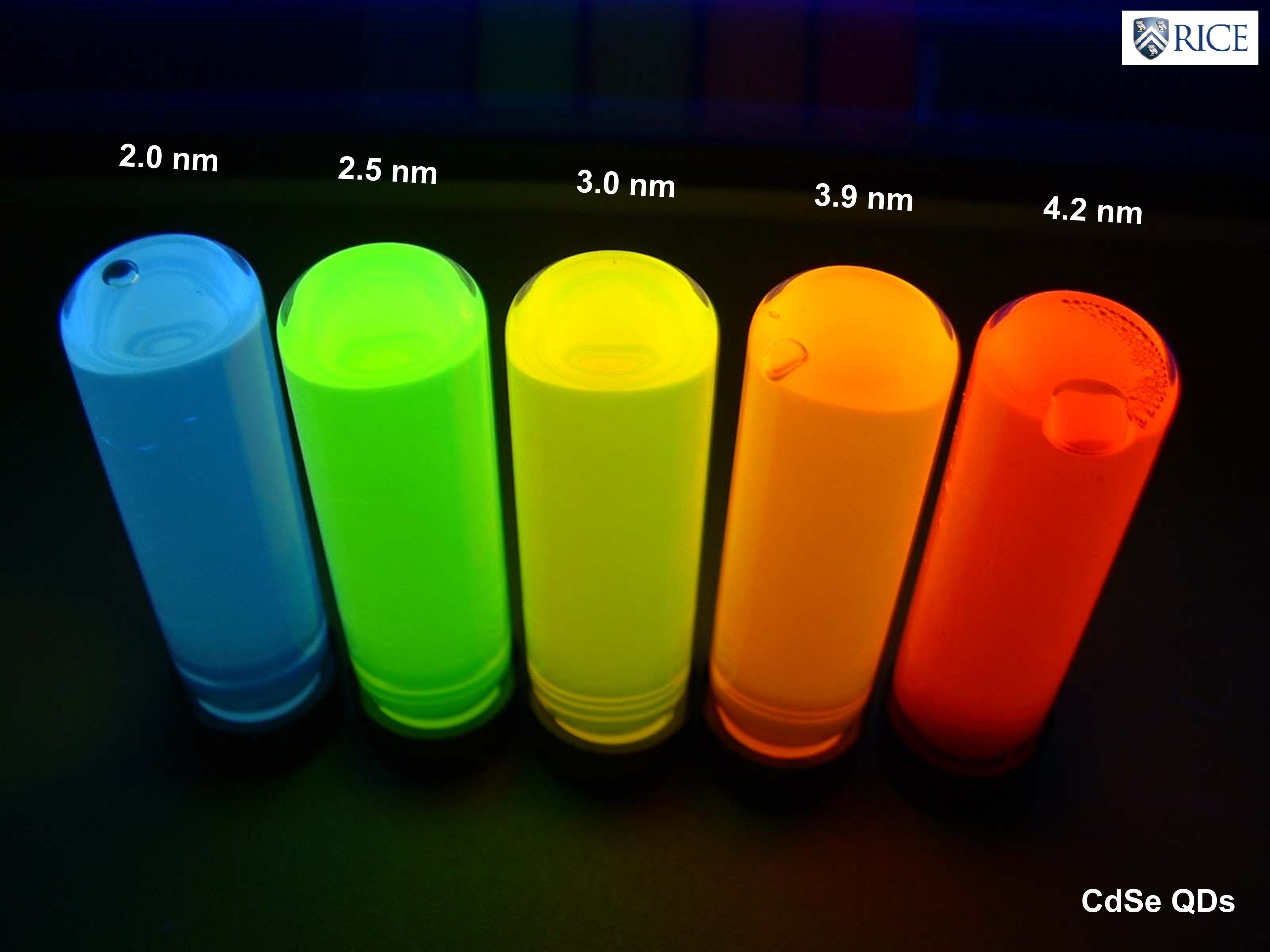
Acknowledgments

RICE



CENTER FOR BIOLOGICAL AND ENVIRONMENTAL NANOTECHNOLOGY
CBEN

- National Science Foundation
- Smalley/Curl Award
- 3M
- Welch Foundation
- SABIC Americas
- WGC
- AEC

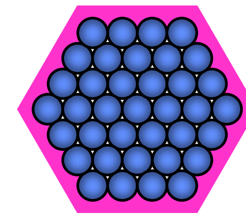


2.0 nm
2.5 nm
3.0 nm
3.9 nm
4.2 nm
CdSe QDs
RICE

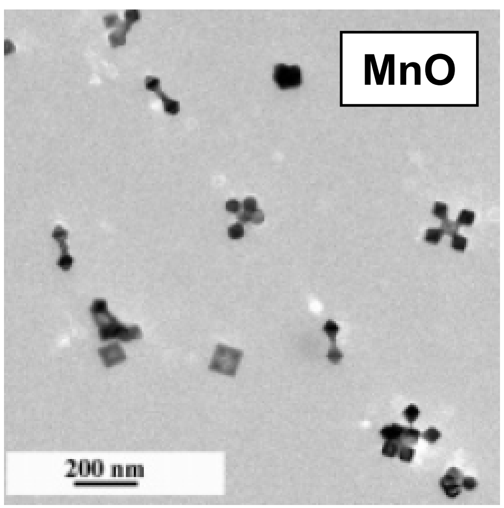
Nanoparticles (NPs)

- 1-100 nm in all three dimensions
- Can be prepared with uniform sizes…
  - *σ as low as 5%*
- … and with uniform shapes
  - *spherical*
  - *rod-shaped (>100 nm = nanowires)*
  - *e.g., arrows, tetrapods, stars, cubes, triangles*
- Synthesized and handled in a liquid as a sol

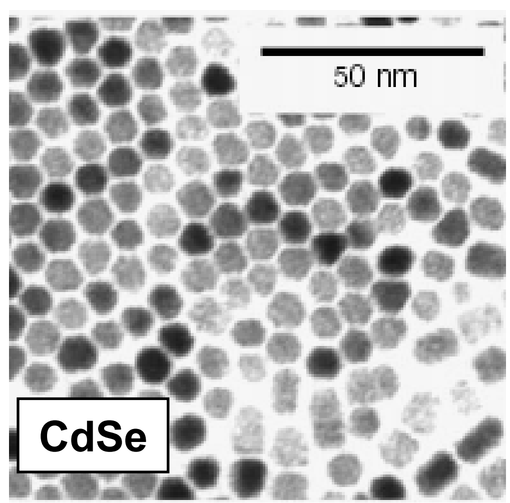
NPs have a surface coating



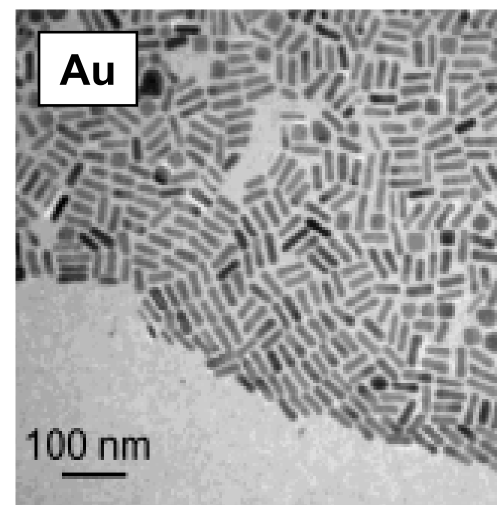
e.g., surfactant, polymer, ionic species



(Whitmire and co-workers, 2006)



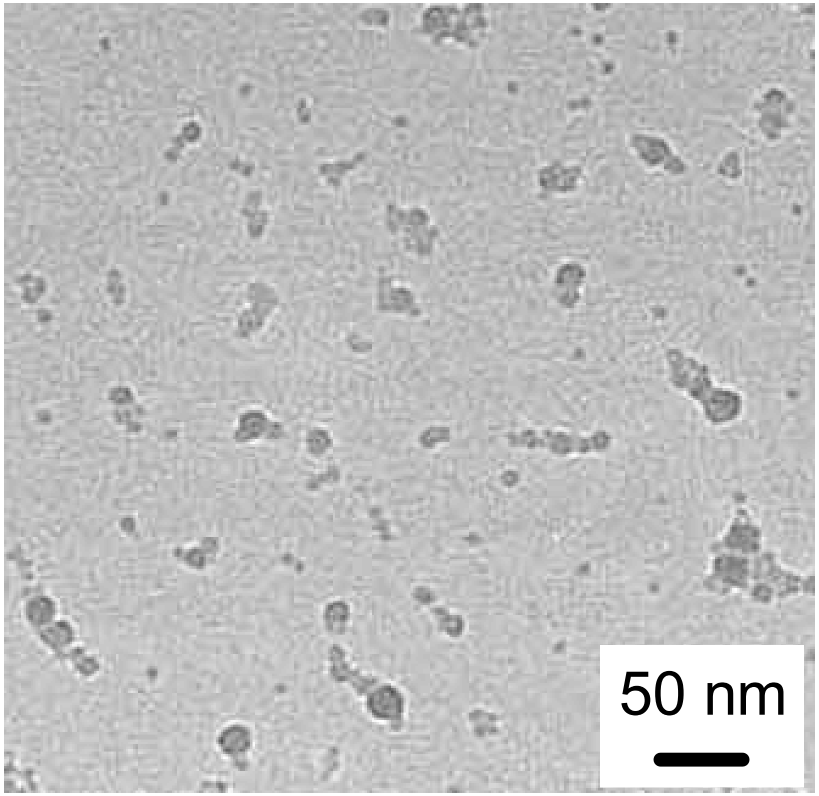
(Alivisatos and co-workers, 2000)



(Murphy and co-workers, 2003)

What do NPs look like macroscopically?

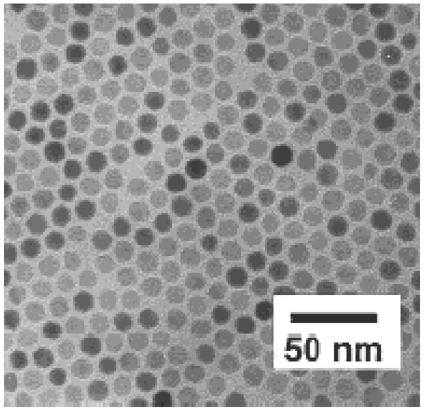
SiO_2 nanoparticles (NPs)



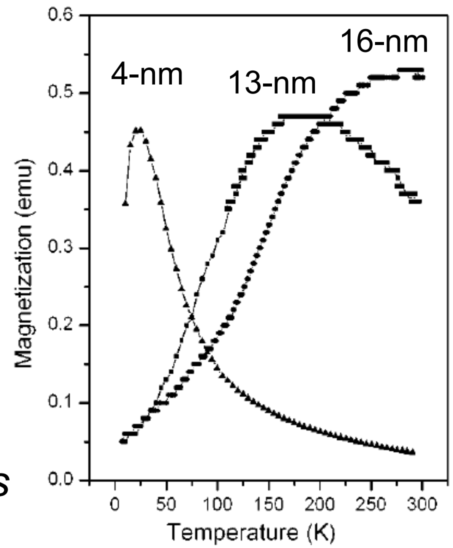
...as a clear suspension in water

Size-dependent properties of NPs

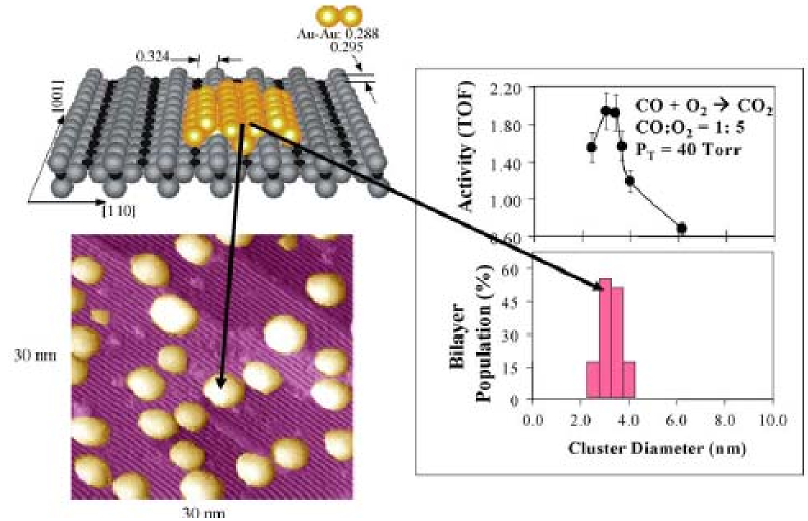
γ-Fe_2O_3 NPs (magnetism)



Hyeon and co-workers



TiO_2-supported Au NPs (catalysis)

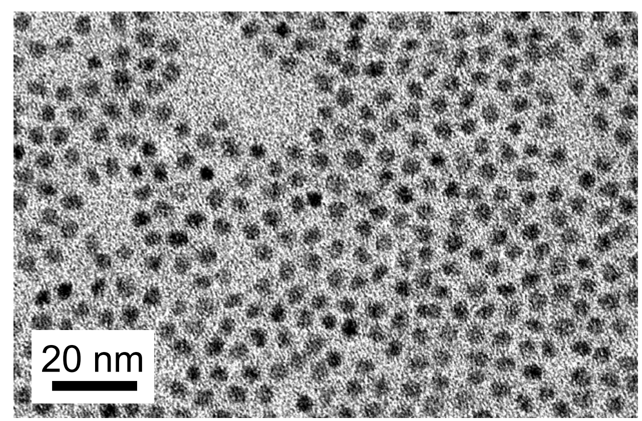


Goodman and co-workers

Gold-shell/SiO_2-core particles (absorbance)

Halas, West, and co-workers

CdSe quantum dots (emission)

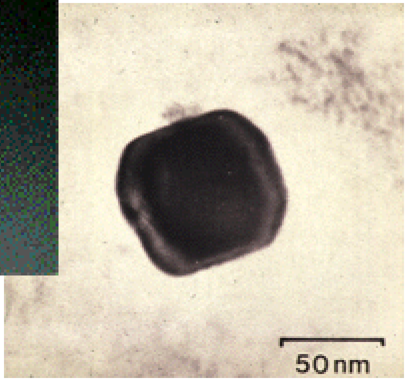


NPs pre-date “nanotechnology”

Original Au NP suspensions prepared by Michael Faraday in 1856

The Royal Institution of Great Britain, Faraday Museum (www.rigb.org)

The Lycurgus Cup, made by Roman glass makers in 4th century AD

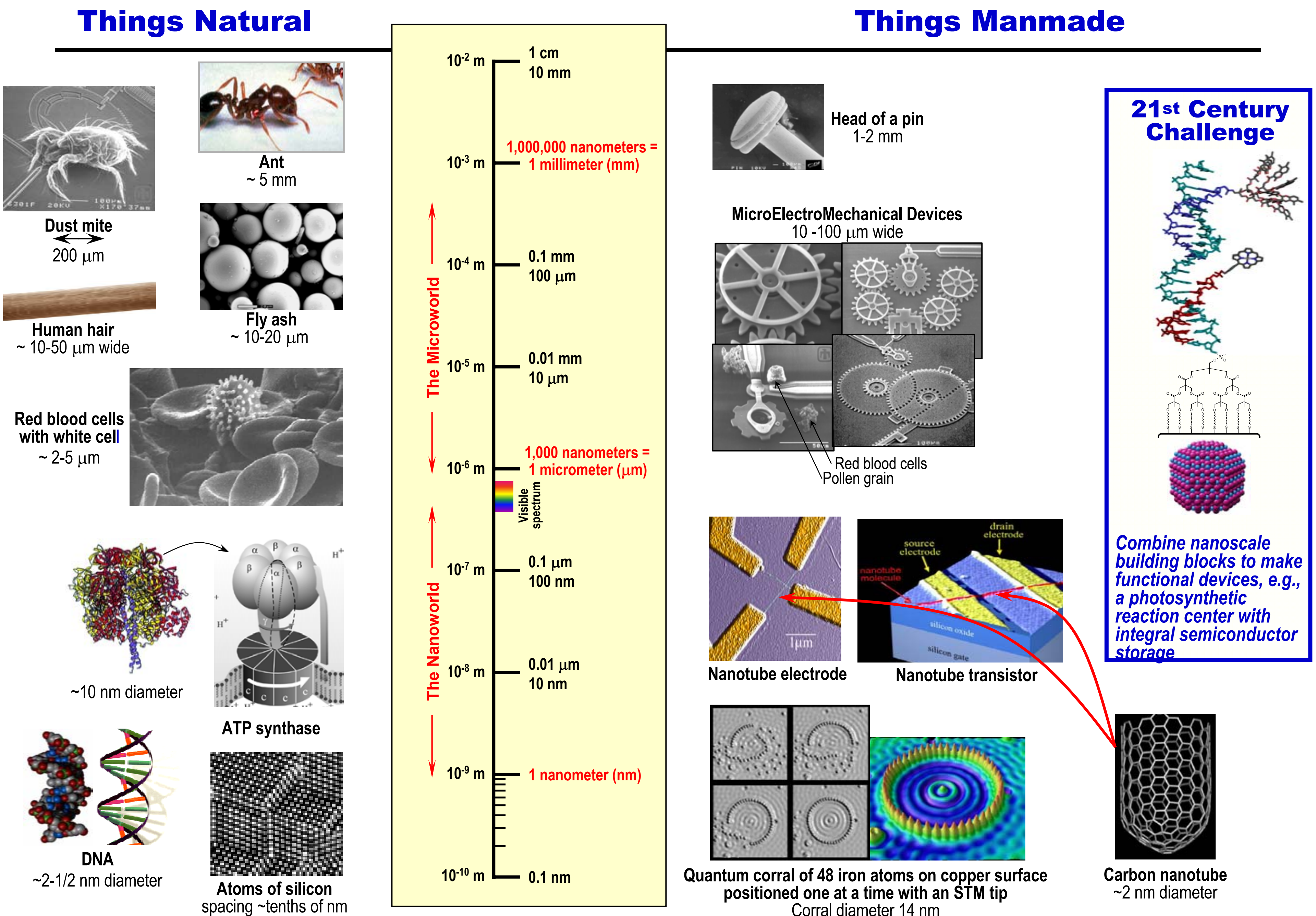


Size ~ 70 nm
Composition: 70% Ag, 30% Au

The British Museum (www.british-museum.ac.uk)

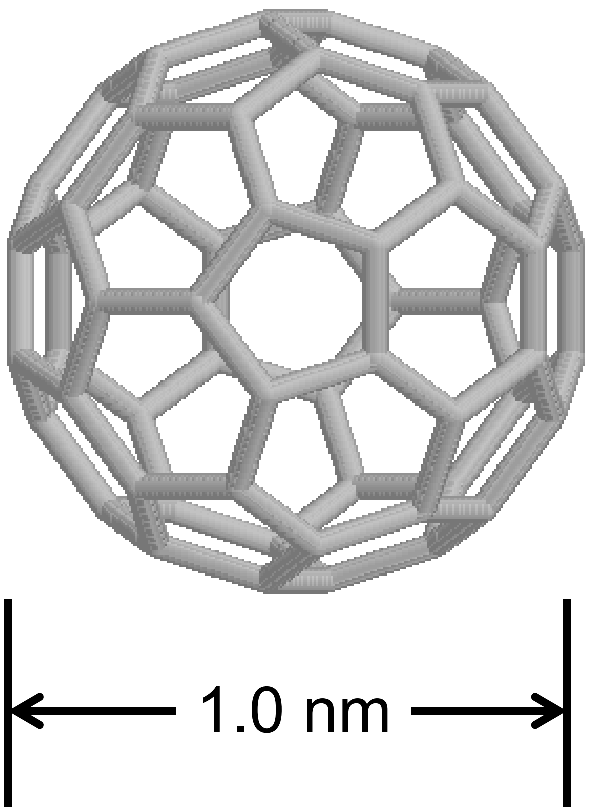
The Scale of Things -- Nanometers and More

(Ref.: Dept. of Energy Office of Science)

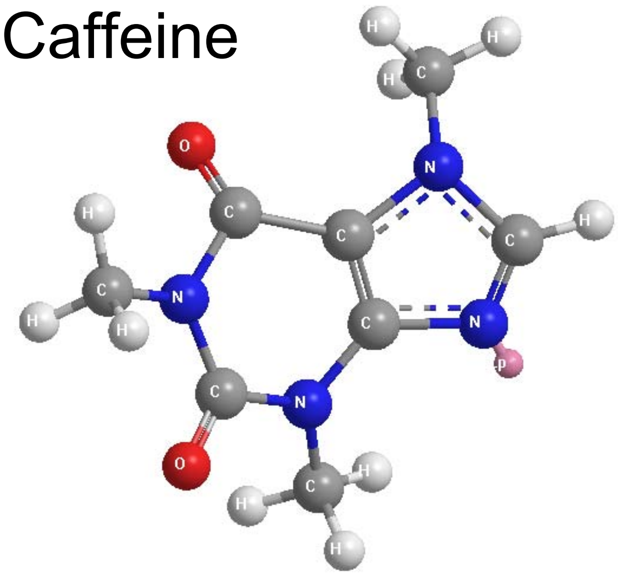


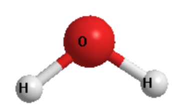
Can molecules be called nanomaterials?

Buckyball, C60



Caffeine



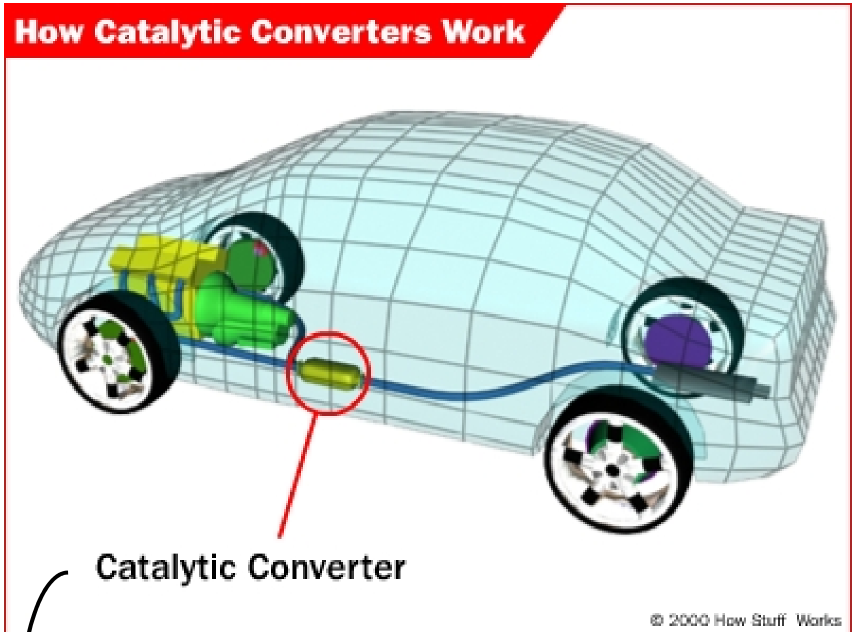


Water

(to scale)

(Technically yes, but it makes most sense if there is some size-dependent property that is shown)

Are catalysts nanomaterials? YES!



Reactions to remove undesirables:

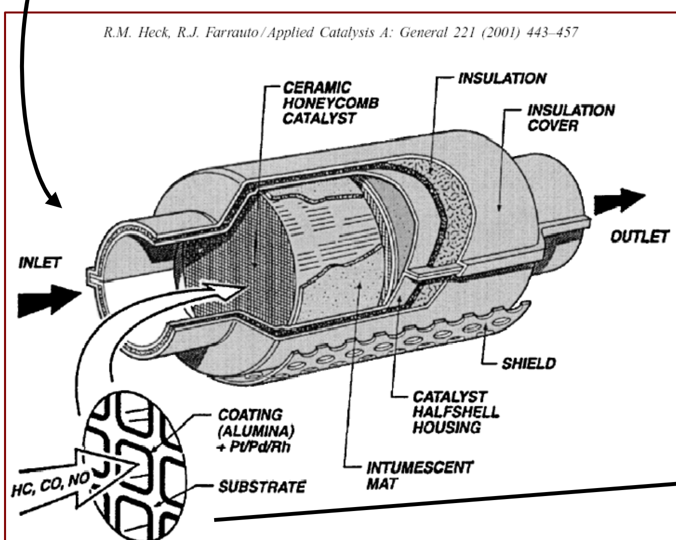
$2CO + O_2 \rightarrow 2CO_2$

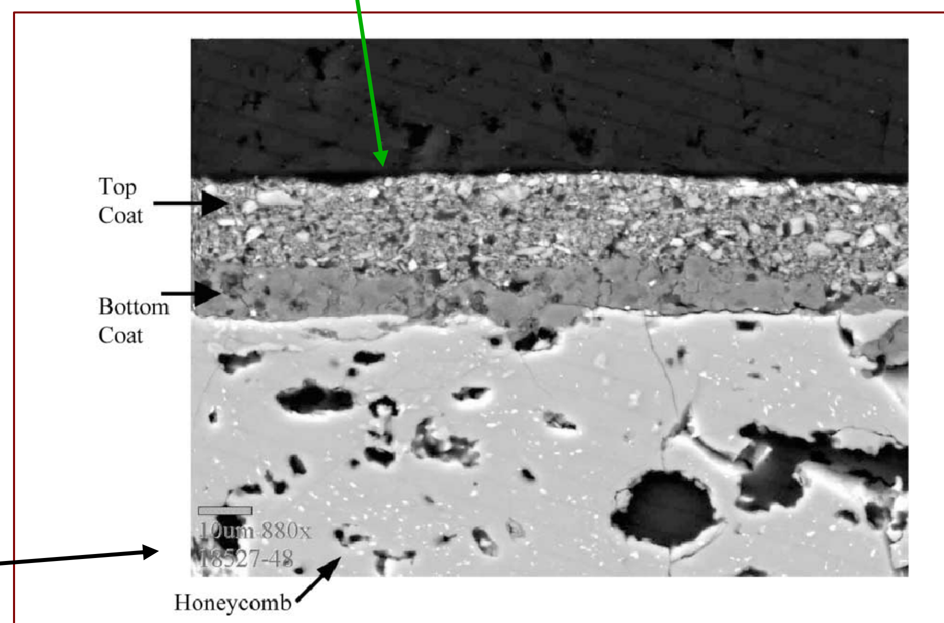
Hydrocarbon + $O_2 \rightarrow CO_2, H_2O$

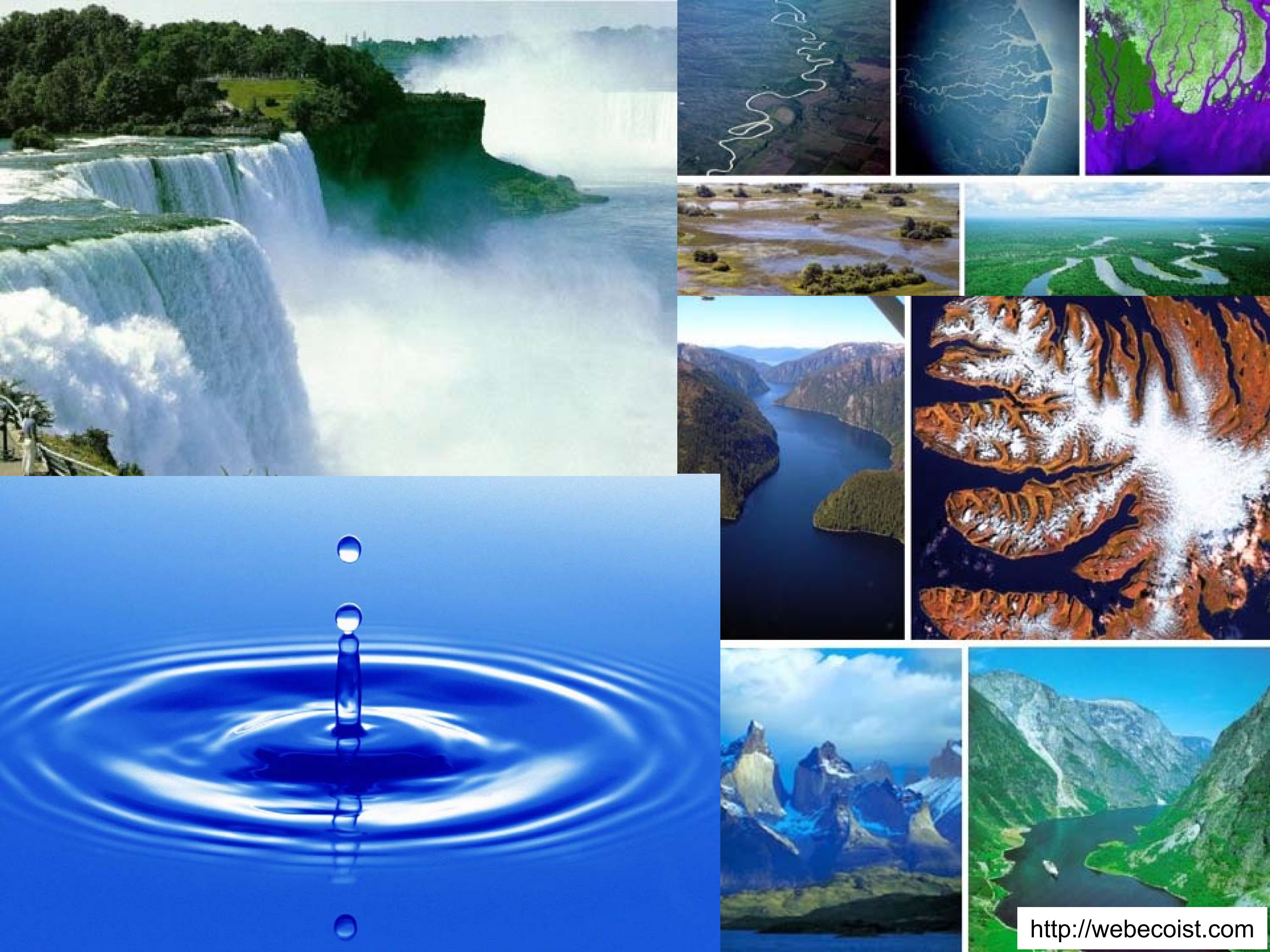
$2NO + 2CO \rightarrow 2CO_2 + N_2$

NO + hydrocarbon $\rightarrow CO_2, H_2O, N_2$

Catalyst = Pt,Rh,Pd nanoparticles

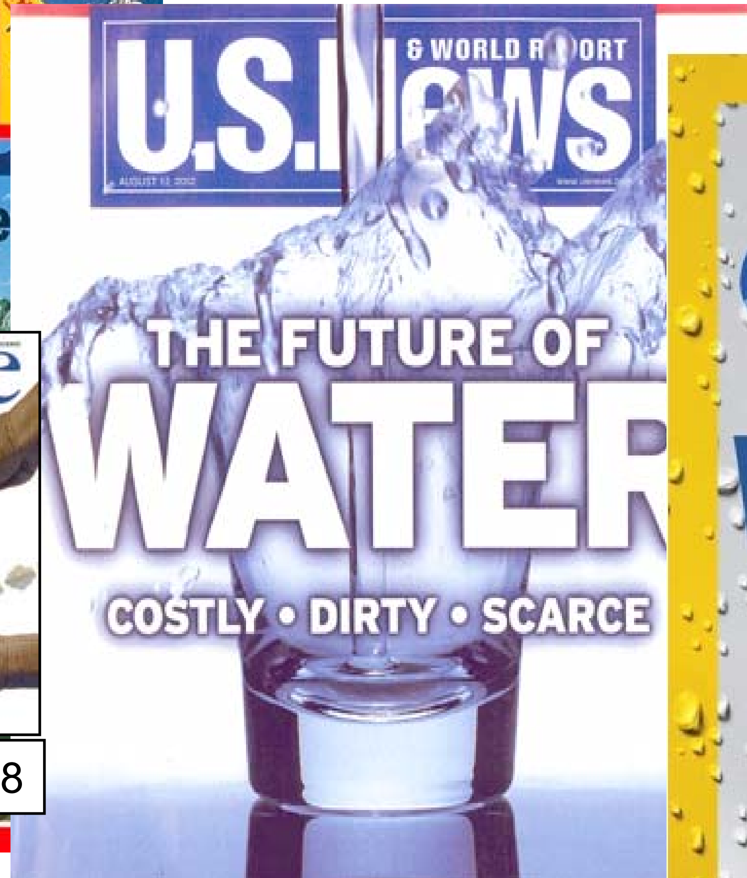




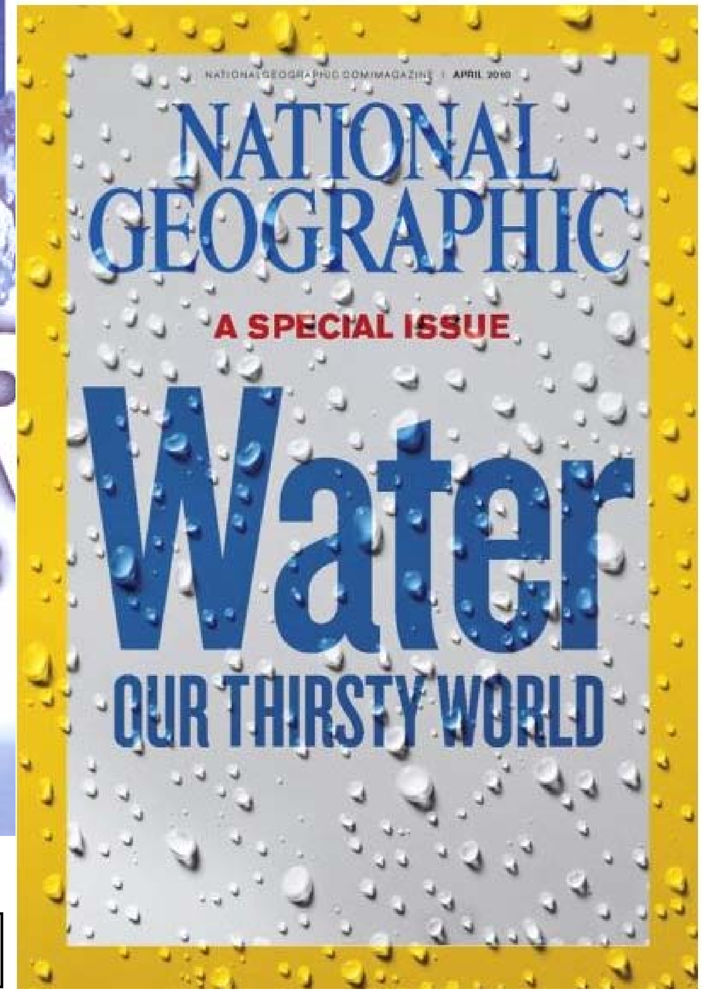

http://webecoist.com

20 March, 2008

Sep. 22, 1980



Aug. 12, 2002



April 2010

http://projects.nytimes.com/toxic-waters

Toxic Waters

A series about the worsening pollution in American waters and regulators' response

http://www.un.org/waterforlifedecade/

Groundwater considerations

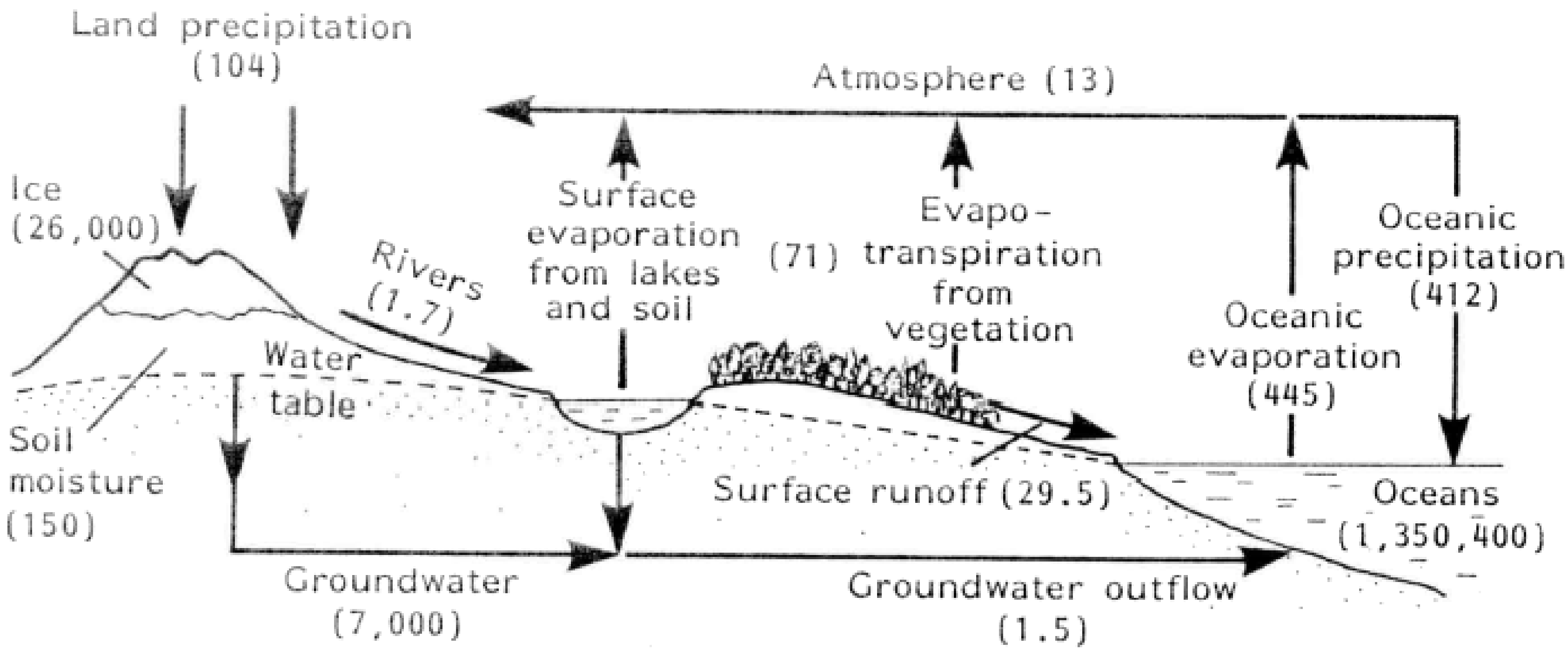


Figure 2.1. Hydrological cycle showing the volume of water stored and the amount cycled annually. All volumes are expressed as 10^3 km^3

(from N. F. Gray, "Drinking Water Quality" (1994)

Groundwater used in industrial, agricultural, and commercial applications

"…ground water is a drinking-water source for about one-half of the Nation's population… Ground water is important as a drinking-water supply in every State."
National Water-Quality Assessment Program of the U.S. Geological Survey, Circular 1292 (2006)

Partial list of groundwater pollutants

Chlorinated methanes
- Carbon tetrachloride (CCl_4)
- Chloroform ($CHCl_3$)
- Dichloromethane (CH_2Cl_2)
- Chloromethane (CH_3Cl)

Chlorinated benzenes
- Hexachlorobenzene (C_6Cl_6)
- Pentachlorobenzene (C_6HCl_5)
- Tetrachlorobenzenes ($C_6H_2Cl_4$)
- Trichlorobenzenes ($C_6H_3Cl_3$)
- Dichlorobenzenes ($C_6H_4Cl_2$)
- Chlorobenzene (C_6H_5Cl)

Pesticides
- DDT ($C_{14}H_9Cl_5$)
- Lindane ($C_6H_6Cl_6$)

Organic dyes
- Orange II ($C_{16}H_{11}N_2NaO_4S$)
- Chrysoidine ($C_{12}H_{13}ClN_4$)
- Tropaeolin O ($C_{12}H_9N_2NaO_5S$)
- Acid Orange
- Acid Red

Heavy metal ions
- Mercury (Hg^{2+})
- Nickel (Ni^{2+})
- Silver (Ag^{+})
- Cadmium (Cd^{2+})

Trihalomethanes
- Bromoform ($CHBr_3$)
- Dibromochloromethane ($CHBr_2Cl$)
- Dichlorobromomethane ($CHBrCl_2$)

Chlorinated ethenes
- Tetrachloroethene (C_2Cl_4)
- Trichloroethene (C_2HCl_3)
- *cis*-Dichloroethene ($C_2H_2Cl_2$)
- *trans*-Dichloroethene ($C_2H_2Cl_2$)
- 1,1-Dichloroethene ($C_2H_2Cl_2$)
- Vinyl chloride (C_2H_3Cl)

Other polychlorinated hydrocarbons
- PCBs
- Dioxins
- Pentachlorophenol (C_6HCl_5O)

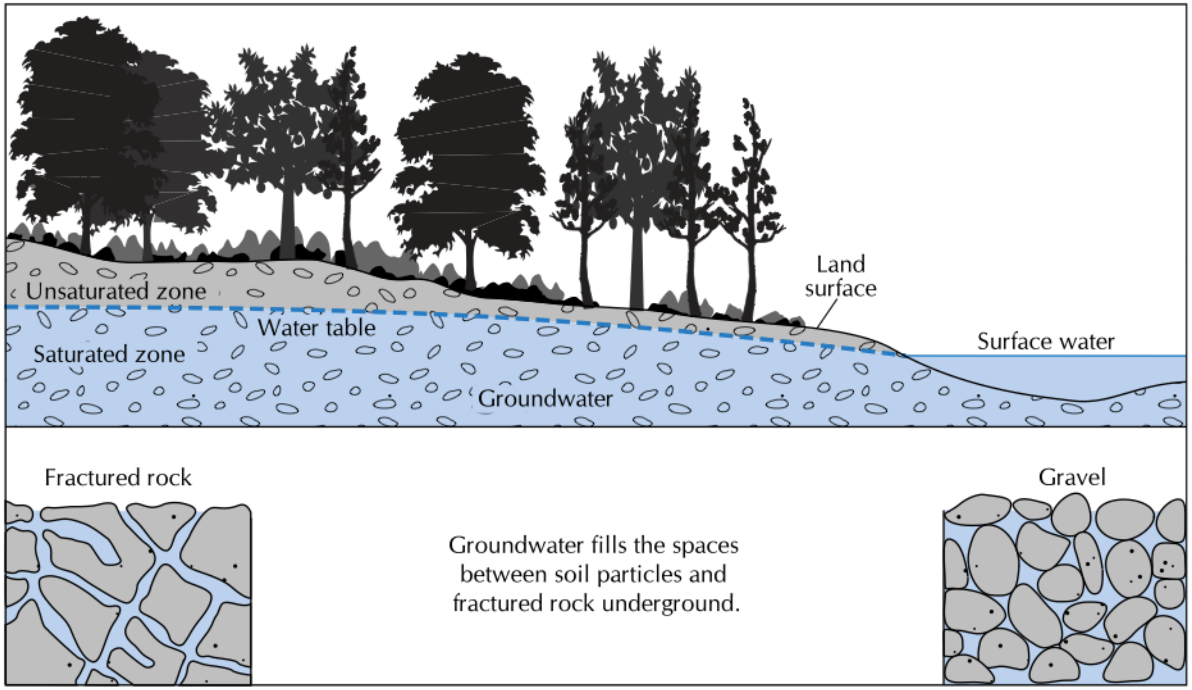
Other organic contaminants
- N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_2O$)
- TNT ($C_7H_5N_3O_6$)

Inorganic anions
- Dichromate ($Cr_2O_7^{2-}$)
- Arsenic (AsO_4^{3-})
- Perchlorate (ClO_4^-)
- Nitrate (NO_3^-)

W.-X. Zhang, *J. Nanopart. Res.* **2003**, 5, 323-332

DNAPL – Major groundwater contaminant

- Dense Non-Aqueous Phase Liquid
- One of the major forms of groundwater contamination
- Migrates deeply below the water table
- Slightly soluble in water, slowly dissolves in the groundwater for long-term contamination
- Common for industrial uses: some oils (creosote, polychlorinated biphenyls), coal tar, and other chlorinated hydrocarbon solvents



2007 CERCLA list

- **DNAPL**: **21** out of top 30
- Chlorinated hydrocarbons: 16 out of top 30

Rank	Substance Name
1	Arsenic
2	Lead
3	Mercury
4	Vinyl Chloride
5	**Polychlorinated Biphenyls (PCB)**
6	Benzene
7	Cadmium
8	**Polycyclic Aromatic Hydrocarbons**
9	**Benzo(A) Pyrene**
10	**Benzo(B) Fluoranthene**
11	**Chloroform**
12	**DDT, P,P'-**
13	**Aroclor 1254**
14	**Aroclor 1260**
15	**Dibenzo(A,H) Anthracene**
16	**Trichloroethylene (TCE)**
17	**Dieldrin**
18	Chromium, Hexavalent
19	Phosphorus, White
20	**Chlordane**
21	**DDE, P,P'-**
22	**Hexachlorobutadiene**
23	**Coal Tar Creosote**
24	**Aldrin**
25	**DDD, P,P'-**
26	**Benzidine**
27	**Aroclor 1248**
28	Cyanide
29	**Aroclor 1242**
30	**Aroclor**

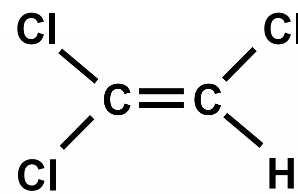
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) list at website of Agency for Toxic Substances and Disease Registry (http://www.atsdr.cdc.gov/cercla/).

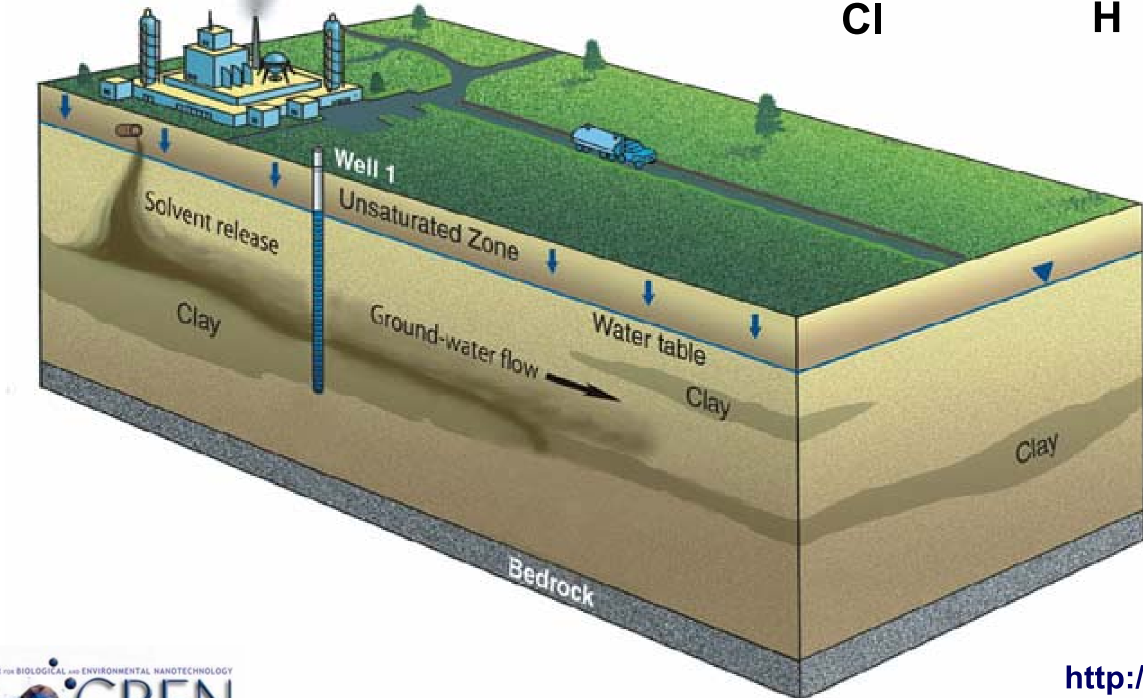
Trichloroethene (TCE) problem

Widely used as a degreasing solvent

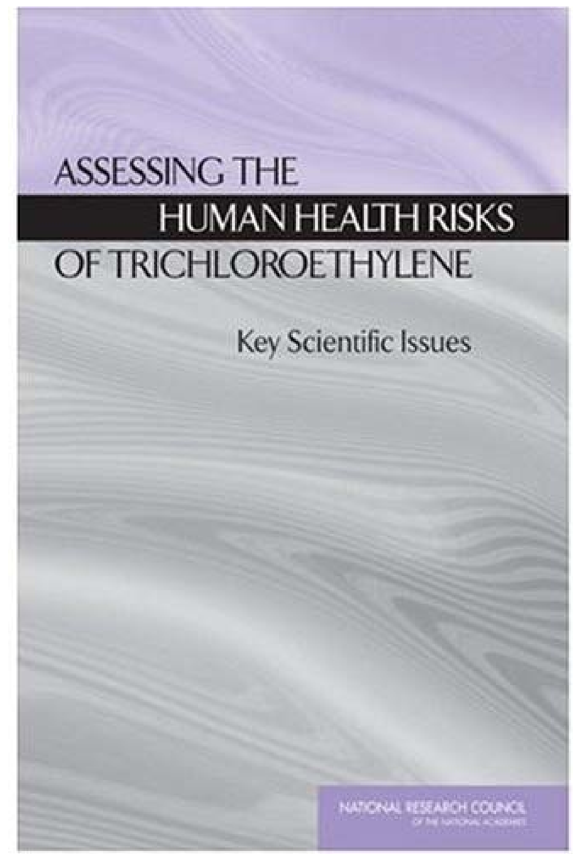
Found in 60% of Superfund sites

Highly persistent in groundwater, difficult to remove





Health effects: cancer, organ damage, developmental toxicity



(NRC, July 2006)

http://water.usgs.gov/nawqa/vocs/national_assessment/report/chapter5.html

EPA Administrator Jackson Outlines New Vision for Clean, Safe Drinking Water

Release date: 03/22/2010

Contact Information: Enesta Jones, jones.enesta@epa.gov, 202-564-7873, 202-564-4355 En español: Lina Younes, younes.lina@epa.gov 202-564-9924, 202-564-4355

WASHINGTON - In a speech today at the Association of Metropolitan Water Agencies (AMWA) annual conference in Washington, D.C., U.S. EPA Administrator Lisa P. Jackson announced the agency is developing a broad new set of strategies to strengthen public health protection from contaminants in drinking water. The aim is to find solutions that meet the health and economic needs of communities across the country more effectively than the current approach. EPA is also announcing a decision to revise the existing drinking water standards for four contaminants that can cause cancer.

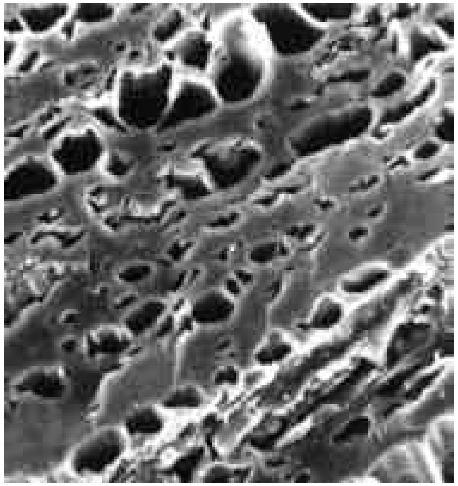
While exploring this shift in strategy, EPA continues to look for opportunities to increase protection using traditional approaches. In the newly finalized review of existing drinking water standards, EPA determined that scientific advances allow for stricter regulations for the carcinogenic compounds tetrachloroethylene, trichloroethylene, acrylamide and epichlorohydrin. Tetrachloroethylene and trichloroethylene are used in industrial and/or textile processing and can be introduced into drinking water from contaminated ground or surface water sources. Acrylamide and epichlorohydrin are impurities that can be introduced into drinking water during the water treatment process. Within the next year, EPA will initiate rulemaking efforts to revise the

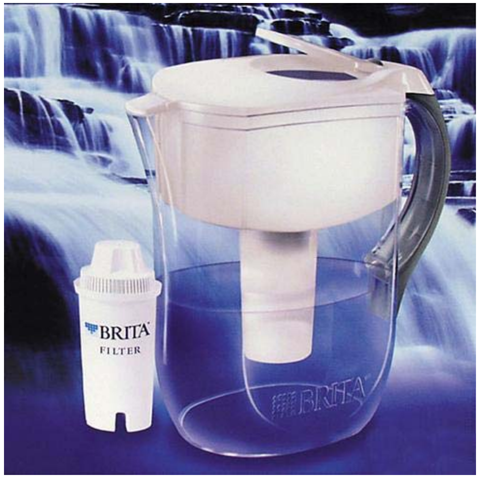
Water remediation strategy: adsorption

- Adsorption using activated carbon

www.activated-carbon.com

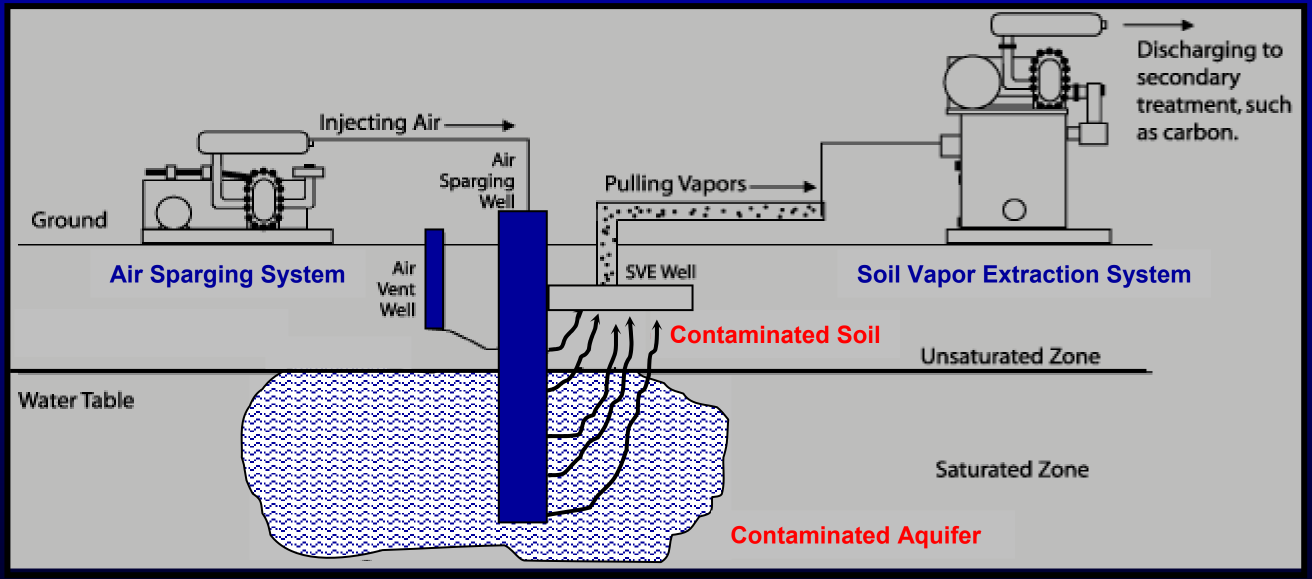
www.tigg.com





Remediation technologies

- Carbon adsorption
  - Contaminated groundwater is pumped out of the aquifer and into a series of carbon beds (*i.e. ex situ* treatment)
  - TCE is transported from liquid to solid phase
- Air stripping
  - Contaminated groundwater is contacted with an air stream
  - In aquifer remediation possible (*in situ* treatment)
  - TCE is transported from liquid to gas phase



➡ Major drawback is the required further treatment (i.e. incineration)

Hydrodechlorination (HDC) of TCE

- Catalysts: Pd black, Pd/alumina[1,2]
  - Remediated chlorinated ethenes, CCl_4, $CHCl_3$

$$CHCl{=}CCl_2 + 4H_2 \rightarrow CH_3CH_3 + 3\ HCl$$

TCE *ethane*

- Large scale pilot operation showing long term results[3]

- Catalyst cost is an issue

Pd/Al_2O_3 pellets

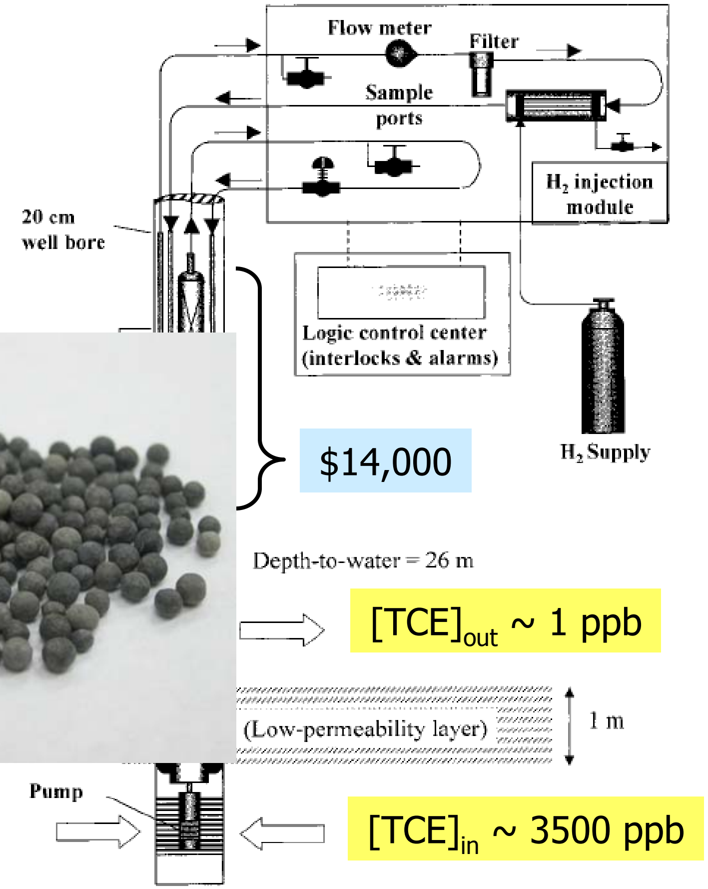


FIGURE 1. Reactive well configuration using catalytic reductive dehalogenation.

1. Lowry and Reinhard, *Environ. Sci. Technol.* (**1999**) 33, 1905
2. Lowry and Reinhard, *Environ. Sci. Technol.* (**2001**) 35, 696
3. McNab et al. *Environ. Sci. Technol.* (**2000**) 34, 149

An example of a catalytic particle in action

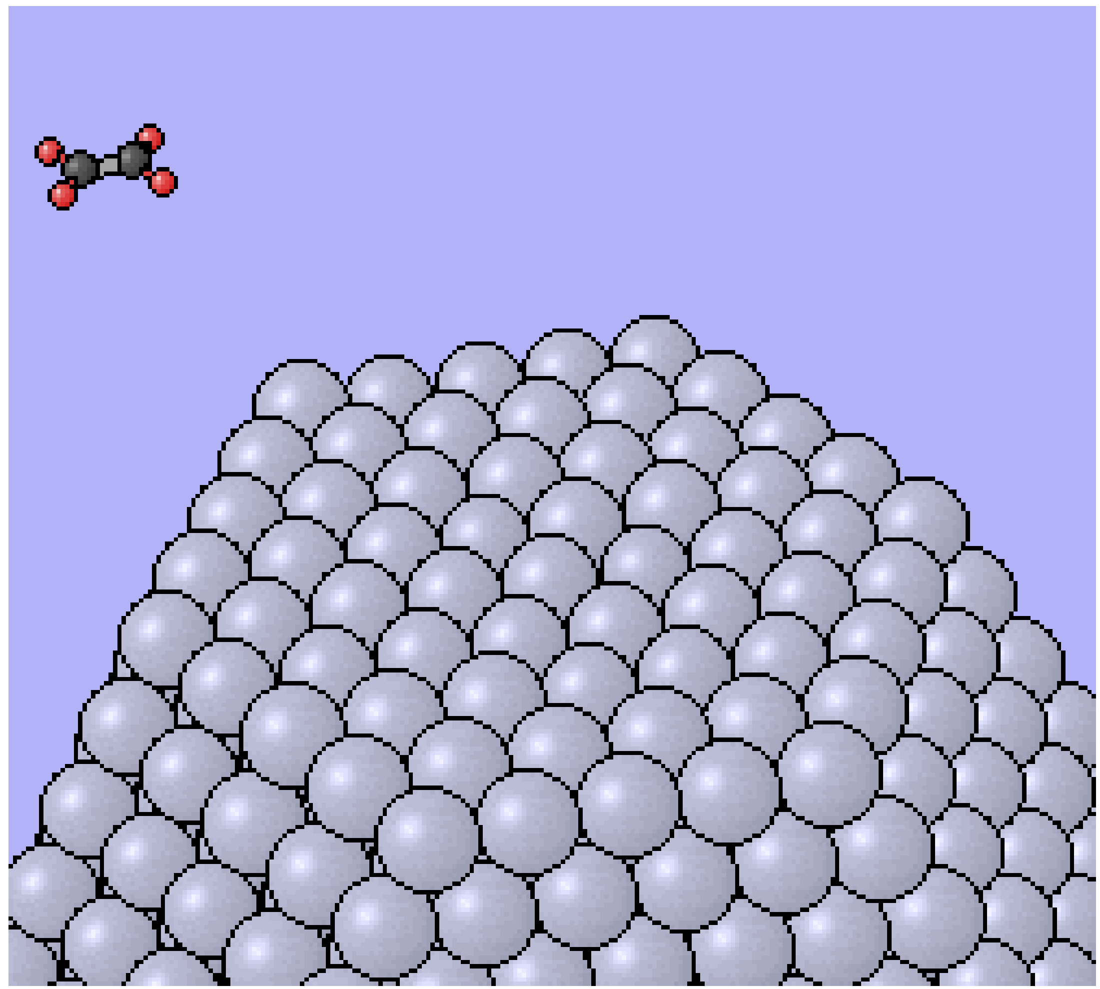
Dehydrogenation of ethylene using Ni nanoparticle catalysts

Ethylene: $H_2C{=}CH_2$

Acetylene: $HC{\equiv}CH$

+

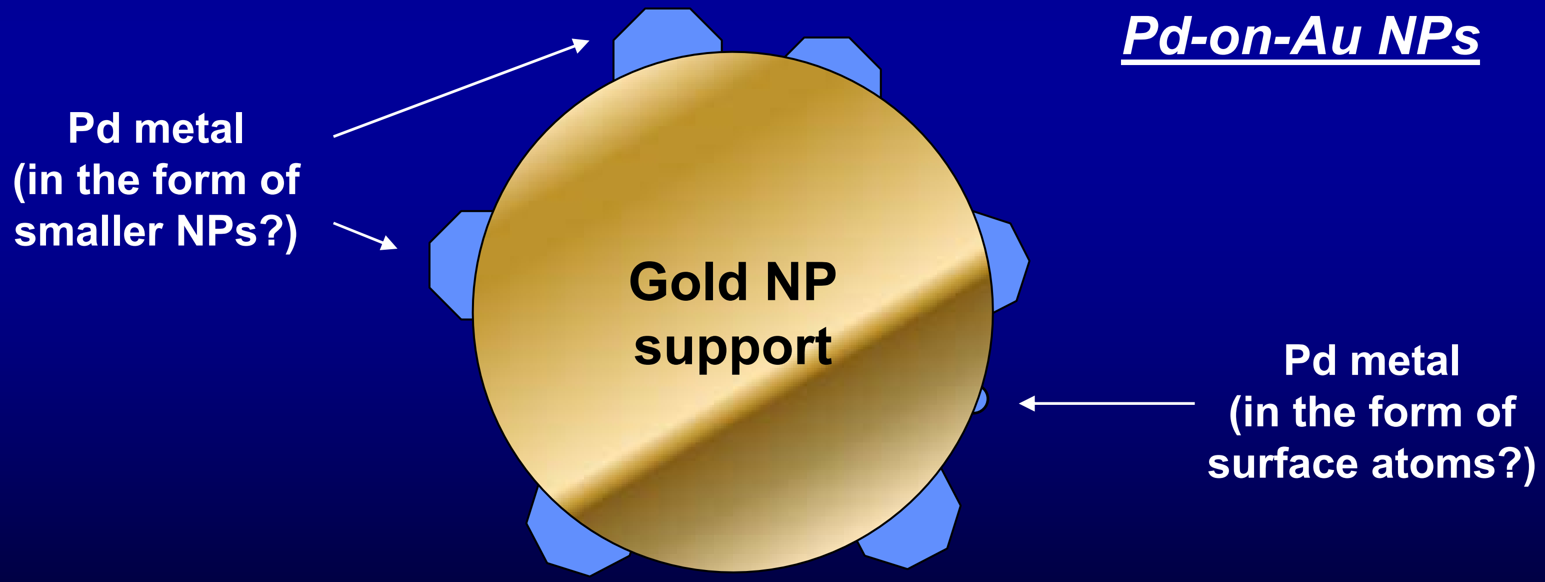
Hydrogen: H_2



http://leung.uwaterloo.ca/CHEM/750/

Our approach: Pd-on-Au NP catalyst

- Coat Au NP surface with Pd
  - Avoids alloy formation
  - Au NPs (Ø ~ 20 nm) can be readily synthesized
  - Au NPs are dispersed in water, handled as a suspension (sol)
  - Electroless plating chemistry is straightforward
  - True catalyst (accelerates reaction, but is not consumed)

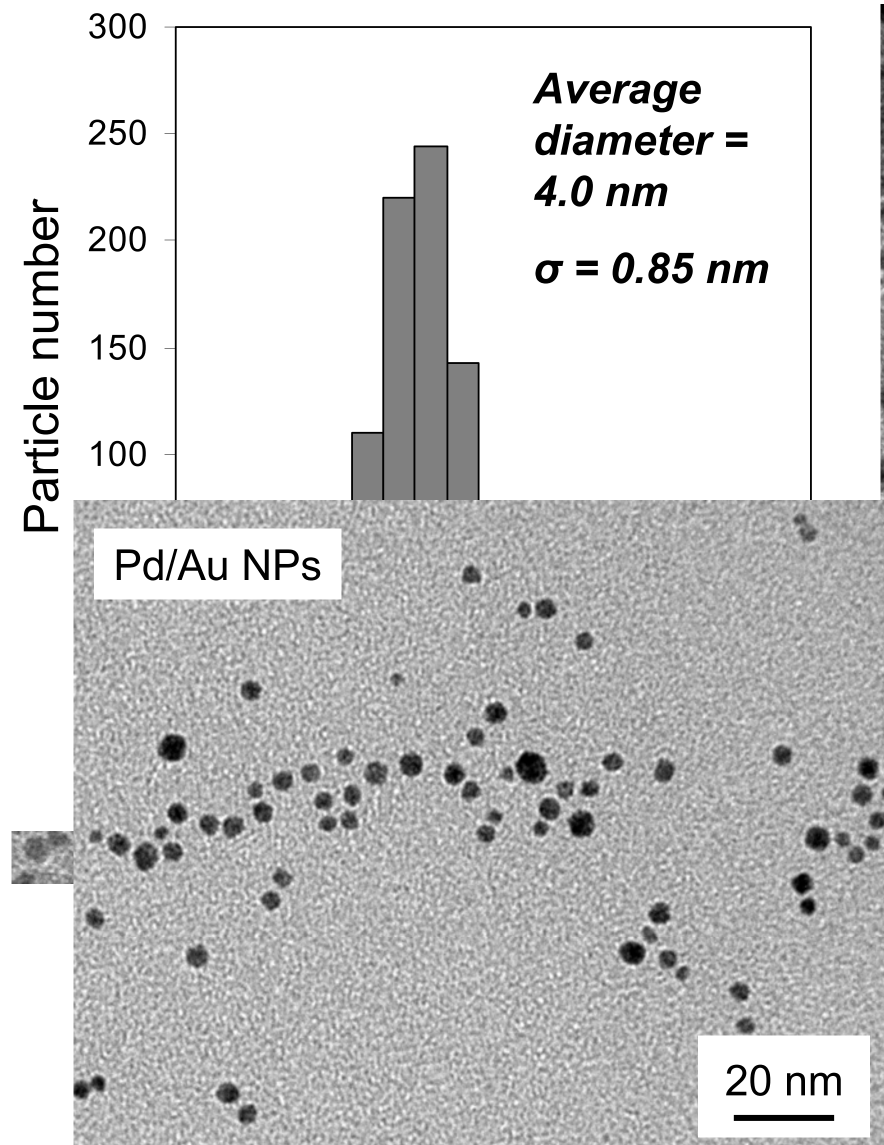


Other Pd NP catalyst synthesis routes: Crooks, El-Sayed, Bönnemann, others

Synthesis of 4-nm Pd-on-Au NPs

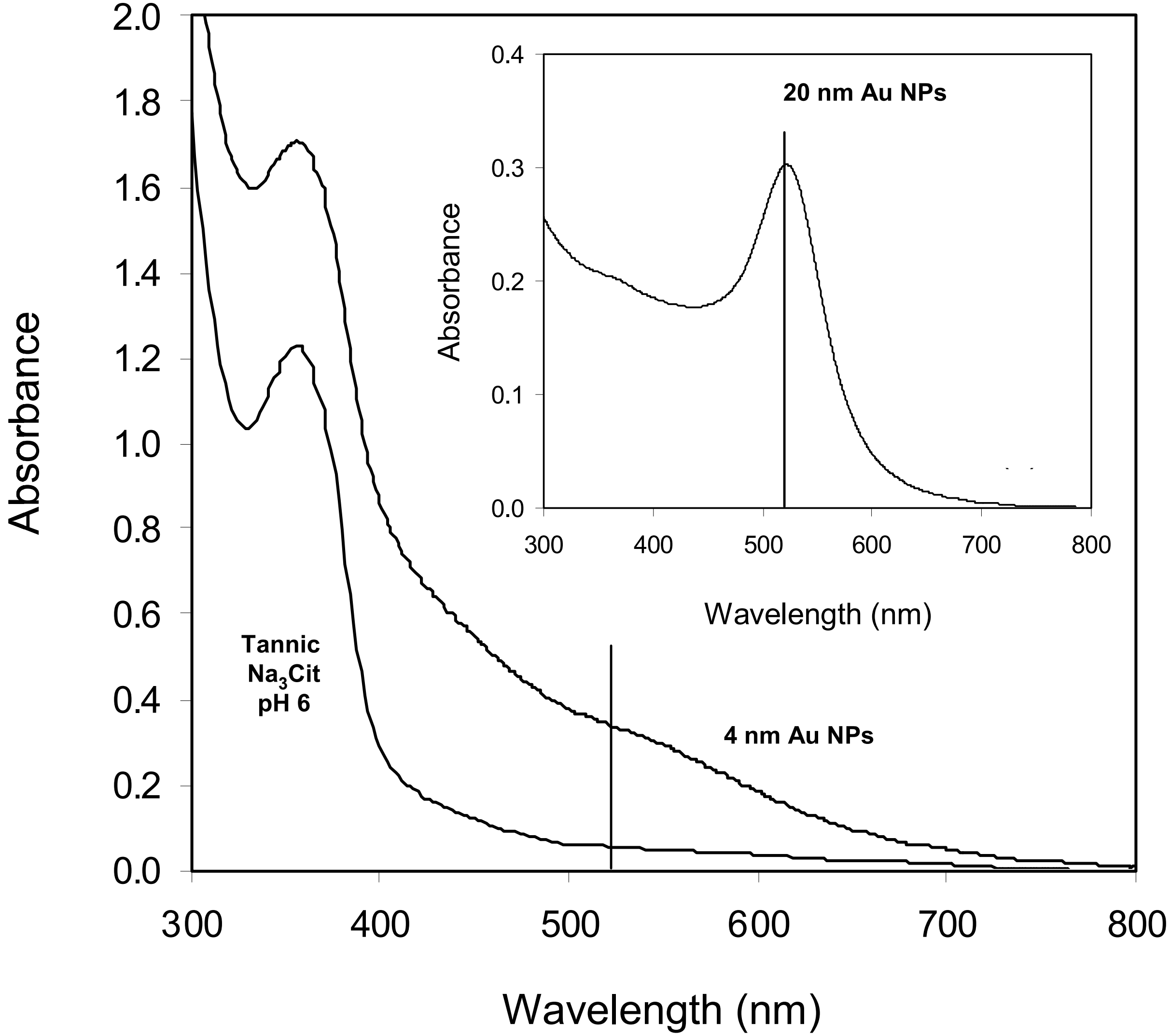
- Tannic acid and sodium citrate as co-reducing agents (Slot-Geuze method)
  - Solution 1 (0.05 g tannic acid, 0.04 g Na_3cit, 0.018 g K_2CO_3 to 20 ml H_2O)
  - Solution 2 (100 ml of 0.296 M $HAuCl_4$, 80 ml H_2O)
  - Heat both at 60 °C and add #1 to #2
  - Bring to a boil for 2 minutes

- $PdCl_4^{2-}$ salt added at RT, followed by H_2 gas contact



Nutt *et al.*, *Appl. Catal. B Env.* **69**, 115-125 (2006)

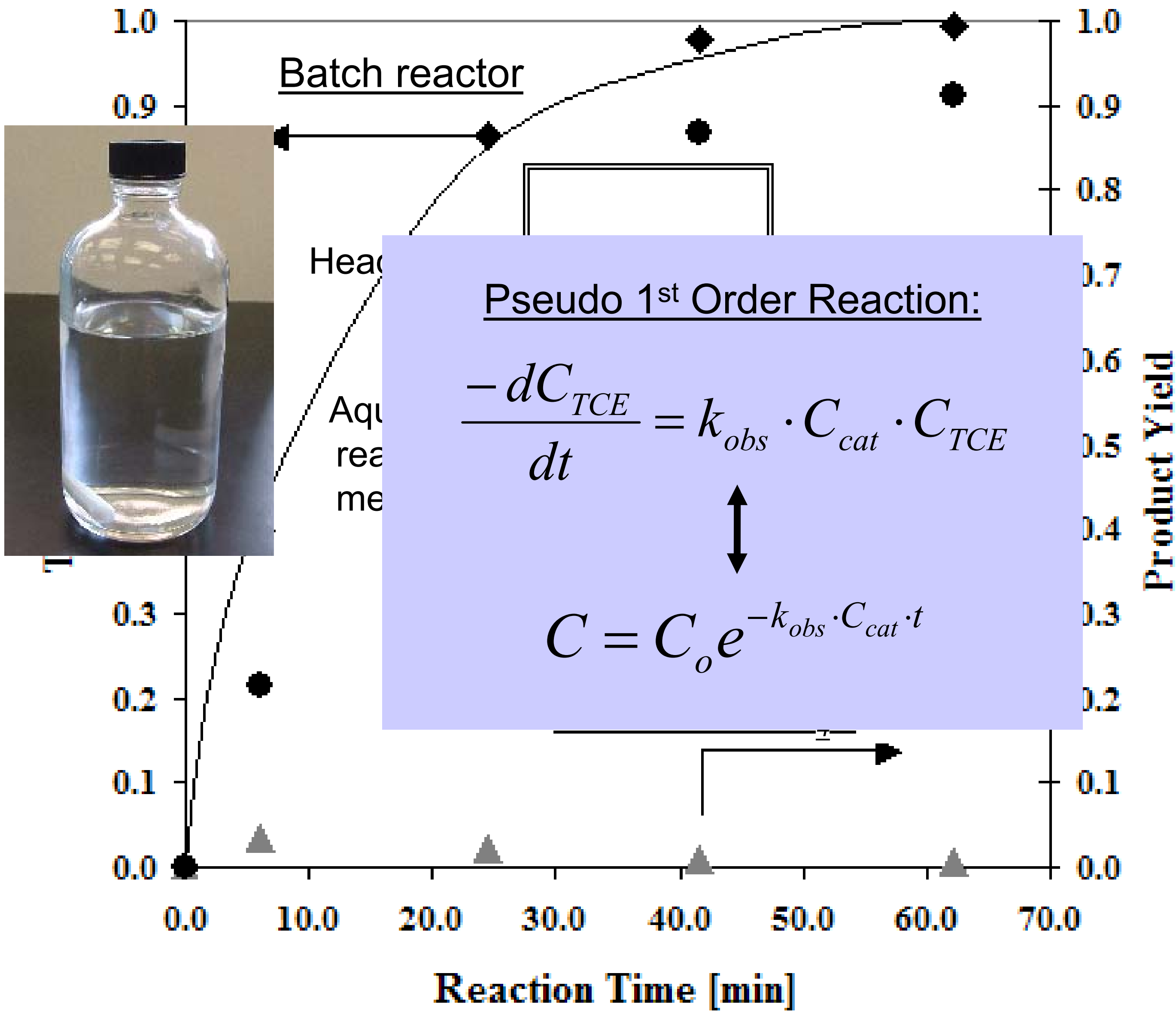
UV-vis spectrum of 4-nm Au NPs



4-nm
Au NPs

4-nm
Pd-on-Au
NPs
(~6 wt% Pd)

TCE HDC reaction analysis



Pseudo 1st Order Reaction:

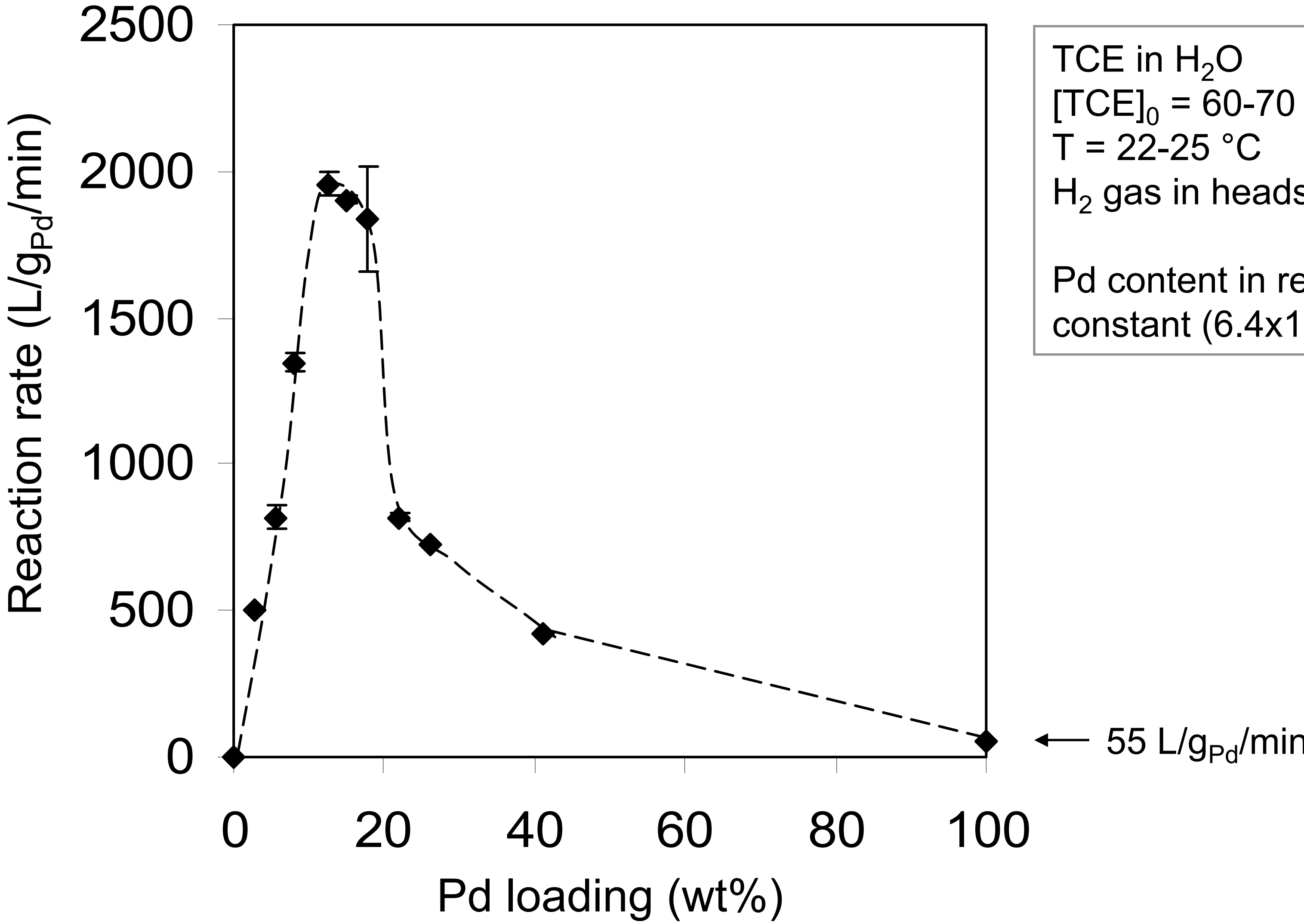
$$\frac{-dC_{TCE}}{dt} = k_{obs} \cdot C_{cat} \cdot C_{TCE}$$

$$\updownarrow$$

$$C = C_o e^{-k_{obs} \cdot C_{cat} \cdot t}$$

4.0-nm Au NPs
11.7 wt% Pd

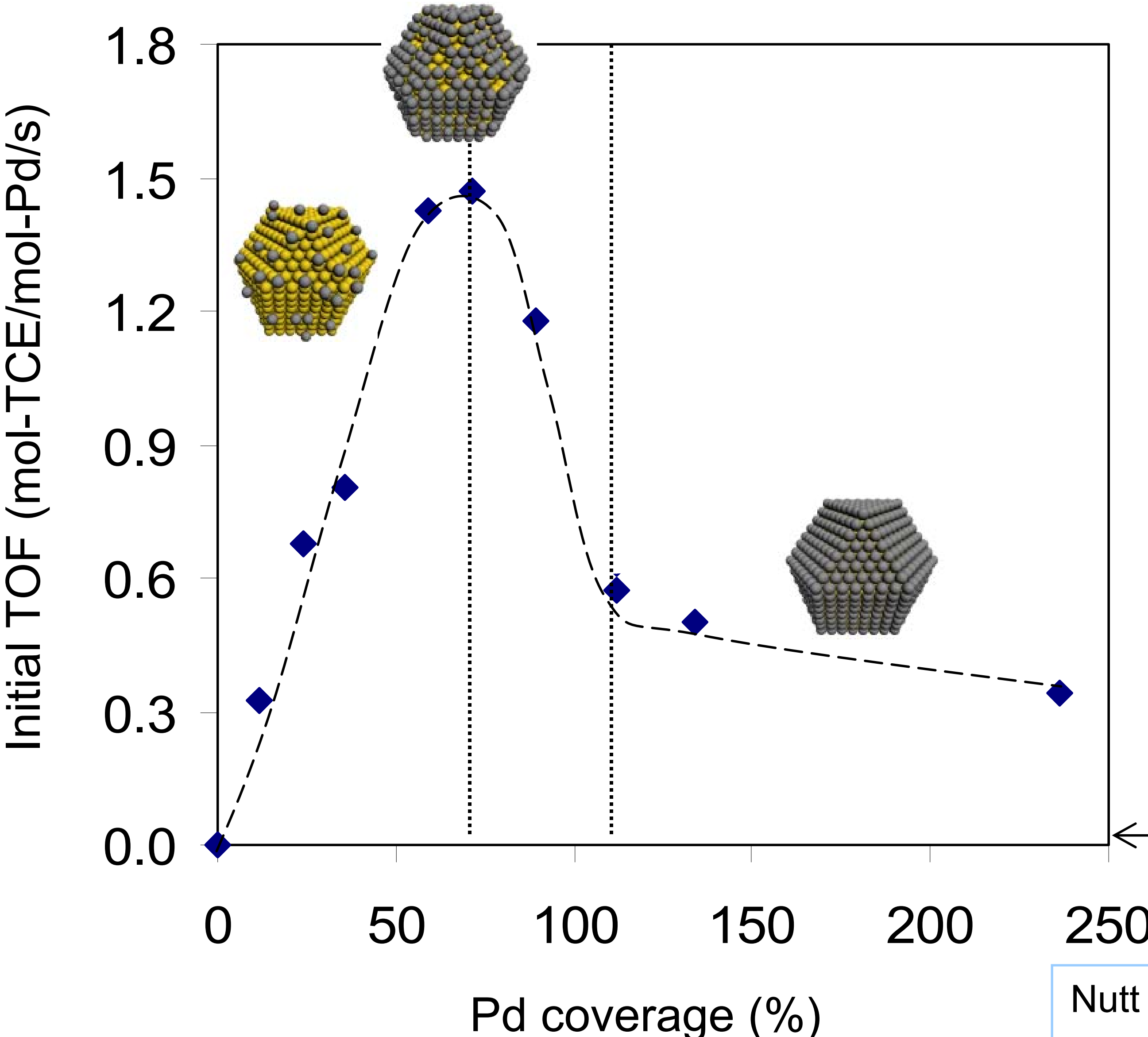
Reaction rate as function of wt% Pd



TCE in H_2O
$[TCE]_0$ = 60-70 ppm
T = 22-25 °C
H_2 gas in headspace

Pd content in reactor was constant (6.4×10^{-8} moles)

Nanostructure has strong influence



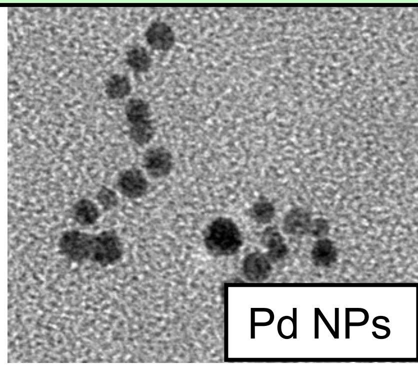
4-nm Pd NPs

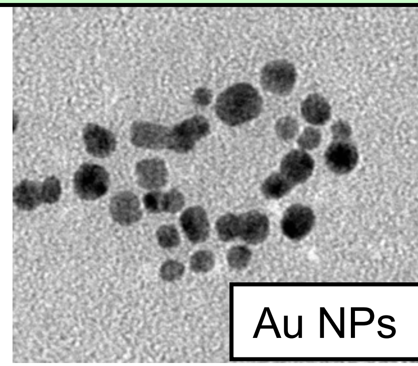
0.044 (mol-TCE/mol-Pd)/s

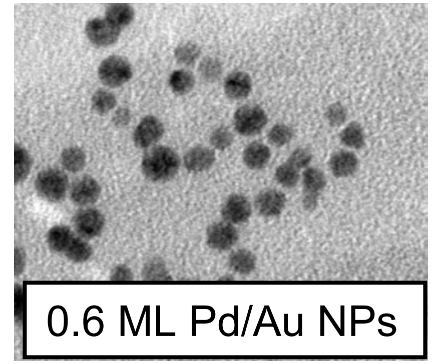
Nutt *et al.*, *Appl. Catal. B Env.* **69**, 115-125 (2006)

Indirect evidence for Pd/Au nanostructure

Pd-on-Au nanostructure not observed through TEM

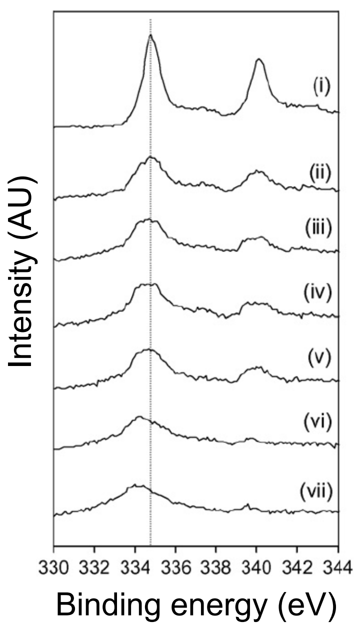






10 nm

XPS shows Pd in contact with Au on Pd/Au NPs



Pd NPs

300% ML Pd/Au NPs

200% ML Pd/Au NPs

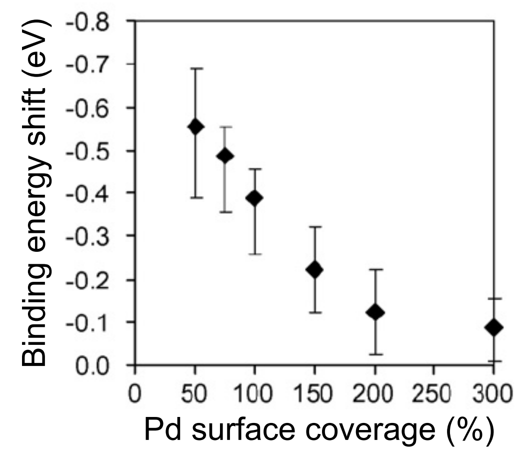
150% ML Pd/Au NPs

100% ML Pd/Au NPs

75% ML Pd/Au NPs

50% ML Pd/Au NPs

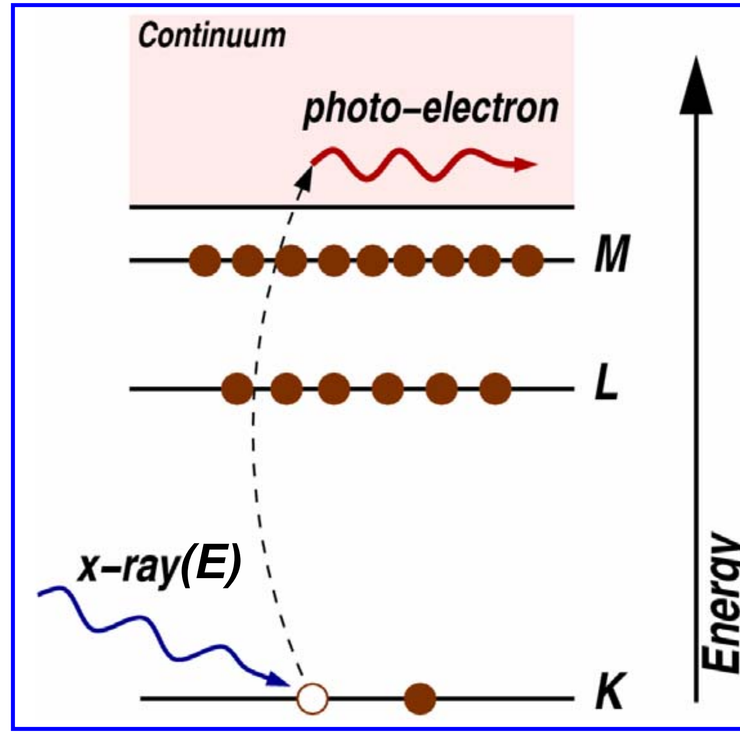
Pd binding energy shifts as a function of Pd surface coverage

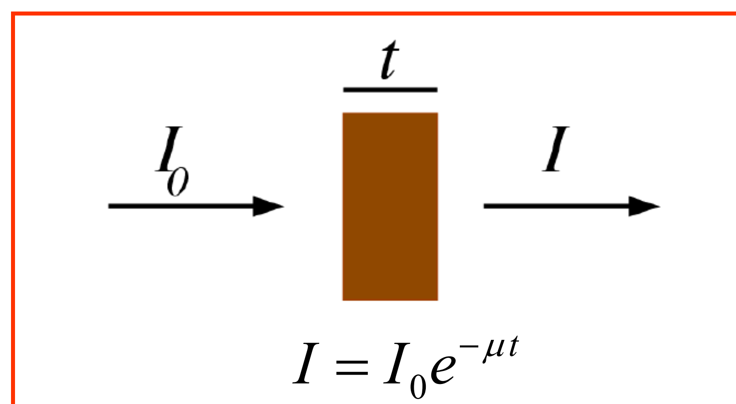


Nutt et al., *Appl. Catal. B: Environ.*, 2006, *69*, 116.

XAFS for nanostructure determination

- XAFS: **X-ray Absorption Fine-structure Spectroscopy**
  - Based on photo-electron effect (an x-ray is absorbed and a core-level electron is promoted out of the atom)
  - Determine nanostructure by measuring absorption coefficient μ as a function of x-ray energy E
  - Provide element-specific bulk information including oxidation state, distance, coordination number, and atom surroundings
  - Good for solid and liquid samples, dilute species, *in situ* measurements





Dr. Jeffrey T. Miller

Argonne NATIONAL LABORATORY

Newville, *Fundamentals of XAFS*, Univ. of Chicago (2004)

EXAFS results – Pd/Au NPs

Calculated from atomic ratio

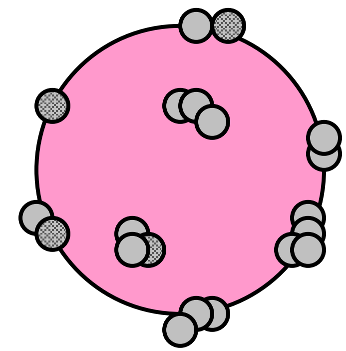
Edge	Treatment	Scattering path	N	N_{random}
Pd	Air RT	Pd-O	0.9	
		Pd-Pd	3.3	**1.3**
		Pd-Au	4.0	**6.0**

Pd ~20% oxidized
Pd islands
(more Pd-Pd neighbors)

Edge	Treatment	Scattering path	N	N_{random}
Au	Air RT	Au-Au	9.6	**8.9**
		Au-Pd	1.3	**2.0**

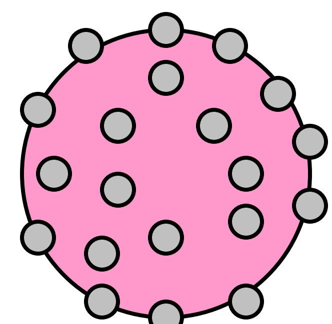
Au 100% metallic
Au-rich core
(therefore, Pd-rich shell)

Pd/Au NPs



4% H_2/He 300°C 30min

He 200°C



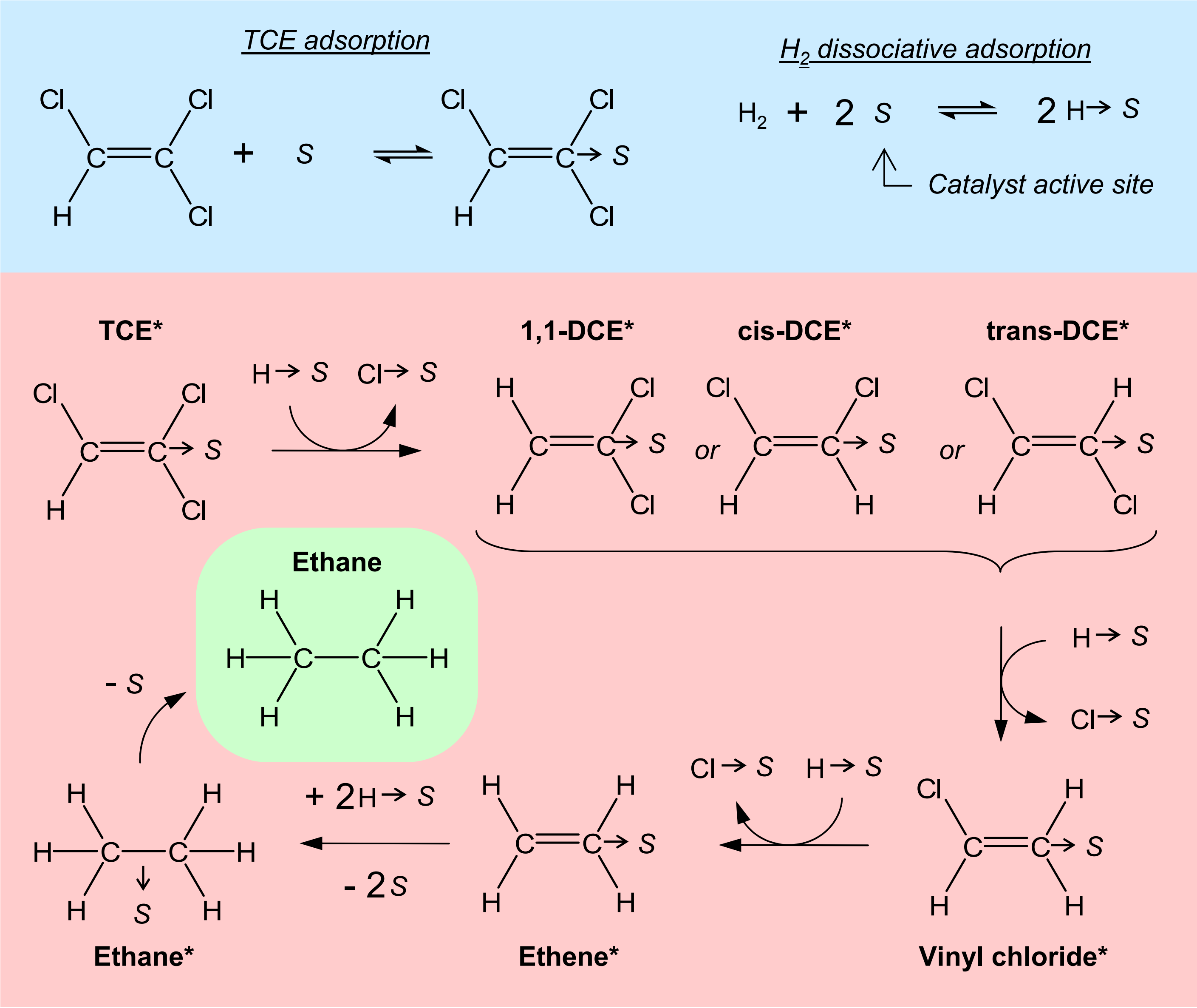
Edge	Treatment	Scattering path	N	N_{random}
Pd	H_2 300 °C, He 200 °C, He RT	Pd-Pd	2.0	**2.0**
		Pd-Au	6.9	**6.9**

Pd 100% metallic
Pd random distribution

Edge	Treatment	Scattering path	N	N_{random}
Au	H_2 300 °C, He 200 °C, He RT	Au-Au	9.3	**8.5**
		Au-Pd	1.6	**2.4**

Au 100% metallic
Au-rich core
(therefore, Pd-rich shell)

TCE HDC proposed reaction mechanism

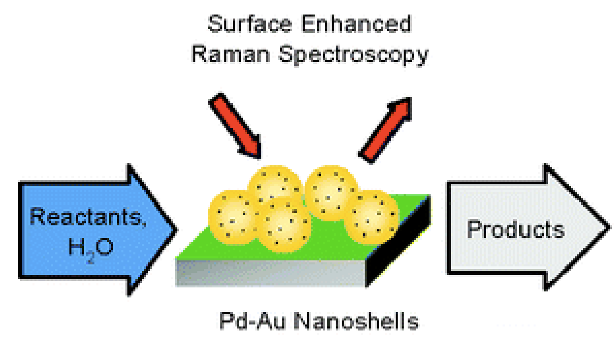


SERS of water-phase reaction

Observing Metal-Catalyzed Chemical Reactions in Situ Using Surface-Enhanced Raman Spectroscopy on Pd–Au Nanoshells

Kimberly N. Heck,[†] Benjamin G. Janesko,[‡] Gustavo E. Scuseria,[‡] Naomi J. Halas,[*,‡,§,∥] and Michael S. Wong[*,†,‡]

Department of Chemical and Biomolecular Engineering, Department of Chemistry, Department of Electrical and Computer Engineering, and Laboratory for Nanophotonics, Rice University, 6100 Main Street, Houston, Texas 77005-1892



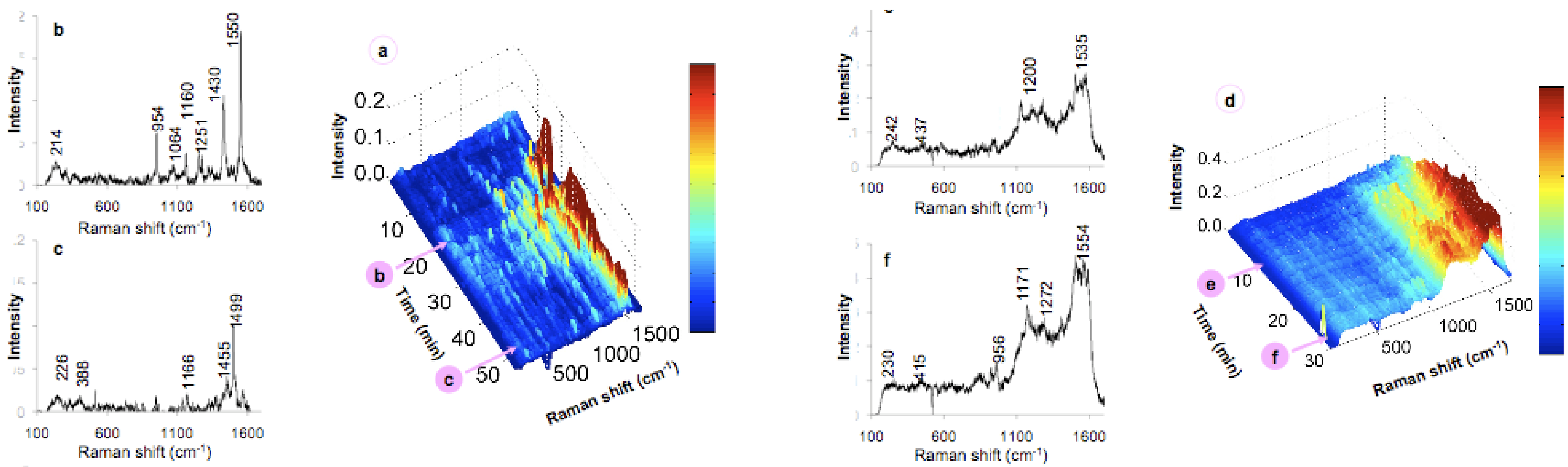
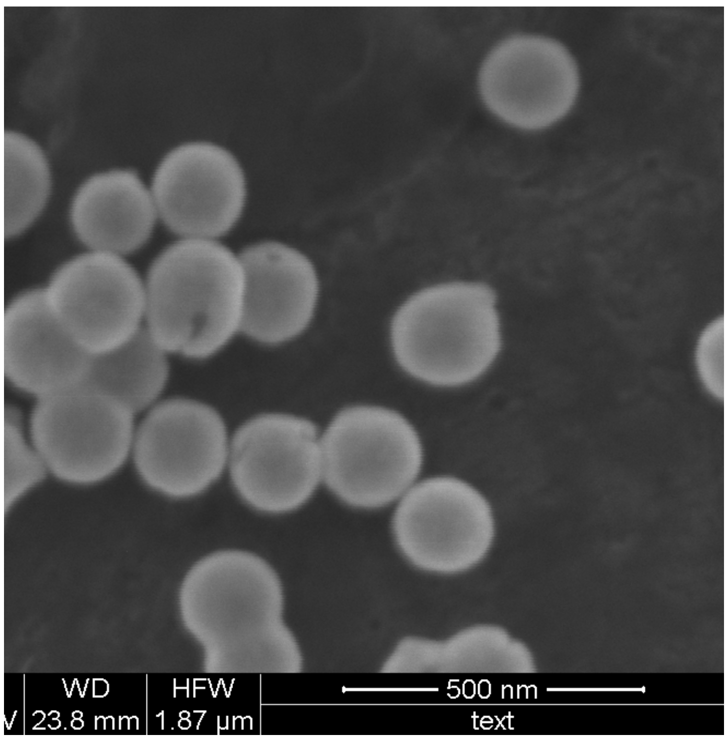
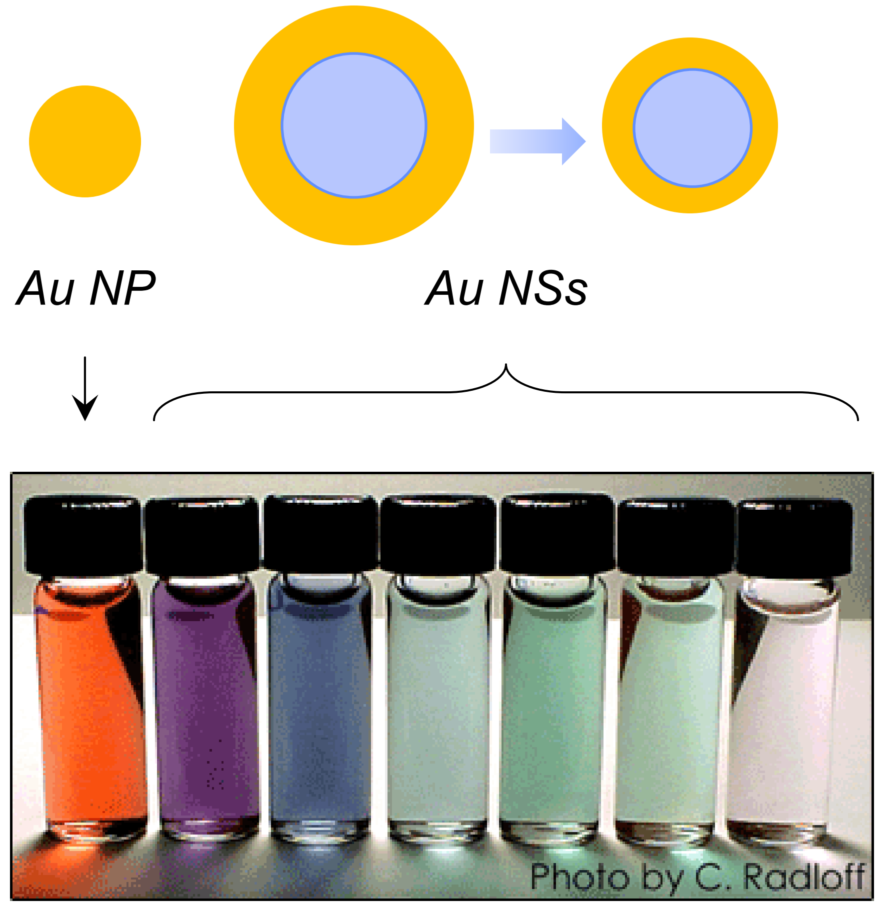


Figure 3. (**a**) Waterfall plot of time-resolved spectra gathered from the chemisorption of 50.9 μM 1,1-DCE on Pd/Au NSs and (**b,c**) individual scans at 20 and 49 minutes after injection of 1,1-DCE solution. (**d**) Waterfall plot of time-resolved spectra gathered from the chemisorption of 254 μM 1,1-DCE and (**e,f**) individual scans at 10 and 28 minutes after injection of 1,1-DCE solution.

Gold nanoshells (Au NSs) for SERS

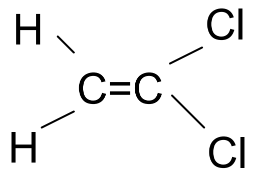
- Colloidal material prepared through wet chemistry
- Nanometer-thick Au shell on a SiO_2 particle (“core”)
- Plasmon resonance = f(core diameter, shell thickness)
  - Useful feature for surface-enhanced Raman spectroscopy (SERS)



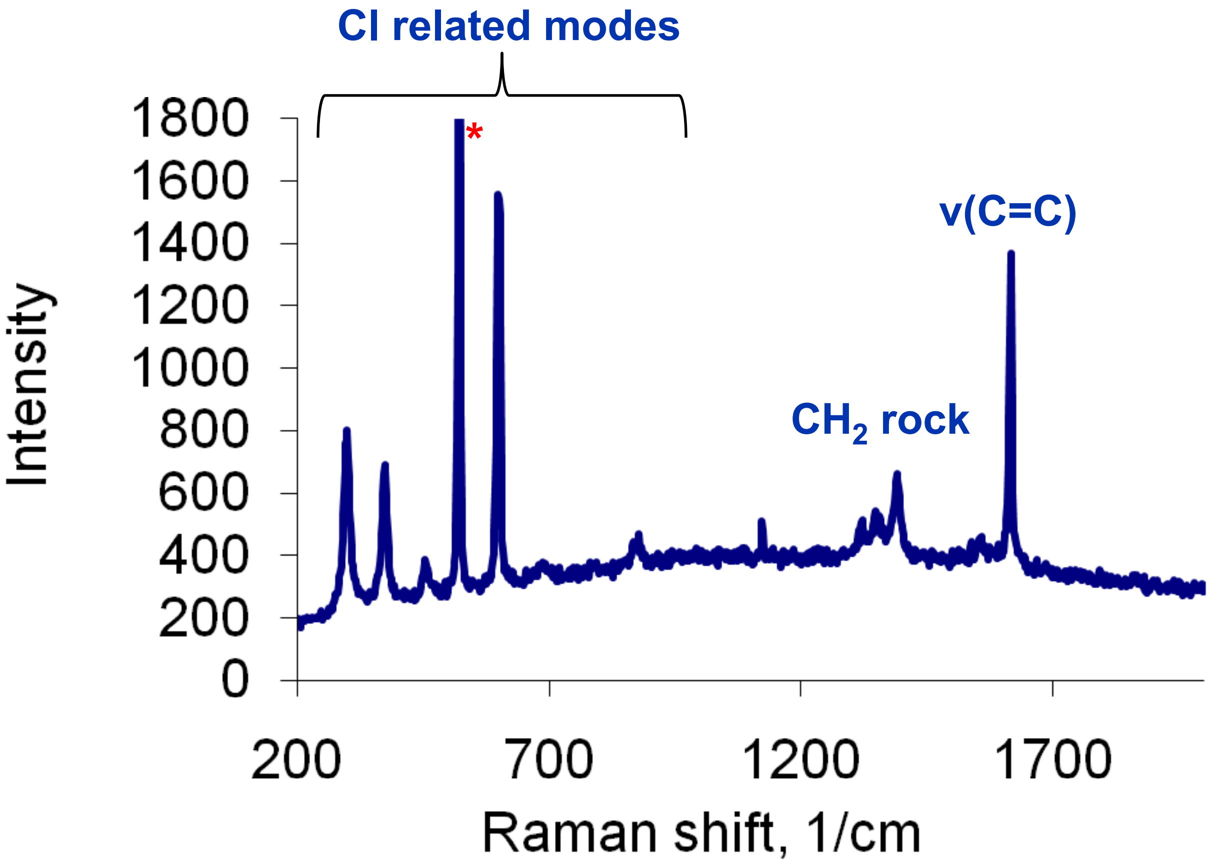


Oldenburg *et al.*, *Chem. Phys. Lett*. **1998**, 288, 243
Wang *et al.*, *Acc. Chem. Res*. **2007**, 40, 53

1,1-Dichloroethylene (DCE)



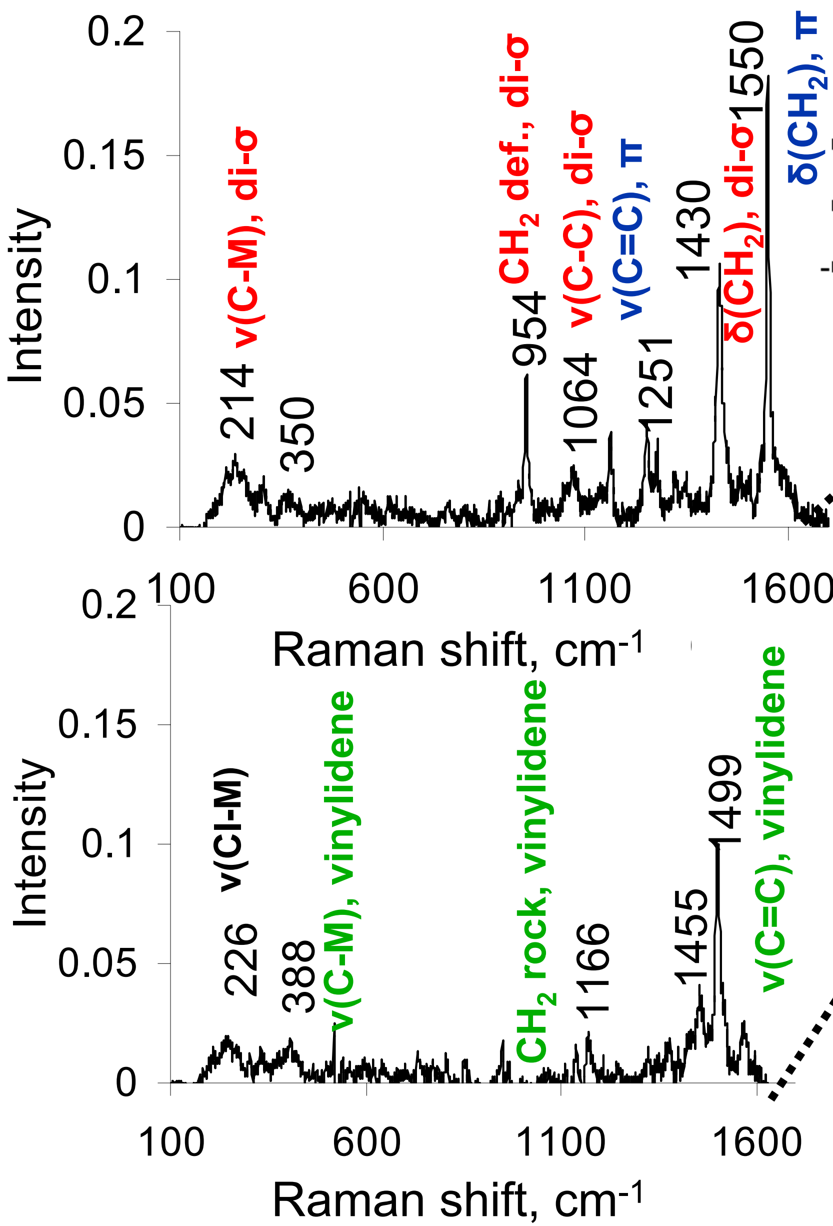
1,1-dichloroethylene

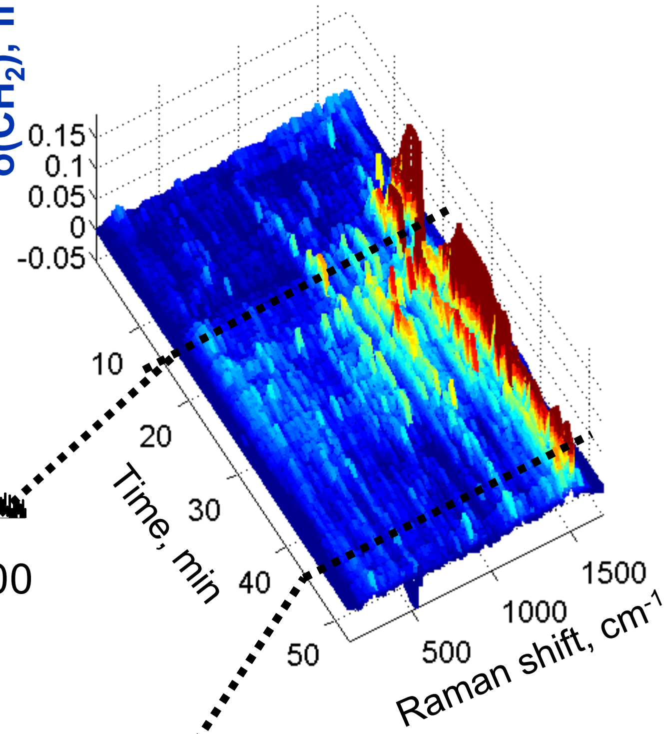


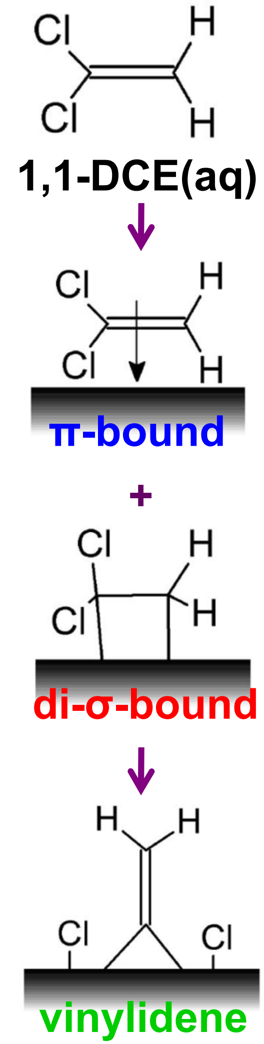
*520 cm^{-1} peak due to Si background

- Similar modes to ethylene (CH_2, C=C) allow literature comparison
- Potential to see evidence of dechlorination

[1,1-DCE] = 50.9 µM



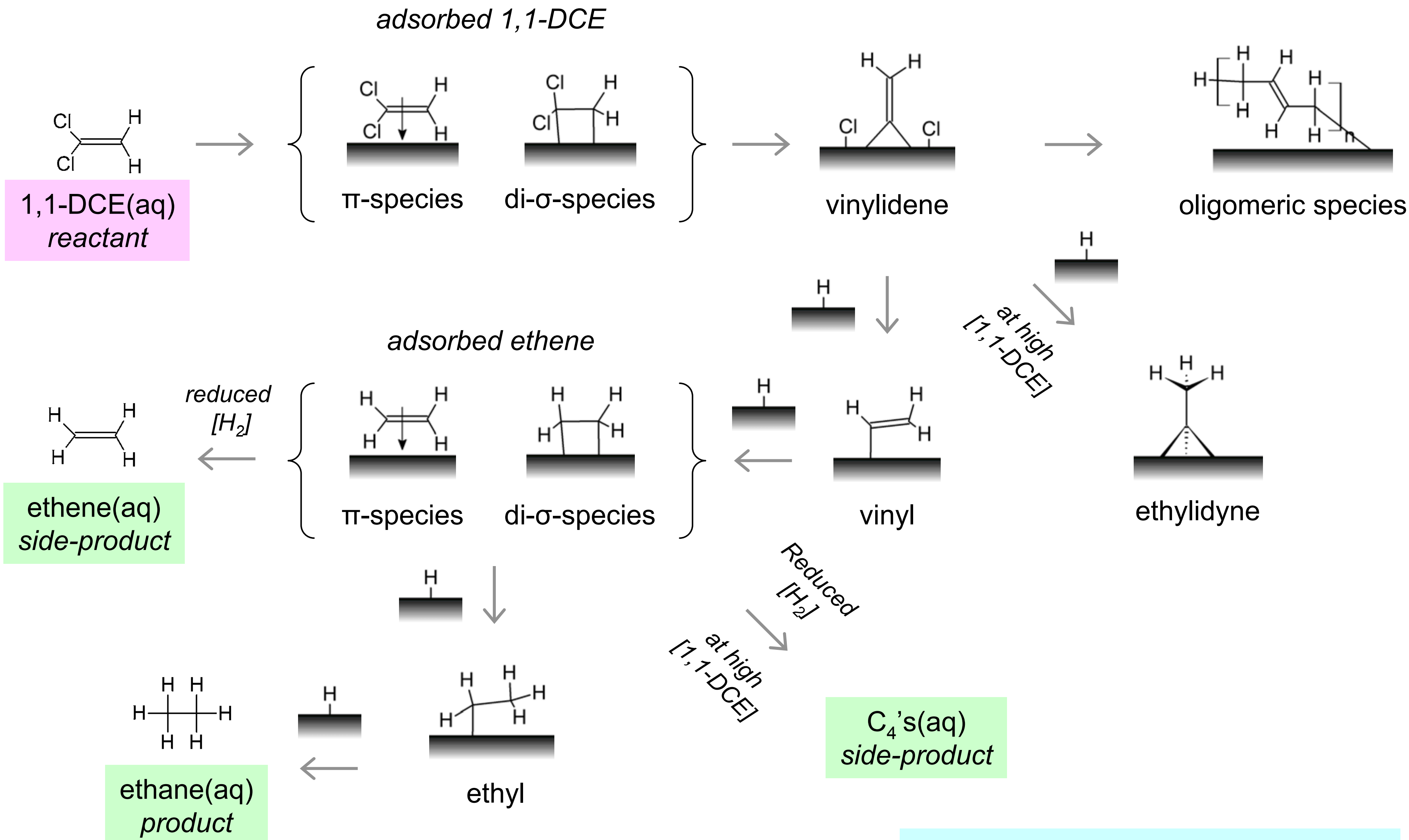




Spectra normalized to 520 cm^{-1} band, and baseline subtracted

Sheppard, *Ann. Rev. Phys. Chem.*, **1998**, 39, 589
Stuve et al., *J. Phys. Chem.*, **1985**, 89,105
Mrozek et al., *J. Phys. Chem. B* , **2001**, 105, 8931
Jungwirthova et al., *J. Phys. Chem. B* , **2001**, 105, 674

From NS-SERS analysis of 1,1-DCE HDC



Heck *et al.*, *JACS*, 2008. **130**: 16592

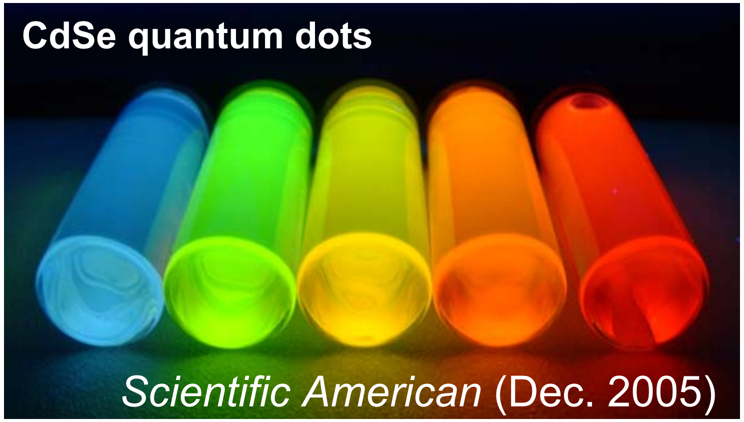
Other chlorinated C_2's can be removed

Table 2. HDC rate constants for selected chlorinated ethenes, using 4 nm Pd-on-Au NPs (with 25% Pd coverage). Reaction conditions are the same as above.[44]

Compound		Rate constant ($L\ g^{-1}_{Pd}\ min^{-1}$)	C–Cl bond strength ($kJ\ mol^{-1}$)[31,45]
PCE	$Cl_2C{=}CCl_2$	270	381
TCE	$ClHC{=}CCl_2$	858	391
1,1-DCE	$H_2C{=}CCl_2$	1519	393
cis-DCE	$ClHC{=}CHCl$	1813	370
trans-DCE	$ClHC{=}CClH$	2303	371

From M.S. Wong, P. J.J. Alvarez, Y.L. Fang, N. Akcin, M. O. Nutt, J. T. Miller, K. N. Heck, "Cleaner Water using Bimetallic Nanoparticle Catalysts"
J. Chem. Tech. & Biotech. 84, 158-166 (2009).

Last slide! Wong's research on NP engineering



NP chemistry and scale-up

Pd-on-Au NPs

Water purification

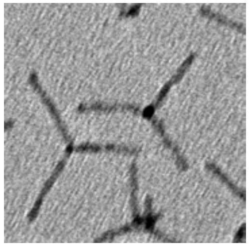
$CHCl{=}CCl_2 + 4H_2$

↓

$CH_3CH_3 + 3\ HCl$

NP catalysis

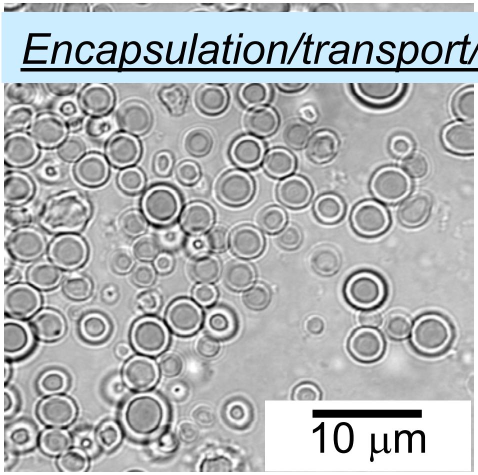
and tetrapods



50 nm

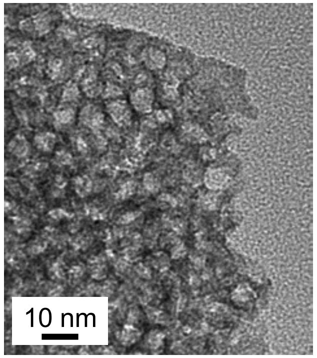
For use in solar cells

Encapsulation/transport/release



NP assembly chemistry

NP-supported metal oxides



Catalysis fundamentals through materials