“Nanoparticle Concepts for Detecting and Removing Oxyanions”

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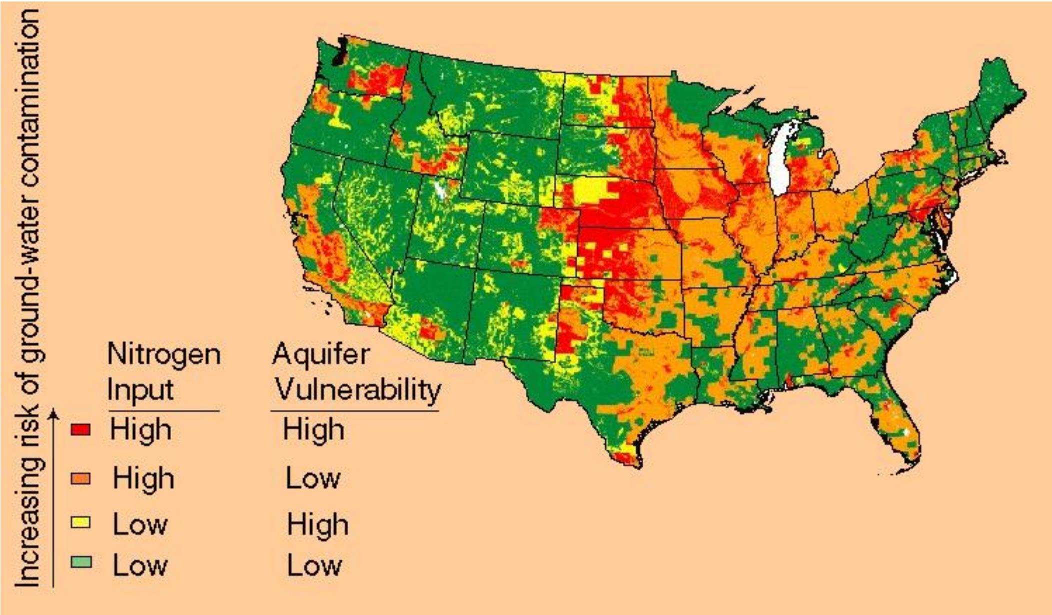
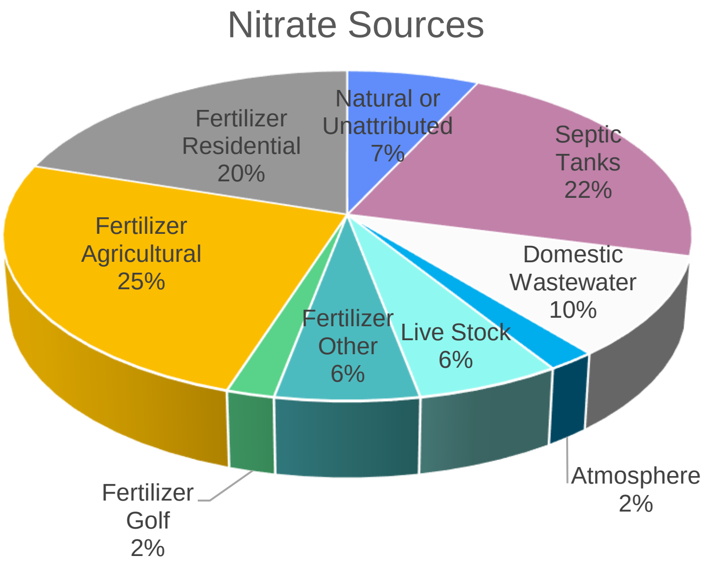
Marina Del Rey, CA
November 5, 2017

The nitrate (NO_3^-) problem

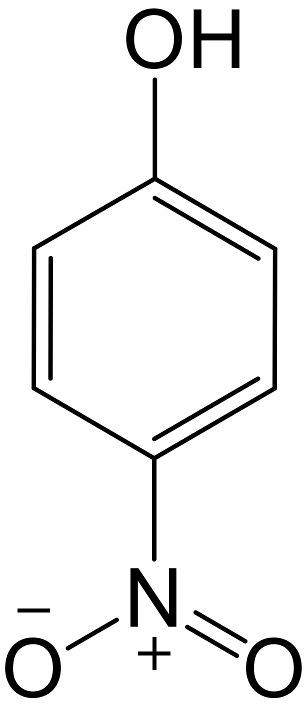
- One of the top 10 contaminants in the US
- Very mobile in water and leaching into groundwater
- Little or no retardation or degradation





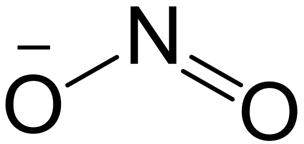
https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants
USGS National water-quality assessment (NAWQA) program

Nitrogen-containing compounds studied



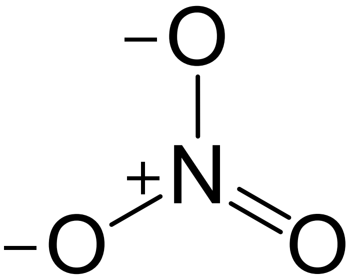
4-Nitrophenol

a 'Priority Pollutant'



Nitrite anion

Maximum Contaminant Level = 1 ppm (1 mg-N/L)

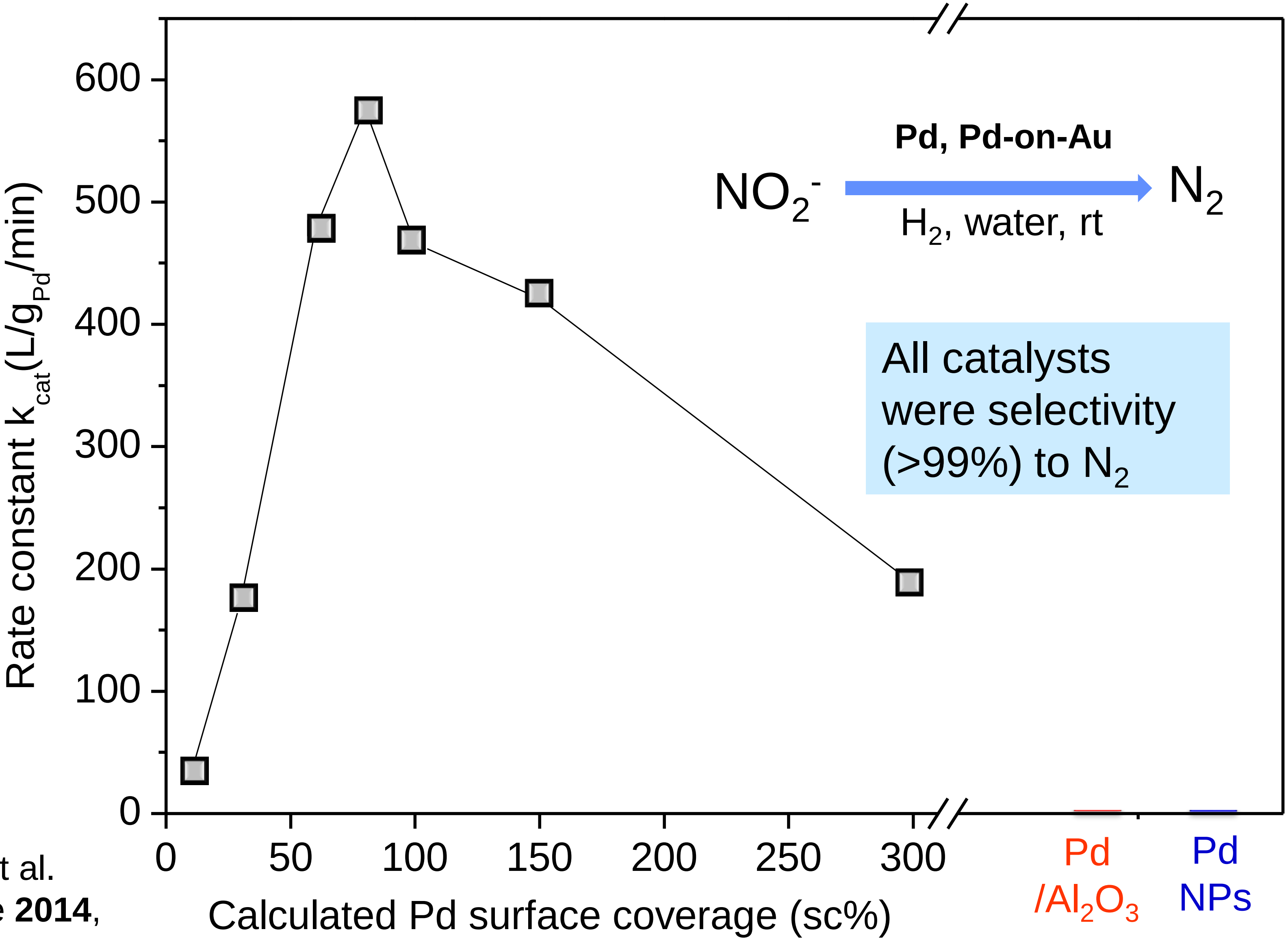


Nitrate anion

Maximum Contaminant Level = 10 ppm (10 mg-N/L)

Regulated by US EPA

Catalytic reduction of nitrite



$NO_2^- \xrightarrow[H_2\text{, water, rt}]{\textbf{Pd, Pd-on-Au}} N_2$

All catalysts were selectivity (>99%) to N_2

(H. Qian et al. Nanoscale **2014**, 6, 358-364)

Catalytic reduction of nitrate

- Adverse health effects: baby blue syndrome, cancer
- EPA MCL = 10 mg-N/L (NO_3^-)
- EPA MCL = 1 mg-N/L (NO_2^-)

General reaction pathway using a Pd-based catalyst

$$NO_3^- + H_2 \xrightarrow{\text{Pd-M}} NO_2^- + H_2O \tag{1}$$

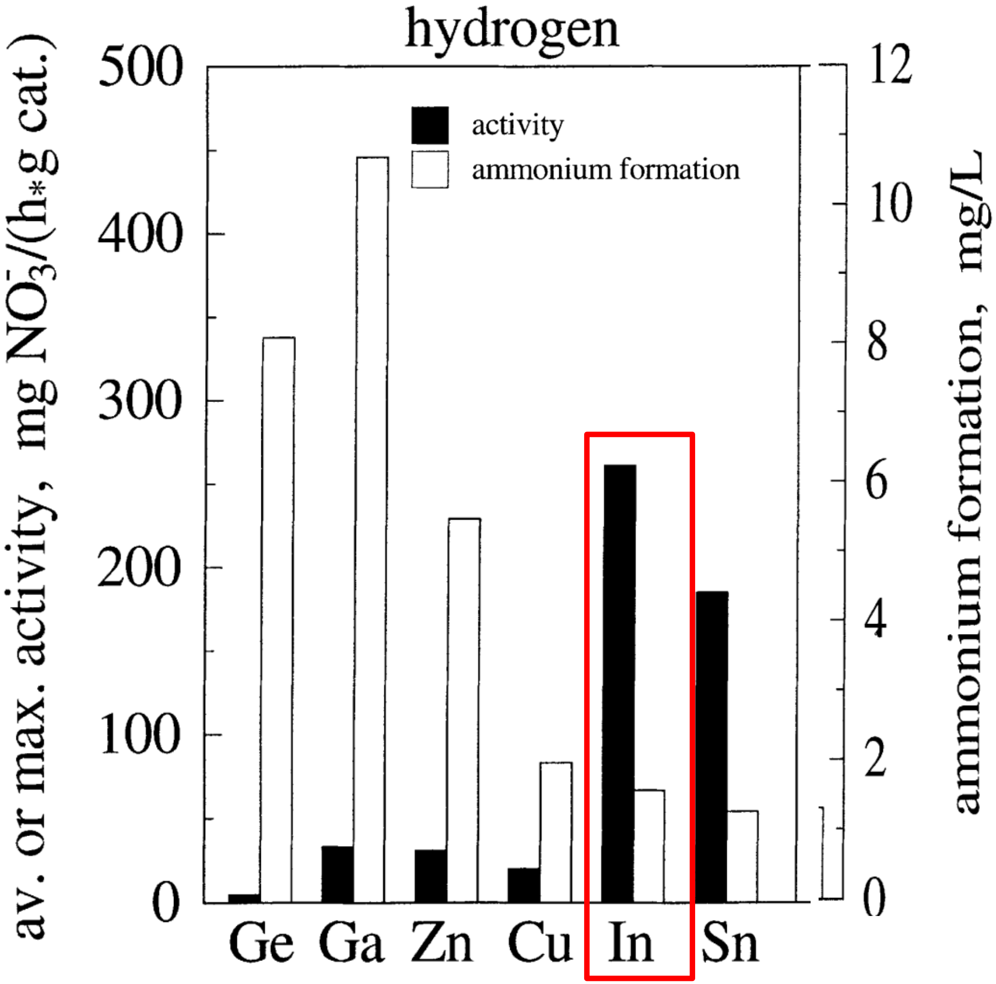
$$2NO_2^- + 3H_2 \xrightarrow{\text{Pd}} N_2 + 2H_2O + 2OH^- \tag{2}$$

$$NO_2^- + 3H_2 \xrightarrow{\text{Pd}} NH_3 + 2H_2O + 2OH^- \tag{3}$$

M = Cu, In and Sn

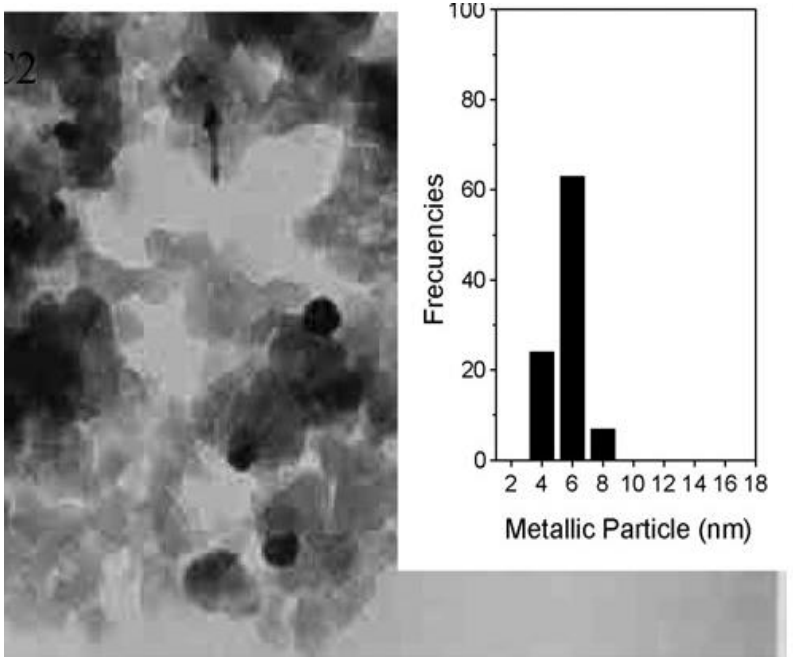
Ref: Vorlop and coworkers, Catal. Today 55, 79 (2000)

Early literature on PdIn catalysts



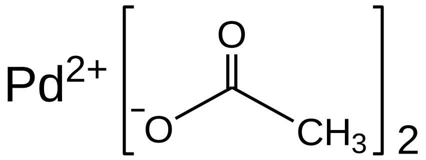
Al_2O_3 support with 5 wt% Pd, 1.25 wt% M

(U. Prüsse et al., Catalysis Today, **2000**, 55, 79)

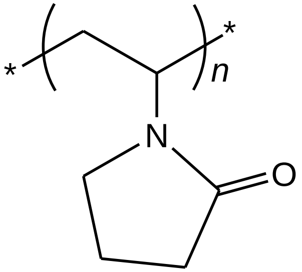


(Marchesini et al., Chemical Engineering Journal, **2010**, 159, 203)

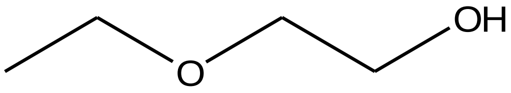
Pd NP synthesis method



$Pd(CH_3COO)_2$ (Pd precursor): 0.1332 g

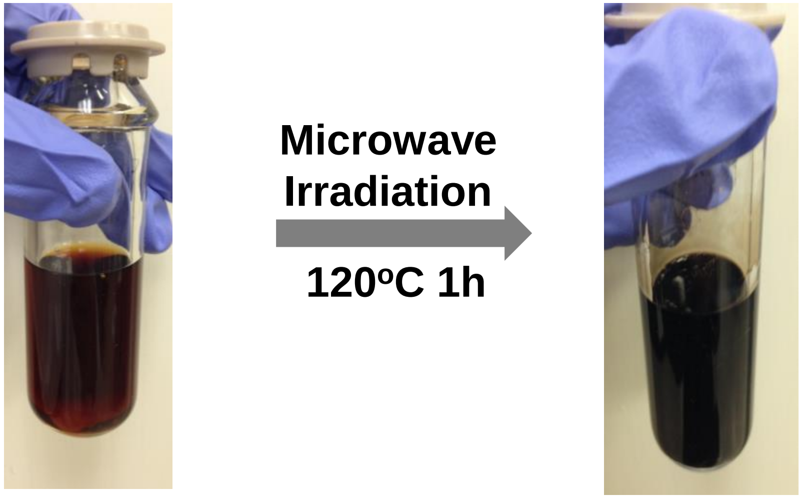


Poly(N-vinyl-2-pyrrolidone) PVP (stabilizer): 0.255 g



2-Ethoxyethanol: 15 mL

(solvent and reducing agent)



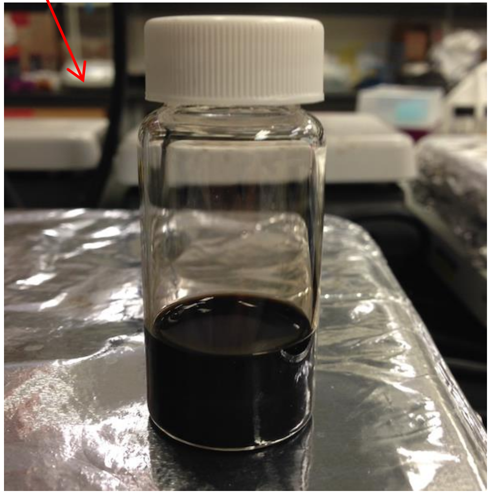
Microwave Irradiation

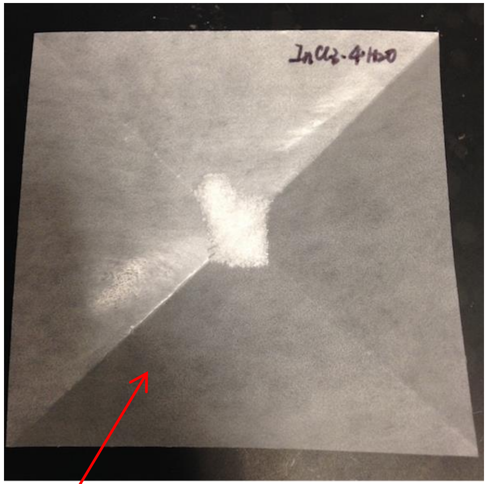
120ºC 1h

Kathryn A. Guy et al. J. Phys. Chem. C **2009,** 113, 8177–8185

Synthesis of In-on-Pd NPs

Pd NPs





$InCl_3$

Add $InCl_3$ to Pd NPs solution

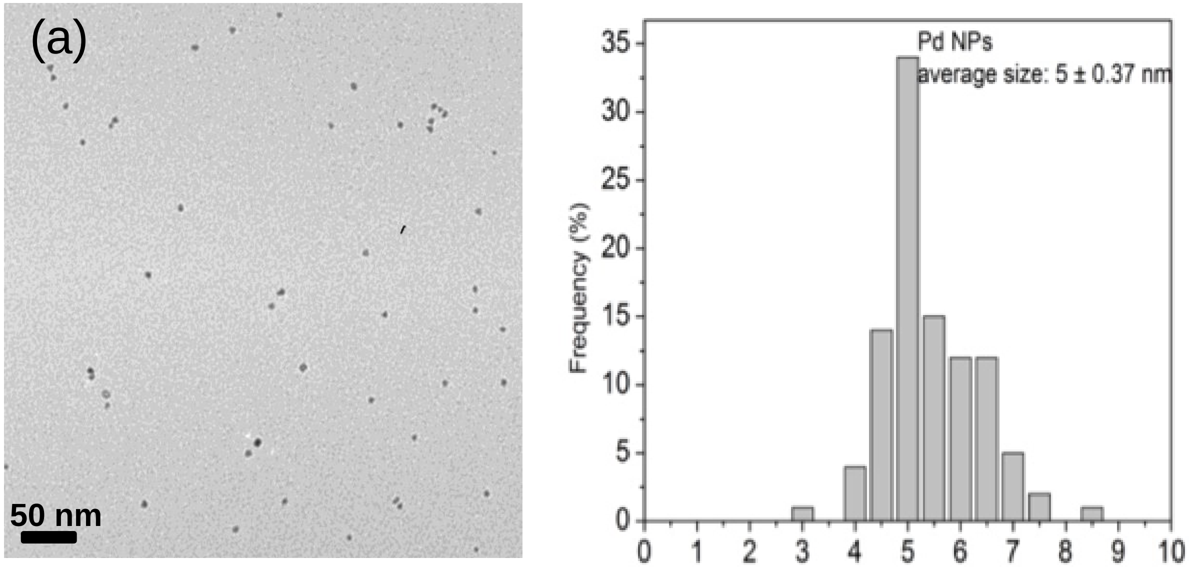
Bubble with **H_2** gas for 30 min

H_2 gas

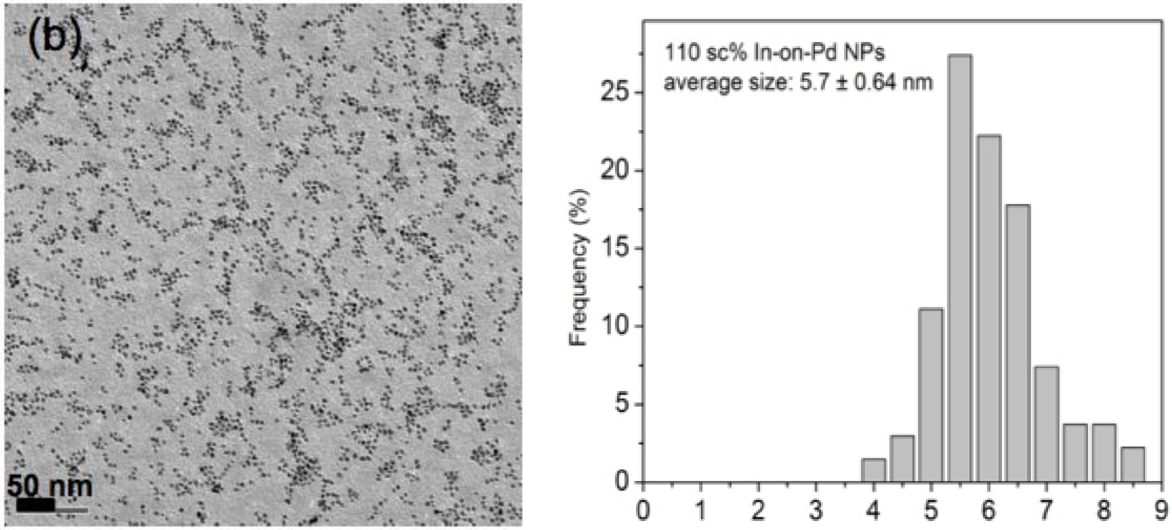
Magnetic Stirrer

10 sc%, 25 sc%, 30 sc%, 40 sc%, 50 sc%, 70 sc%, 110 sc%

Transmission electron microscopy (TEM)



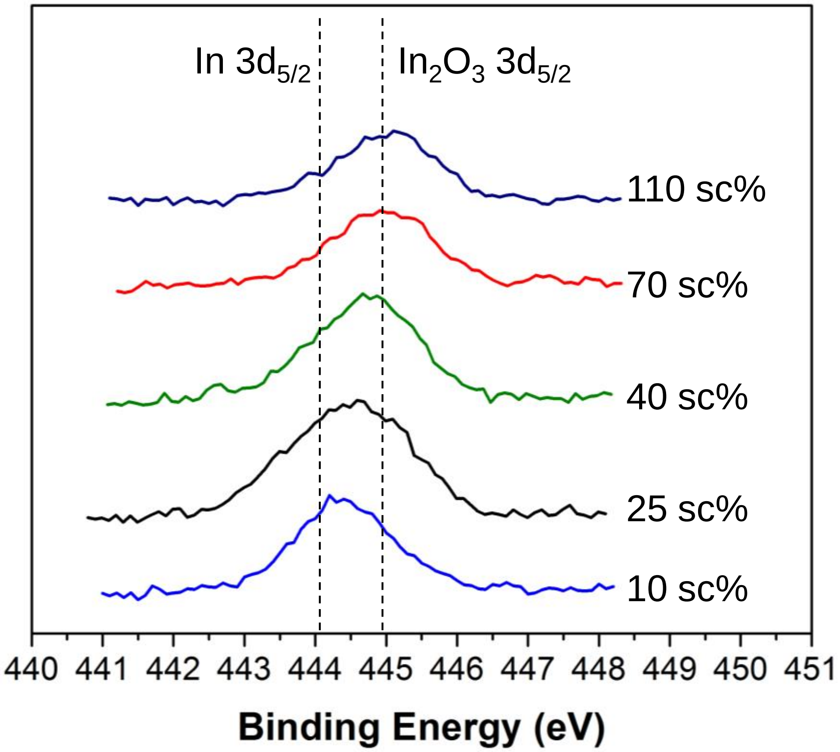
- Pd NPs
  - – mean diameter of 5.0±0.4 nm



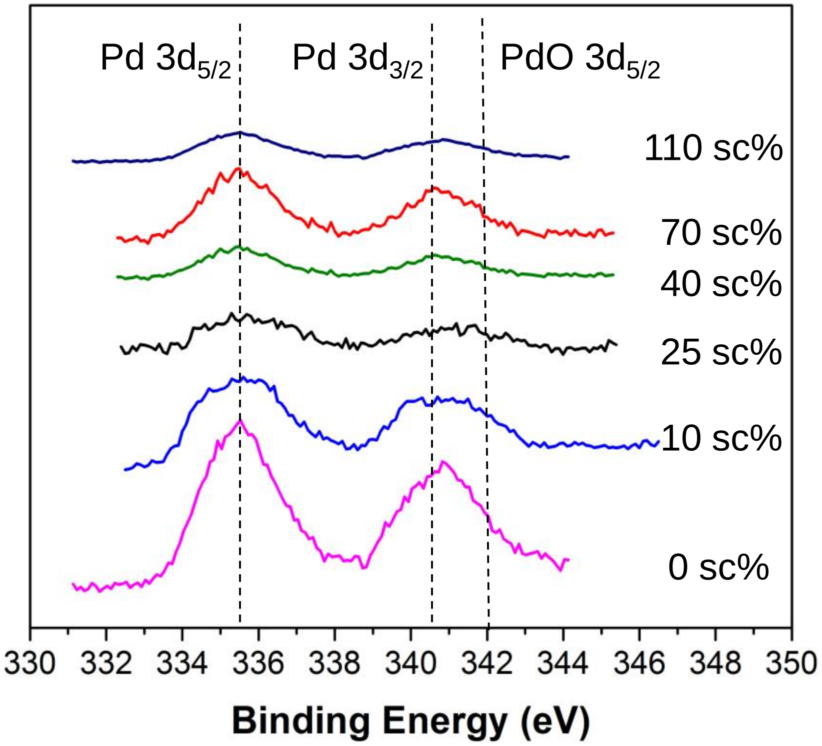
- 110 sc% In-on-Pd NPs
  - – mean diameter of 5.7±0.6 nm

XPS of In-on-Pd NPs

Indium

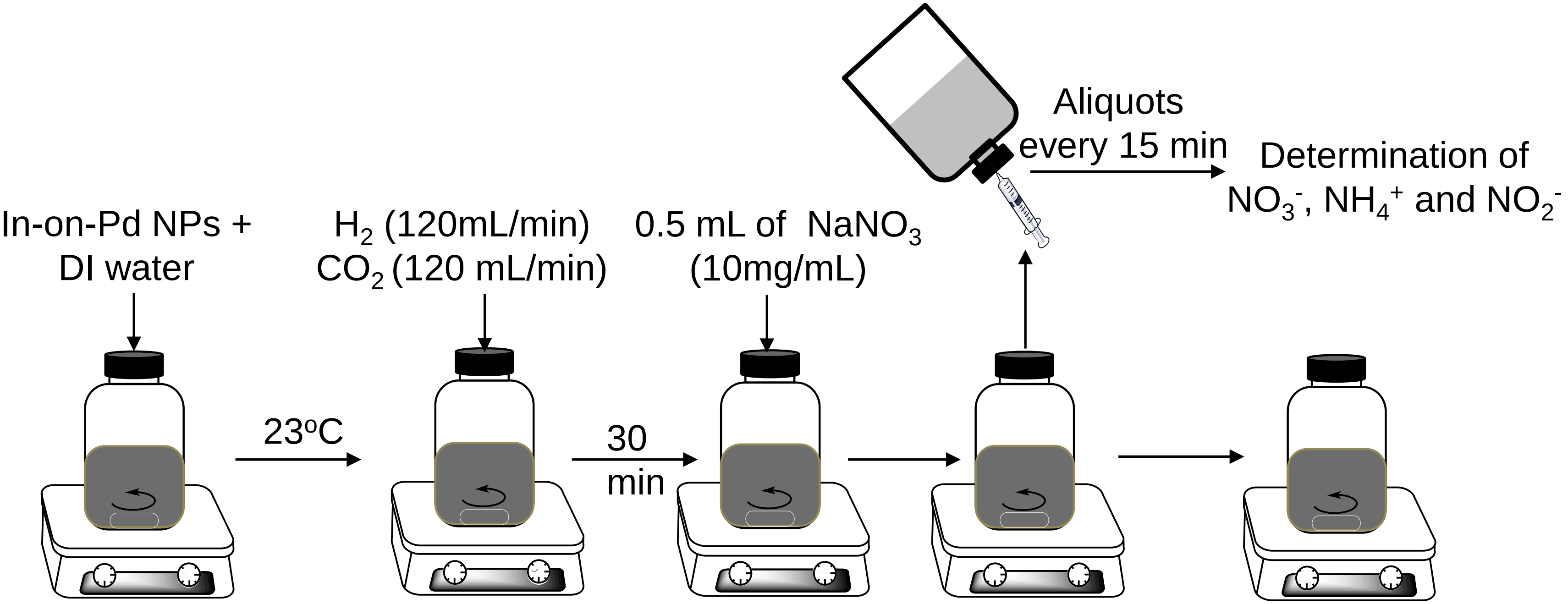


Palladium



- In atoms were more reduced at the lower In loadings
- The electronic state of Pd was unaffected by the In

Batch nitrate reduction experiments



In-on-Pd NPs + DI water

23^oC

H_2 (120mL/min) CO_2 (120 mL/min)

30 min

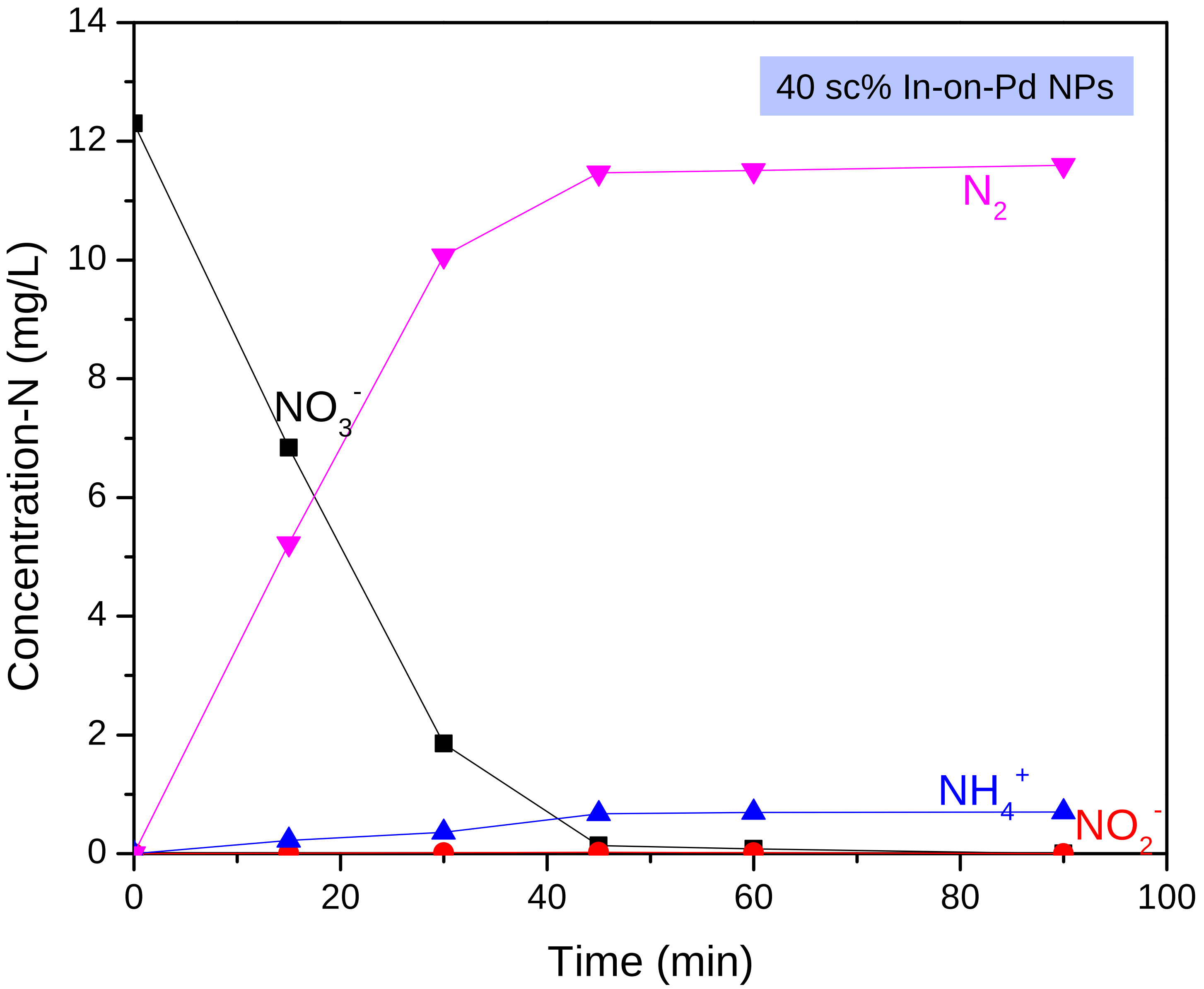
0.5 mL of $NaNO_3$ (10mg/mL)

Aliquots every 15 min

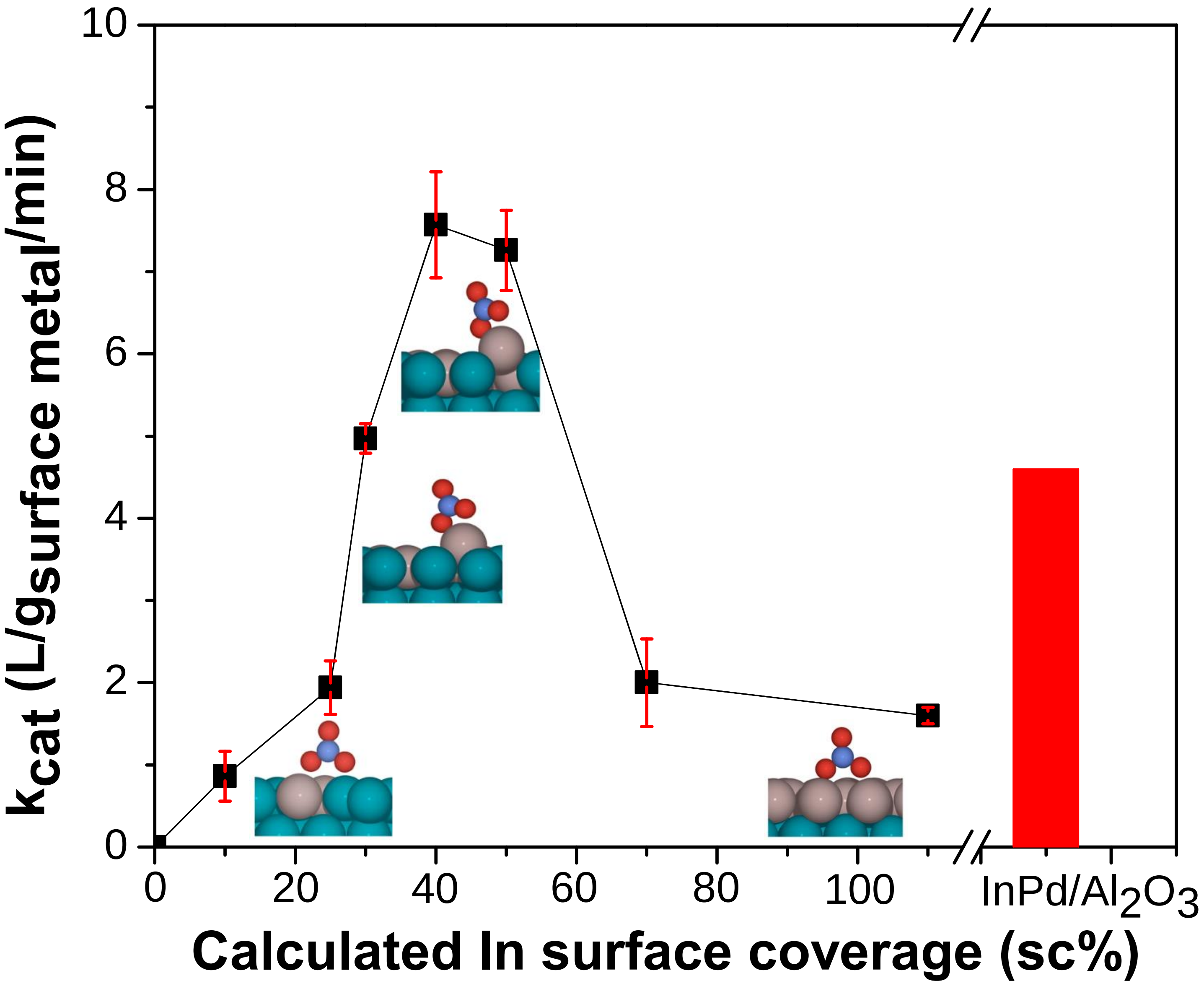
Determination of NO_3^-, NH_4^+ and NO_2^-

- Total solution in the reactor: 100 mL
- Bubble simultaneously with 120mL/min H_2 and 120mL/min CO_2 ~30 min (pH 4~6)
- Injected NO_3^- to initiate reaction (50 ppm), 600 rpm
- Surface coverage with 0%,10sc%, 25sc%, 30sc%, 40sc%, 50sc%, 70sc% and 110sc%
- NO_3^-, NO_2^-, NH_4^+ and pH monitored over time

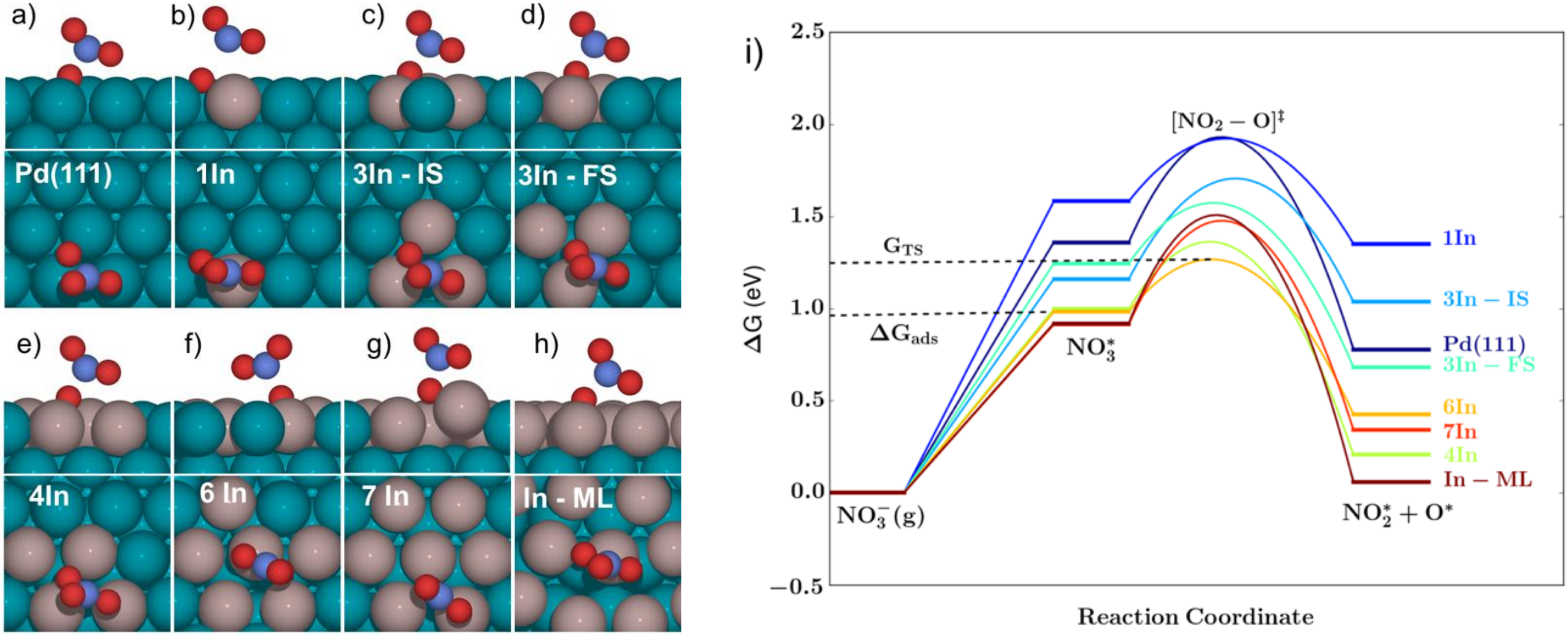
Example concentration-time profile



Volcano-shape dependence on In sc%



Transition states and free energy diagram



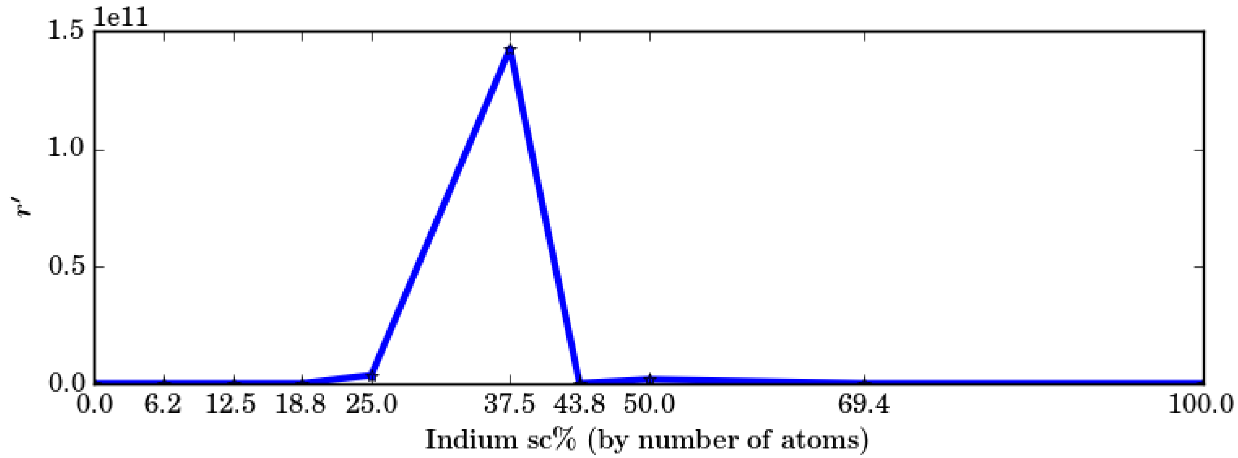
$$NO_3^- + * \leftrightarrow NO_3^*$$

r.l.s. $NO_3^* + * \rightarrow NO_2^* + O^*$

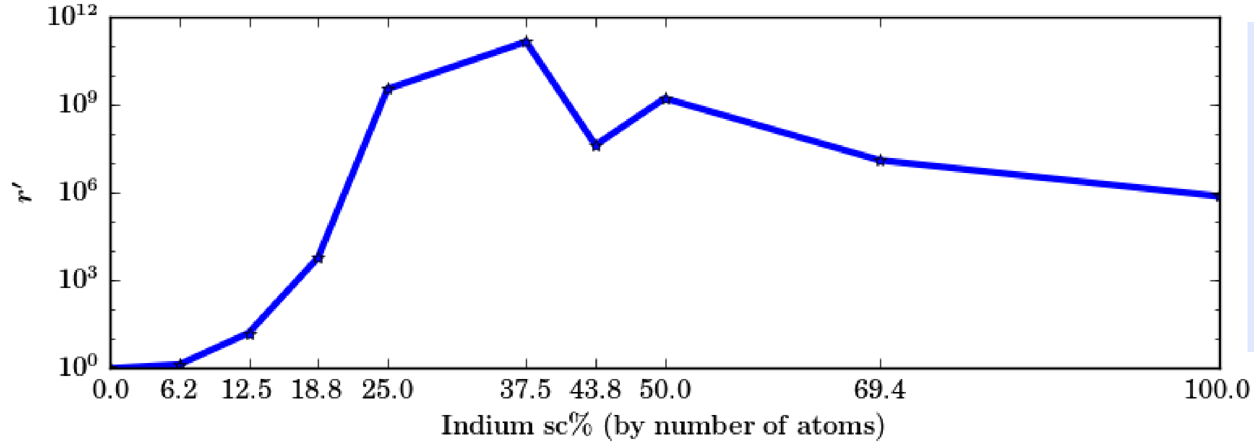
- In (>1 atom) promotes nitrate adsorption
- In ensembles of 4-6 atoms have the lowest activation barrier for N-O bond cleavage

Relative NO_3^- reduction rates from lumped kinetic modeling

Linear scale



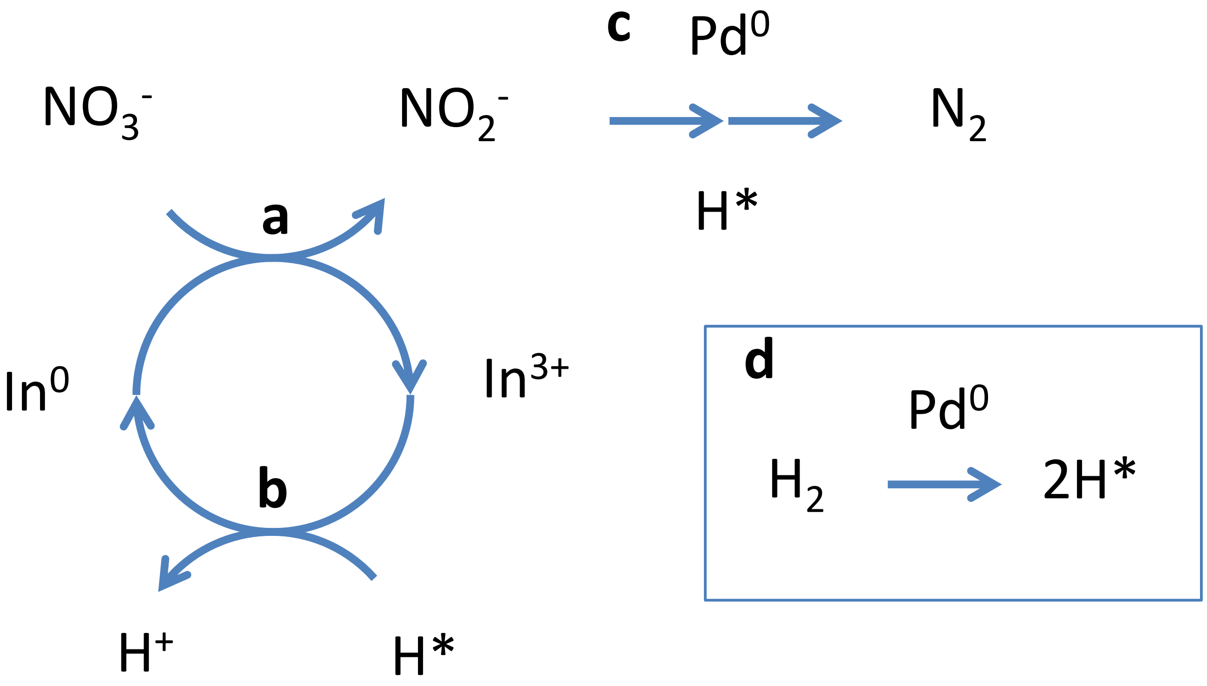
6-atom In ensembles, corresponding to 37.5 sc% coincides with the experimentally determined activity peak between 40-50 sc%



In ensembles of 4 or more atoms (>25 sc%) show a drastically improved nitrate reduction rate (6 orders of magnitude or more) that extends to 100 sc%

Semi-log scale

Model of nitrate reduction catalysis



c Pd^0

NO_3^- NO_2^- $\xrightarrow{}\xrightarrow{}$ N_2

H^*

a

In^0 In^{3+}

b

H^+ H^*

d

Pd^0

$H_2 \xrightarrow{} 2H^*$

a → reduction of nitrate to nitrite and oxidation of In^0 to In^{3+}

b → regeneration of In^0 by H*

c → further reduction of nitrite to dinitrogen over Pd^0

d → dissociation of H_2 into H* over Pd^0

Cr(VI) contamination

Testing chromium(VI) waste polluted water in Yunnan, China in 2011

http://www.greenpeace.org/eastasia/news/stories/toxics/2011/chromium-waste-dumpers-yunnan/

- 5,000 tons of waste containing Cr(VI) was dumped by Yunnan Liuliang Chemical Industry
- Cr(VI) level up to 24.25 ppm (over 400 fold higher than the WHO permissible limit)

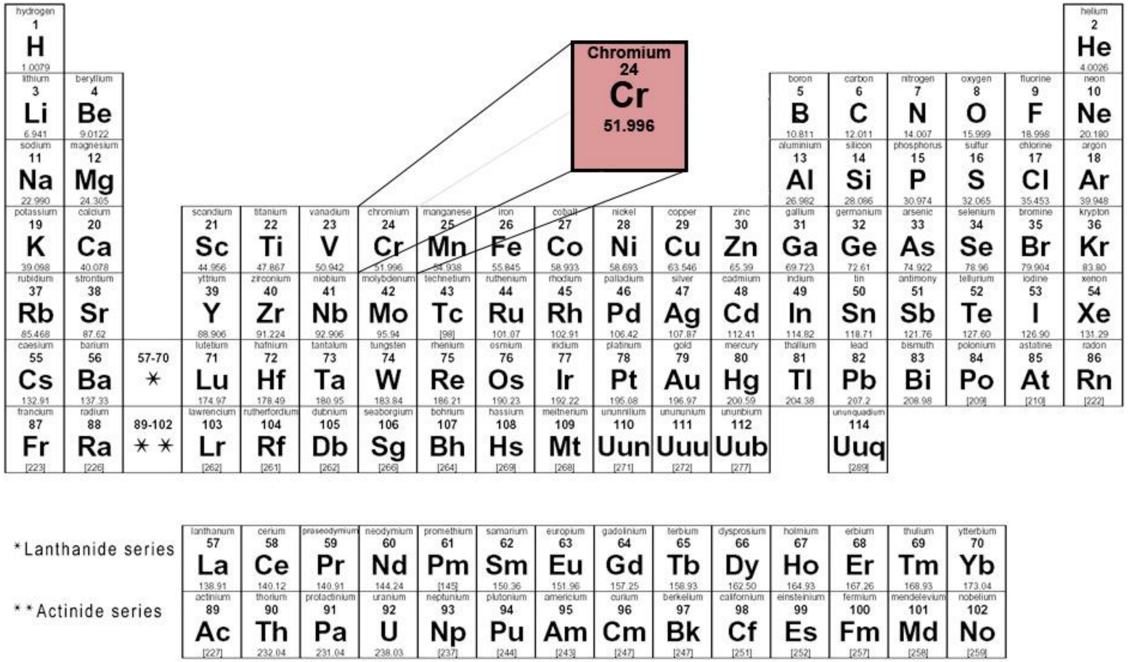
Yellow colored contaminated water from a pump in Kanpur, India in 2012

Sharma, Priti, et al. PloS one 7.10 (2012): e47877.

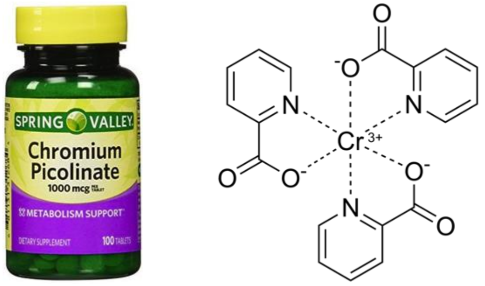
- The waste from tanneries has been illegally dumped in deep borings, open lands and in rivers through decades
- Cr(VI) level up to ~20 ppm (390 fold higher than the WHO permissible limit)

Chromium (Cr)

- A chemical element discovered in 1797 by Louis Nicholas Vauquelin
- Ferrous chromite ($FeCr_2O_4$) mines as the major source (South Africa)
- Trivalent (Cr(III) and hexavalent (Cr(VI)) chromium are most stable
- Cr(III) is a harmless trace element for organism (~6 mg in an adult)
- Cr(VI) is mainly released by human activities and it is extremely toxic




Ferrous chromite



Cr(III) as a dietary supplement

Cr(VI) regulations

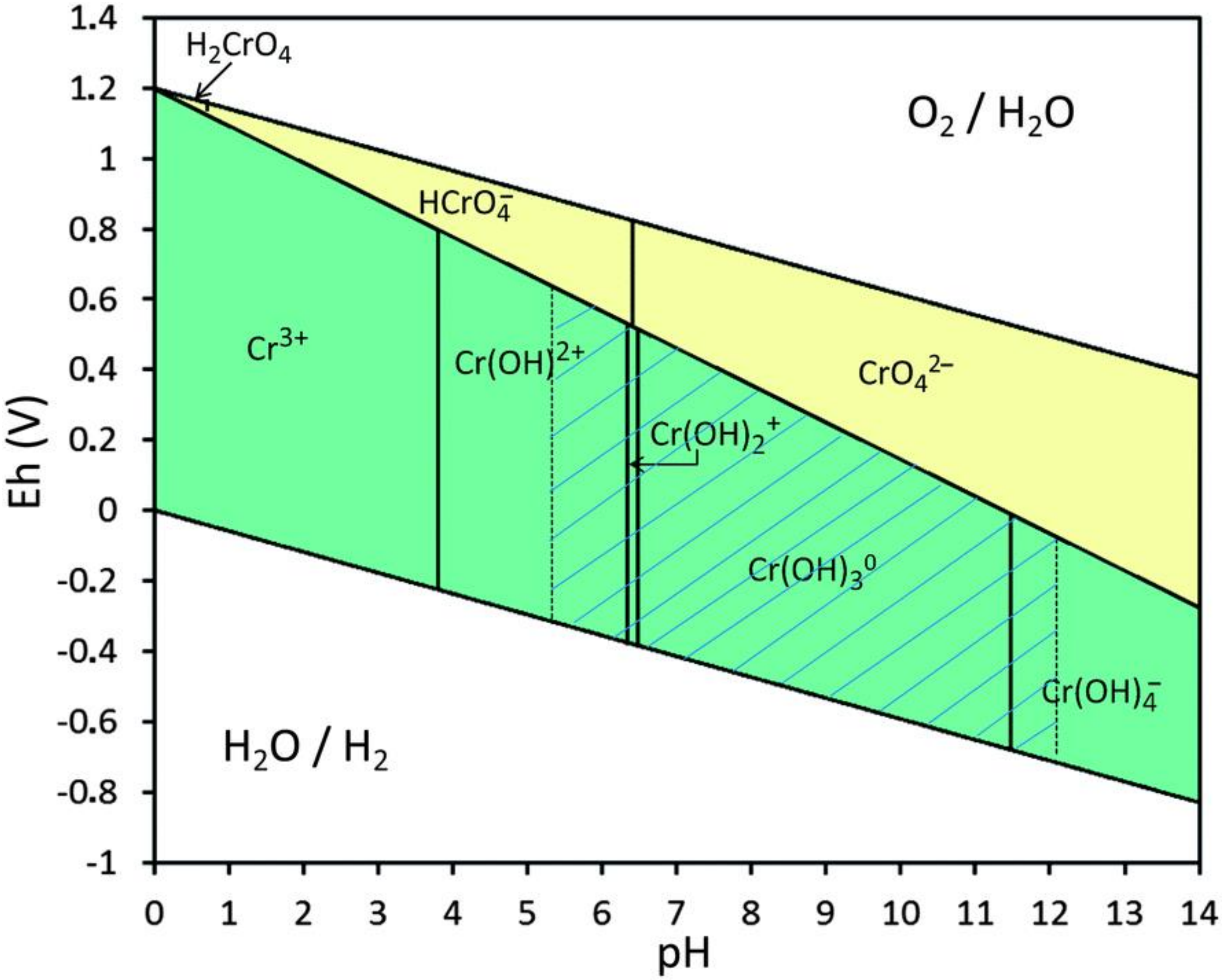
- ***The United States Environmental Protection Agency (US EPA)*** set a maximum contaminant level (MCL) for total chromium (Cr(III)+Cr(VI)) at ***100 ppb***, but no MCL for Cr(VI).

- ***California*** set a MCL for total chromium (Cr(III)+Cr(VI)) at ***50 ppb***, MCL for Cr(VI) is in process.

- ***The Ministry of Environmental Protection of the People's Republic of China*** set limit of Cr(VI) in drinking water to be **50 ppb** and the industrial waste water discharge limit of Cr(VI) to the environmental water bodies at ***100 ppb***.

- ***World Health Organization (WHO)*** set the guideline of Cr(VI) at ***50 ppb***.

Pourbaix diagram for Cr

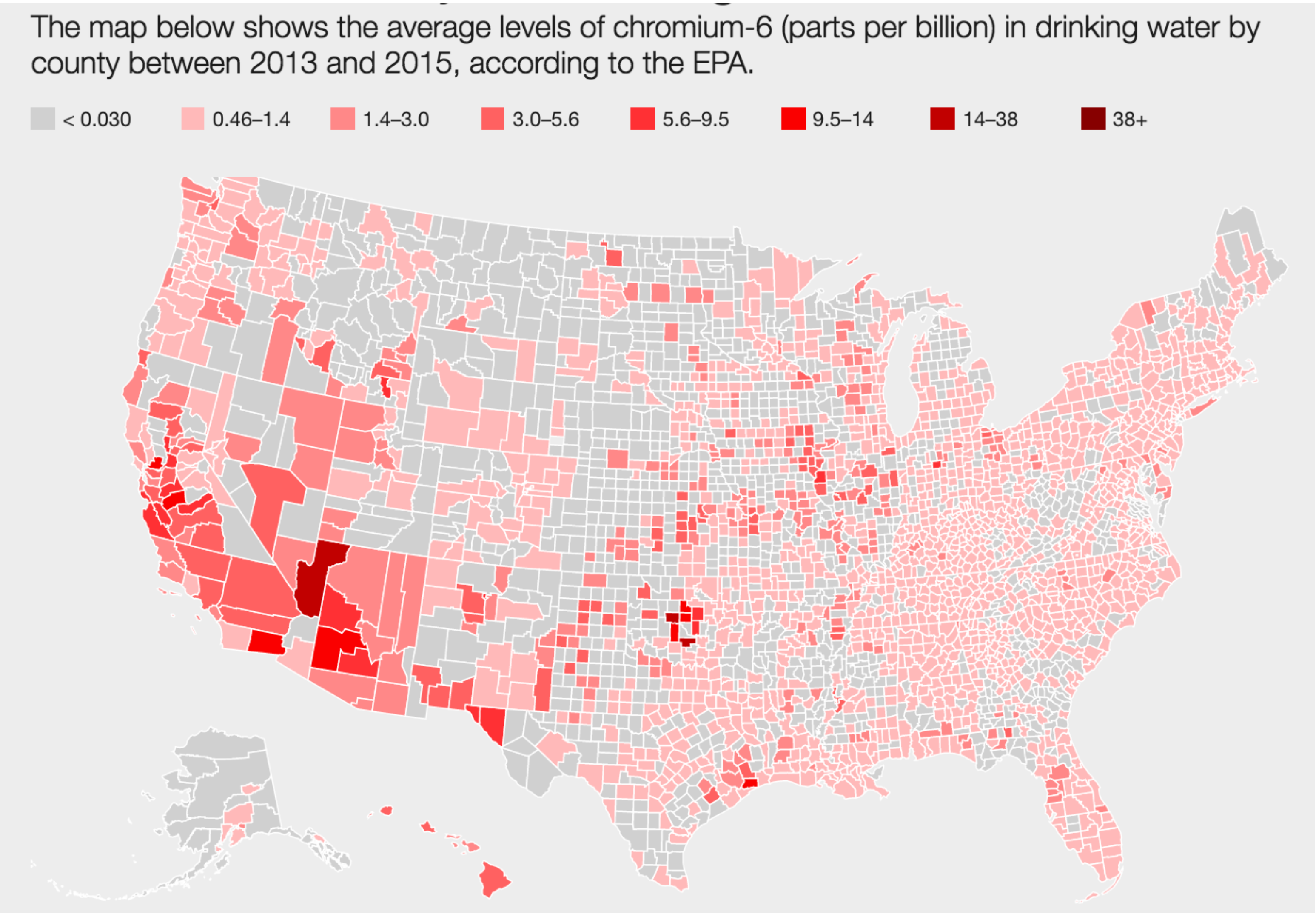


25 ° C
1 Bar
[Cr] = 10^{-6} M

J. Anal. At. Spectrom., 2014, 29, 427–443

Cr(VI) in US drinking water systems

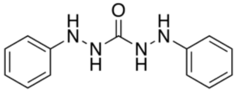
Found in ~90% of the water systems sampled across the nation



The map below shows the average levels of chromium-6 (parts per billion) in drinking water by county between 2013 and 2015, according to the EPA.

http://www.cnn.com/2016/09/21/health/chromium-6-drinking-water-questions/

US EPA methods for Cr(VI) quantification

- **Method 218.6 (1991)**: Determination of dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents by ion chromatography
    - Instrument: Ion chromatography (IC) with an UV-Vis detector
    - Detection mechanism: Cr(VI) post column reaction with diphenylcarbazide (DPC) 
    - Method detection limit (MDL) of Cr(VI): 0.3 µg/L (ppb) as CrO_4^{2-}

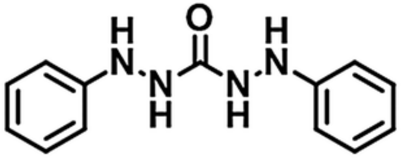
- **Method 218.7 (2011)**: Determination of hexavalent chromium in drinking water by ion chromatography with post-column derivatization and UV–visible spectroscopic detection
    - Improved method detection limit (MDL) of Cr(VI): 0.0044 µg/L (ppb) as CrO_4^{2-}

Disadvantages:
Expensive instrument, complicated operation and knowledge of chemistry

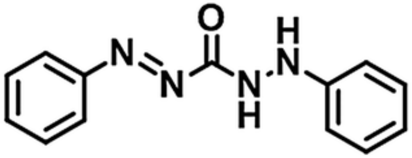
Commercial test kit for Cr(VI)

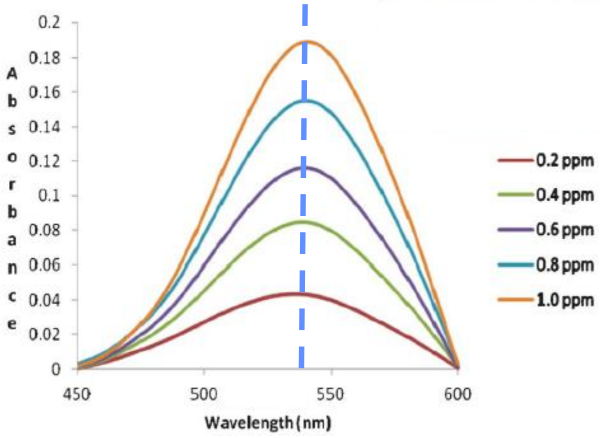
$2CrO_4^{2-}+3H_4L+8H^+=[Cr^{III}(HL)_2]^++Cr^{3+}+H_2L+8H_2O$

H_4L
diphenylcarbazide



H_2L
diphenylcarbazone





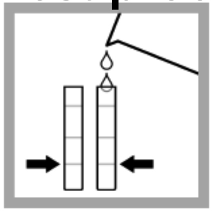
RSC Advances 3(8):2697-2709 , 2013

Chromium Color Disc Test Kit (Hach, Model CH-8)

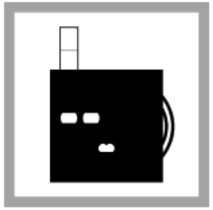
- Detection limit: 0.1 mg/L (ppm)
- Price: $68.75 for 100 test kits

Can we improve?

Test procedure

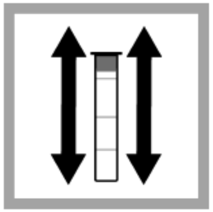


1. Fill two tubes to the first line (5 mL) with sample.



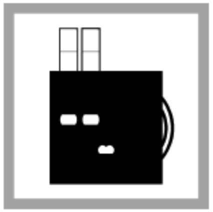
2. Put one tube into the left opening of the color comparator box.

3. Add one ChromaVer 3 Chromium Reagent Powder Pillow to the second tube.



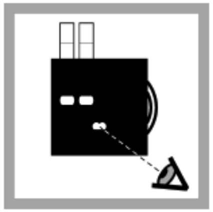
4. Put a stopper on the tube. Shake to mix. A purple color develops.

5. Wait 5 minutes. Read the result within 20 minutes.



6. Put the second tube into the color comparator box.

7. Hold the color comparator box in front of a light source. Turn the color disc to find the color match.



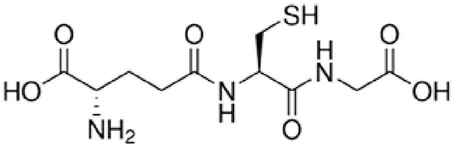
8. Read the result in mg/L in the scale window.

https://www.hach.com/chromium-color-disc-test-kit-model-ch-8/product?id=7640217301

Our Work: Synthesis of GSH-Au NCs

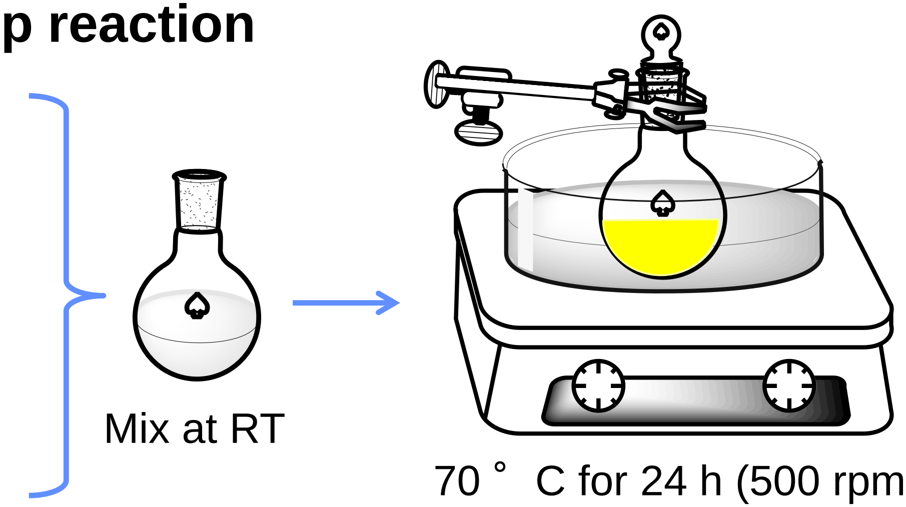
Synthesis by one-step reaction

Glutathione
(GSH, 100 mM, 1.5 mL)



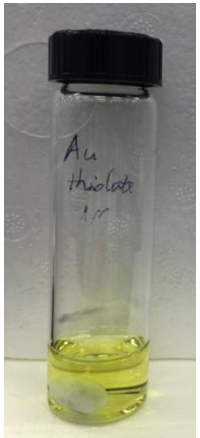
$HAuCl_4$ (20 mM, 5 mL)

DI water (43.5 mL)



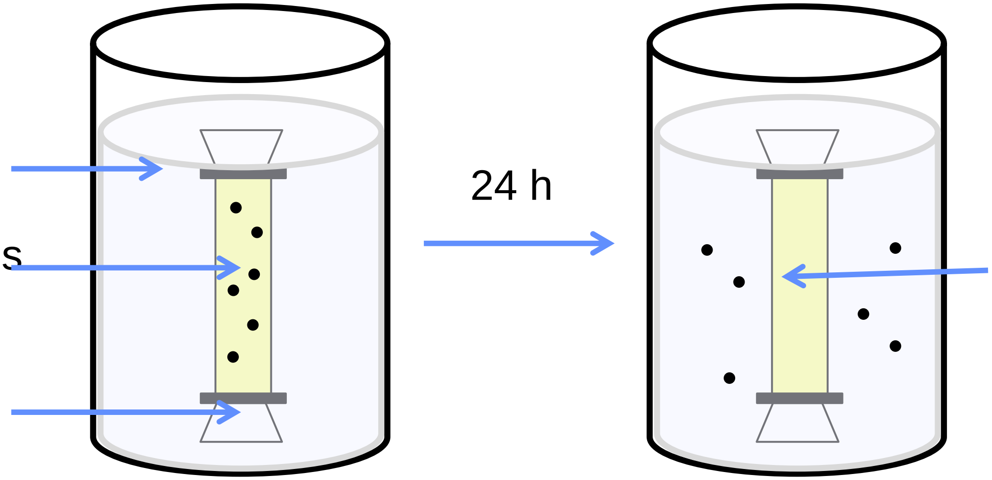
Mix at RT

70 °C for 24 h (500 rpm)



Synthesis method from J. Xie and group: J. Am. Chem. Soc., 2012, 134 (40), pp 16662–16670

Purification by dialysis



DI water (2 L)

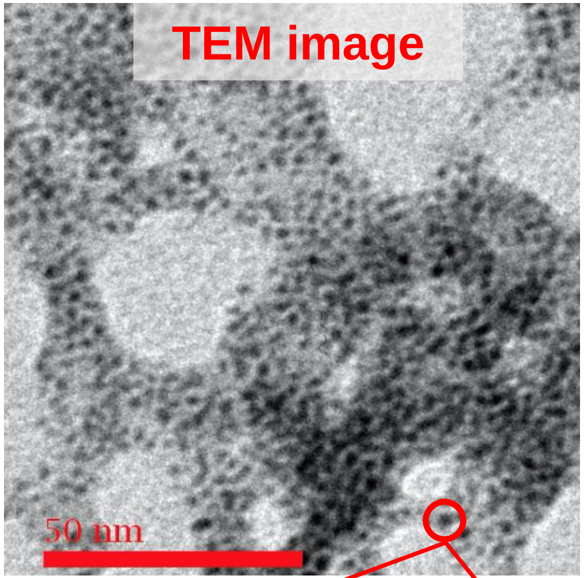
As-synthesized Au NCs solution (50 mL)

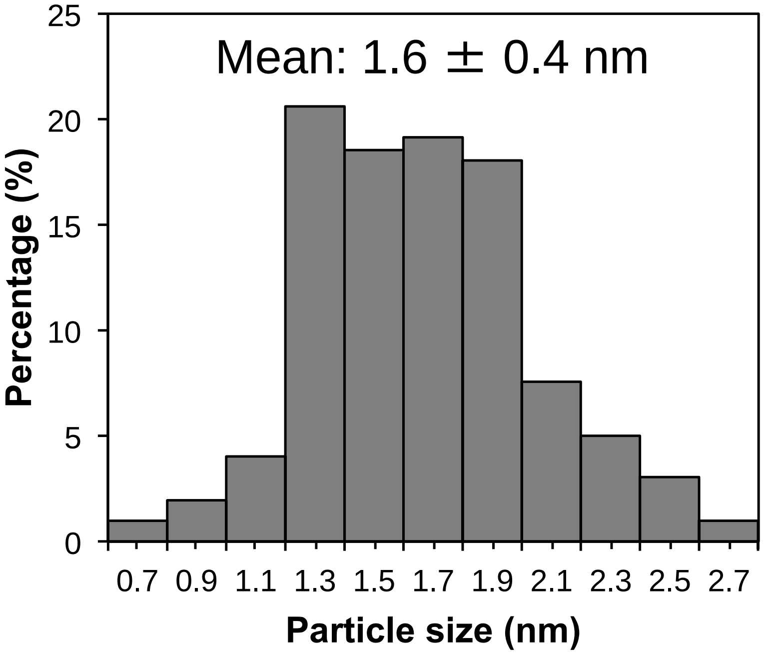
Dialysis bag (MWCO 3500)

24 h

Purified Au NCs solution (50 mL)

Structure of GSH-Au NCs



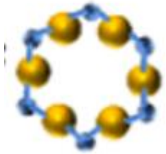


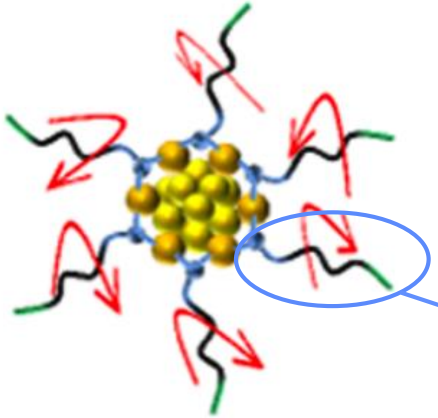
Core-shell structure

Molecular formula

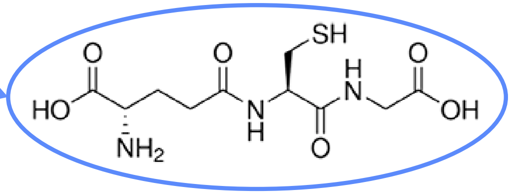
Au core (Au(0))

Staple motif (Au(I)-S-Au(I))

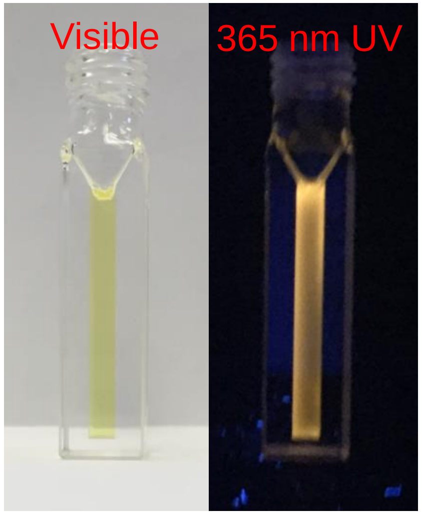


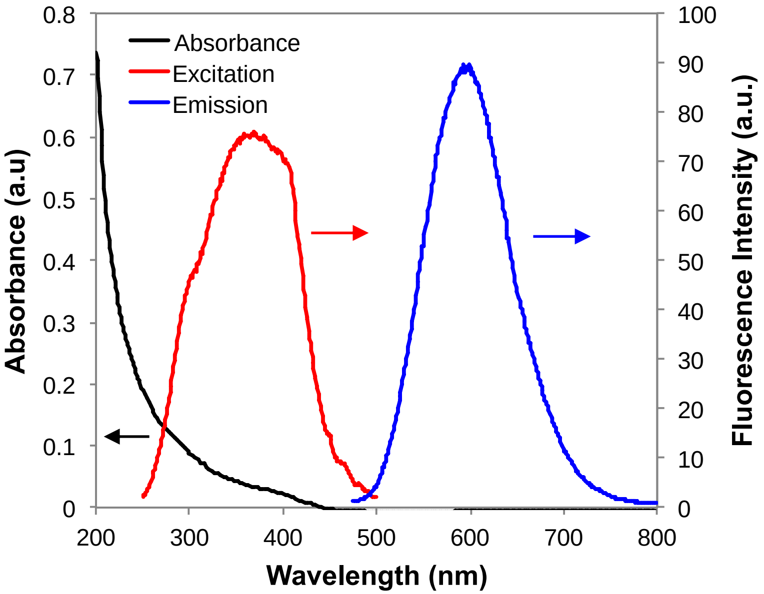


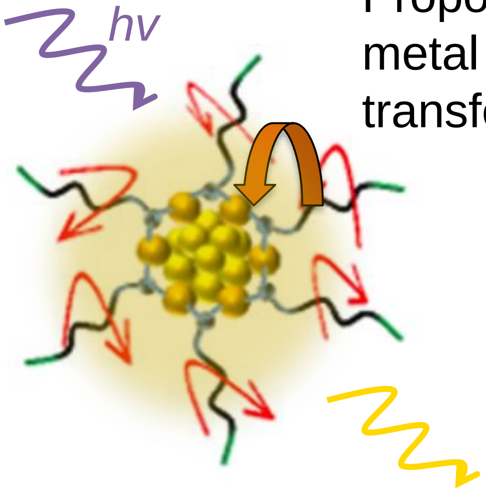
$Au_{29}SG_{27}$, $Au_{30}SG_{28}$, $Au_{36}SG_{32}$, $Au_{39}SG_{35}$, and $Au_{43}SG_{37}$



Optical Properties of GSH-Au NCs

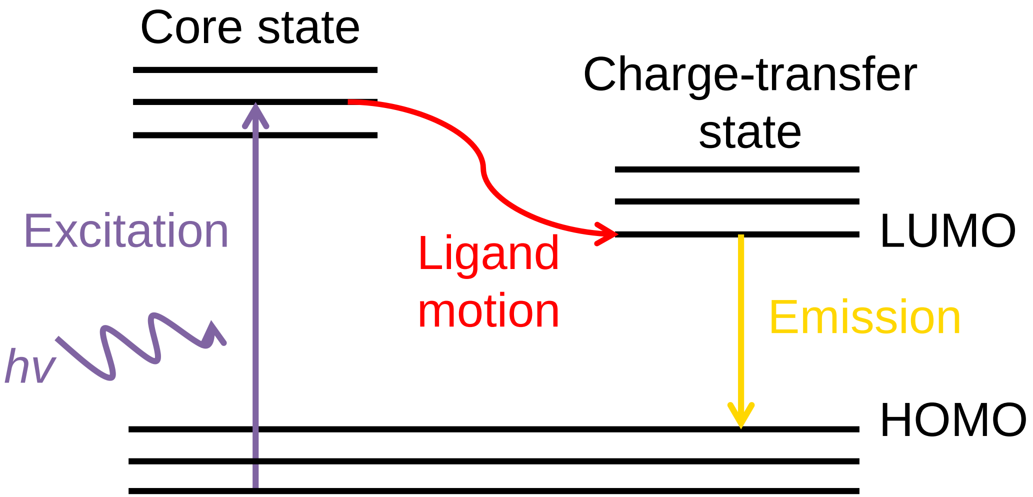






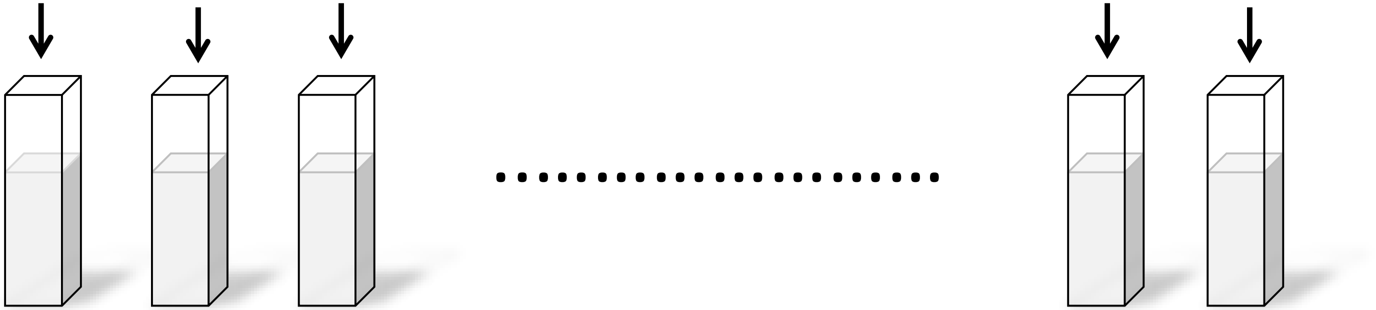
Proposed ligand-to-metal charge transfer (LMCT)

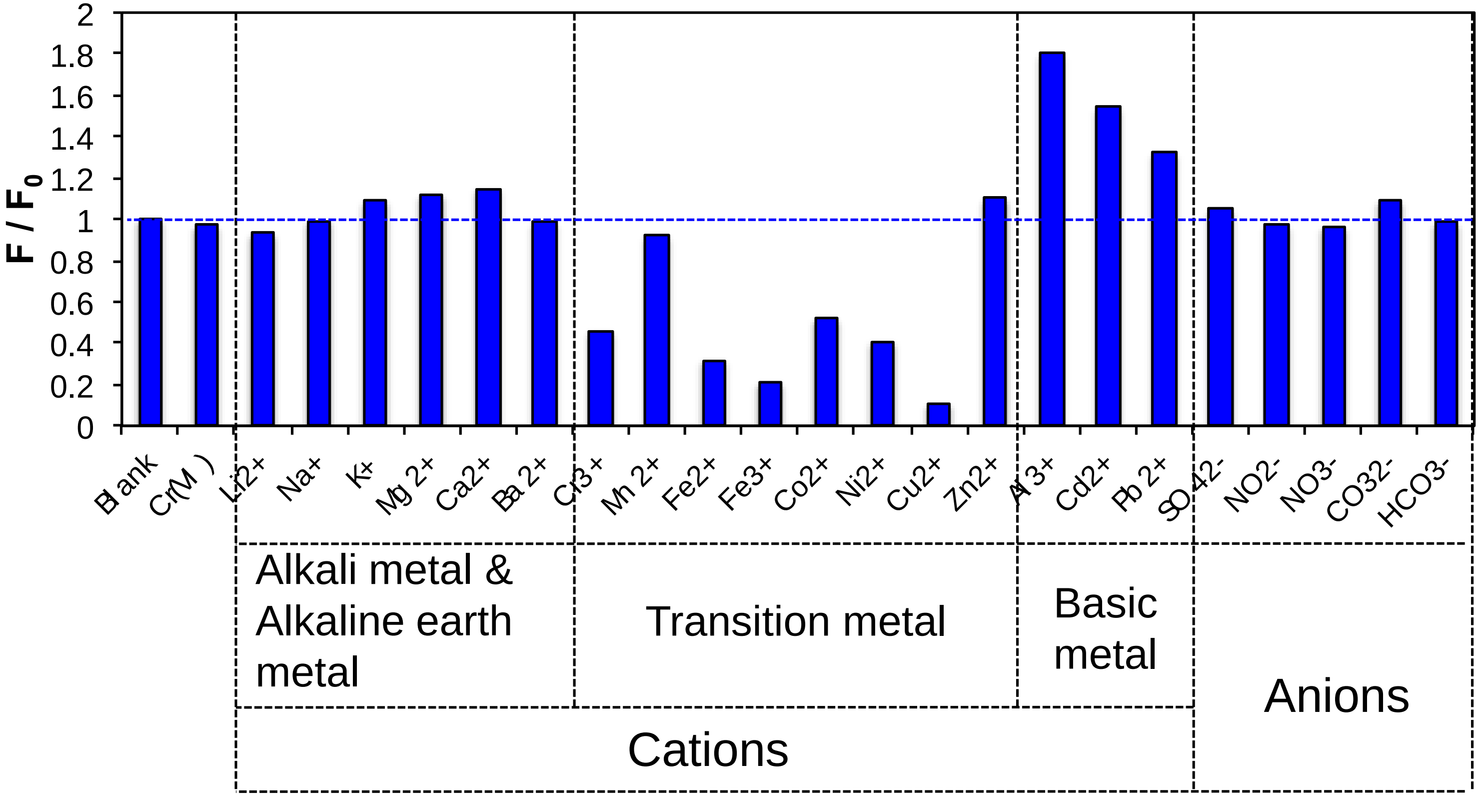
Energy level diagram



Fluorescence sensitivity to inorganic ions

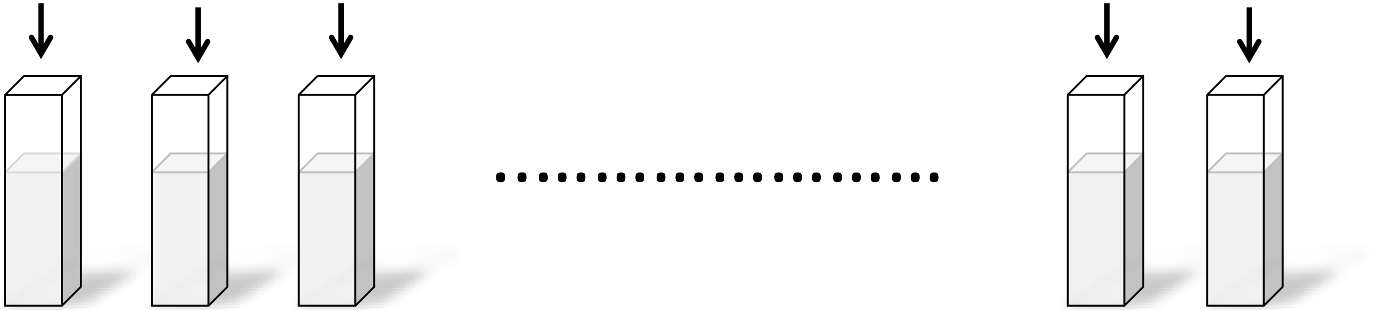
pH~7
20 µM ion conc.
3.3 µM Au

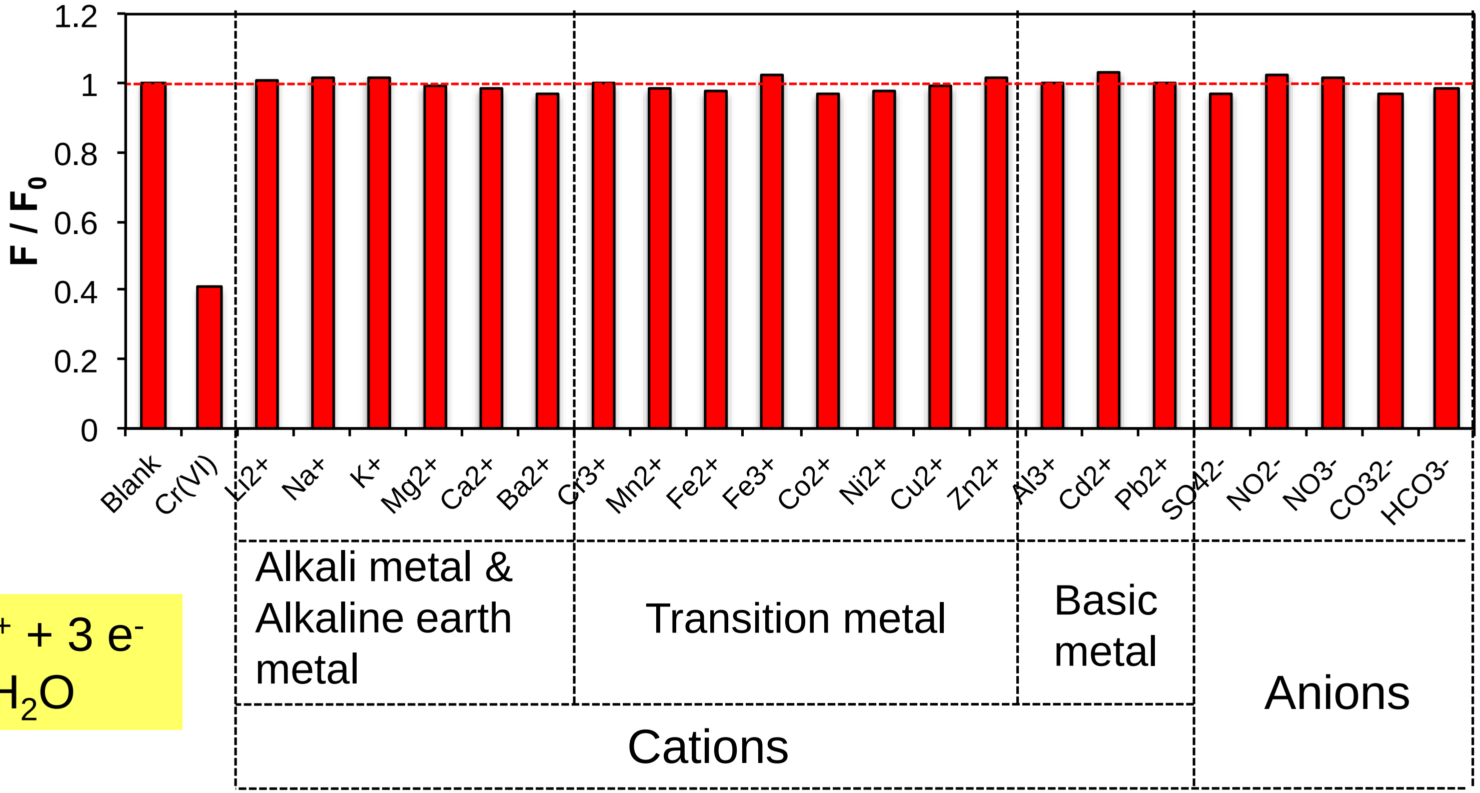




Low pH effect on fluorescence sensitivity

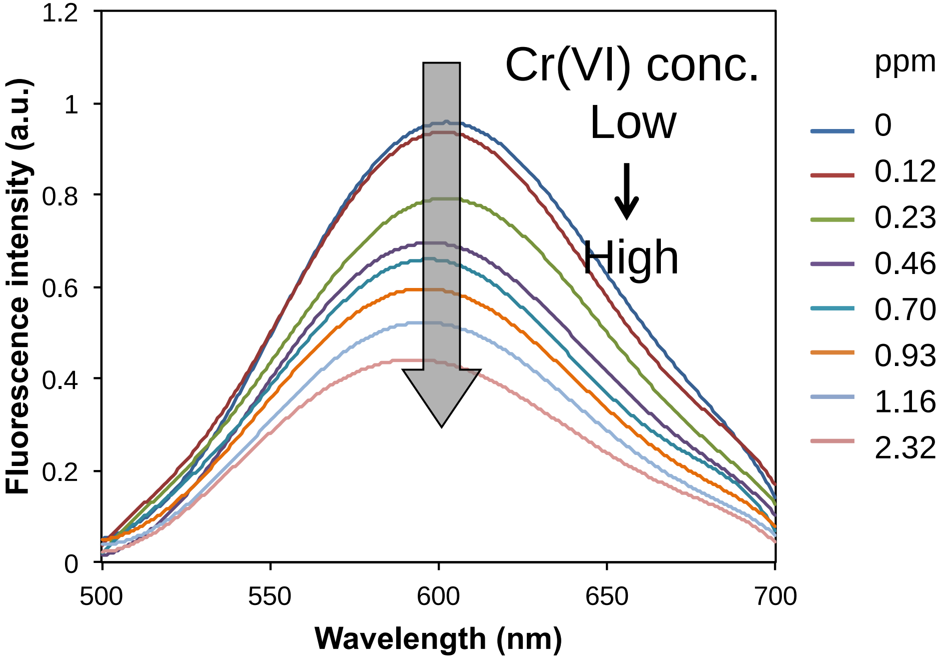
pH~1
20 μM ion conc.
3.3 μM Au

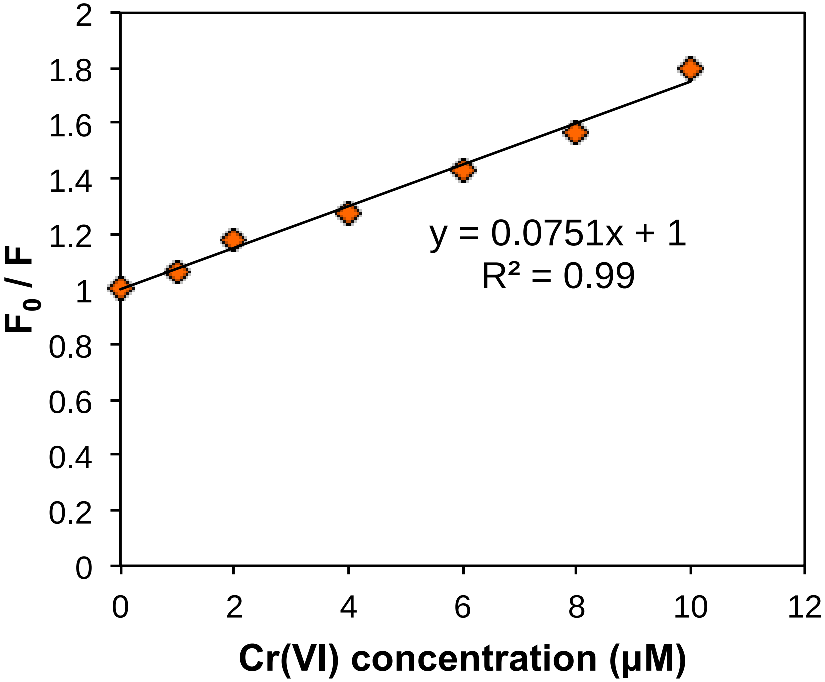




$CrO_4^{2-} + 8H^+ + 3\ e^-$
$\rightarrow Cr^{3+} + 4\ H_2O$

Cr(VI) concentration effect





Stern-Volmer equation

$F_0/F = K_{SV} * [Q] + 1$

K_{SV} the Stern-Volmer quenching constant, which quantifies the quenching efficiency and therefore the sensitivity of the sensor.

LOD (limit of detection) is 0.11 ppm > 0.1 ppm MCL

Other reports of Au NCs for Cr(VI) sensing

Jiyan Liu and coworkers

- Glutathione-stabilized Au NCs (GSH-Au NCs)
- Cr(VI) react with GSH at acid condition to cause the fluorescence quenching
- Limit of detection (LOD) of Cr(VI) is 0.5 µg/L (ppb)

Analytica chimica acta 770 (2013): 140-146.

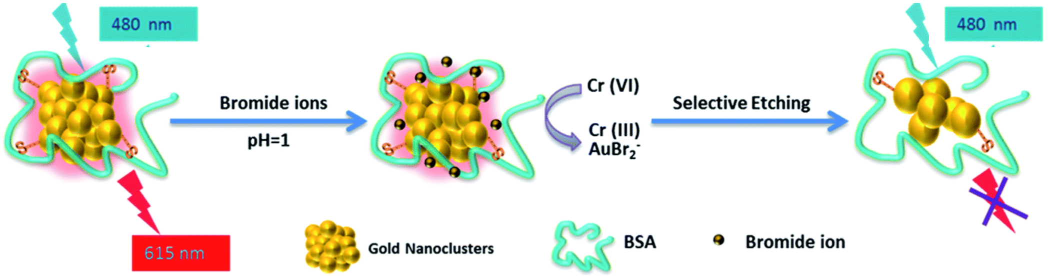
Yongdong Jin and coworkers

- 11-Mercaptoundecanoic acid protected Au NCs (11-MUA-Au NCs)
- Cr(VI) reduced to Cr(III) by ascorbic acid and Cr(III) induced the FL quenching
- Limit of detection (LOD) of Cr(VI) is not reported

J. Mater. Chem. C, 2013,1, 138-143

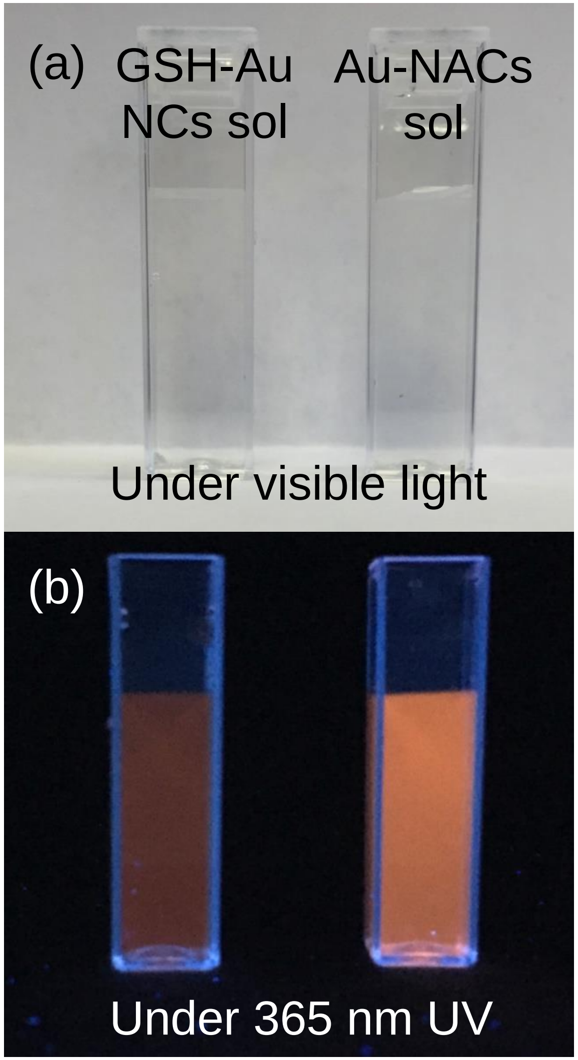
Hou Chang-jun, Yang Mei and coworkers

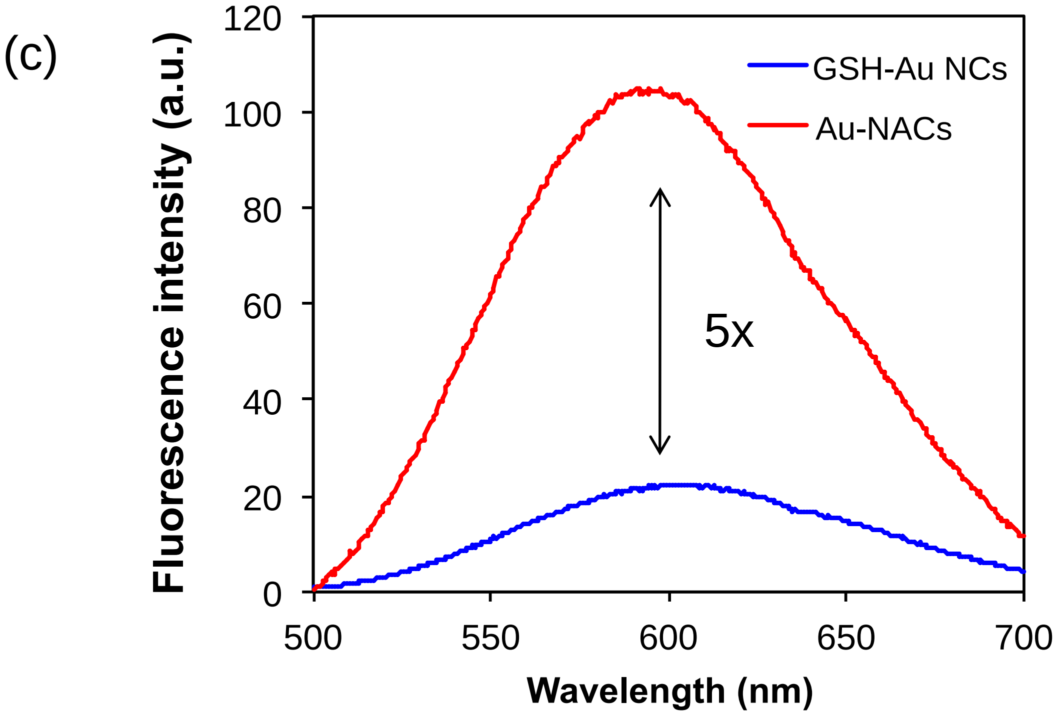
- Bovine serum albumin-stabled gold nanoclusters (BSA-Au NCs)
- Au(0) was oxidized to $AuBr_2^-$ by Cr(VI) in presence of Br^-
- Limit of detection (LOD) of Cr(VI) is 0.6 nM



RSC Adv., 2016,6, 104693-104698

Fluorescence increases after encapsulation

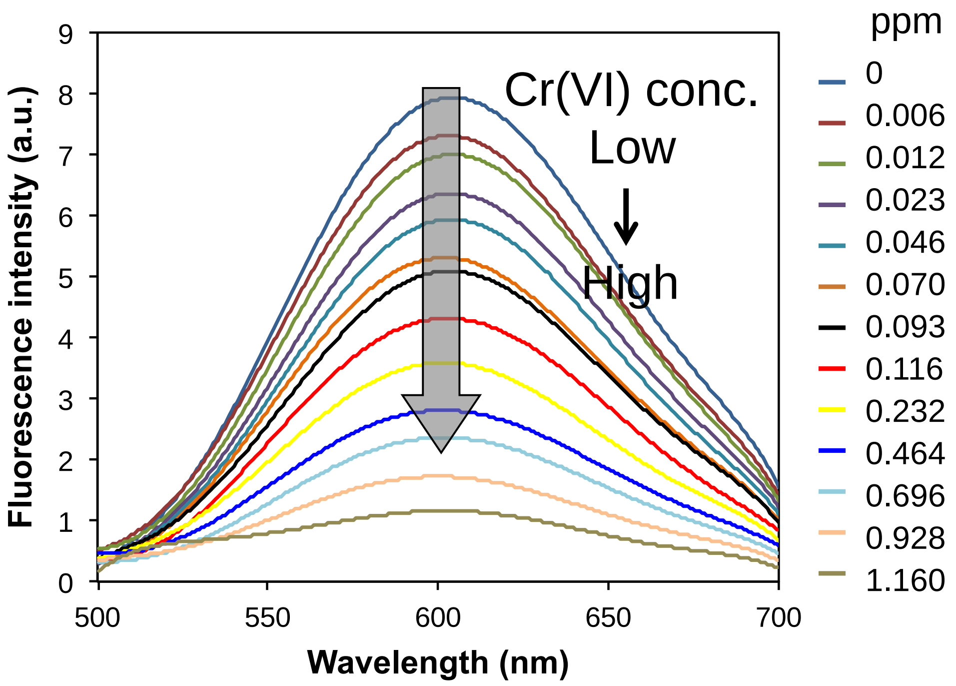


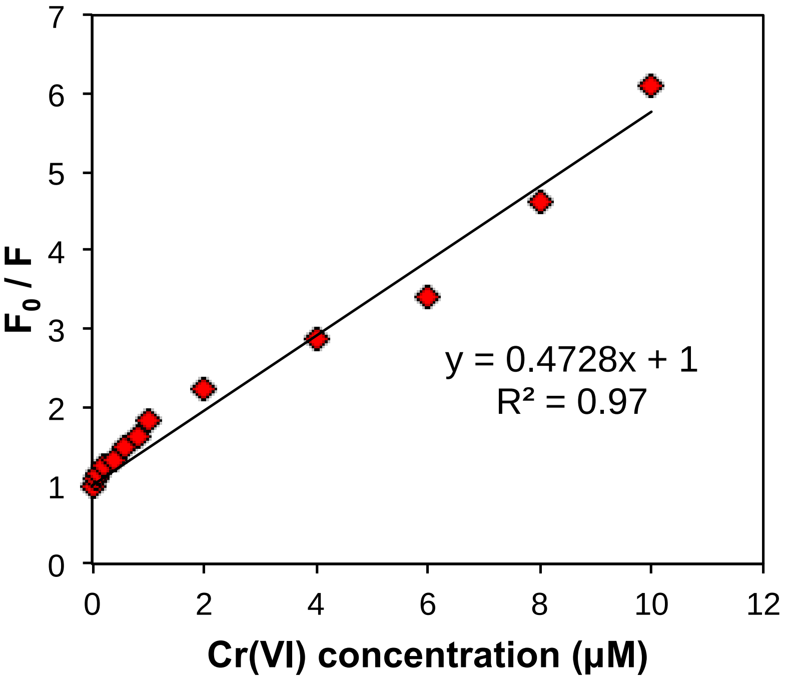


- 50 uL fluorescent Au NCs solution (2 mM Au atom) in 2.95 mL water
- 550 uL Au-NACs in 2.45 mL water

(Au content is 0.033 mM for each case; Au-NACs are synthesized by adding 0.5 mL Au-GSH NCs solution into 0.5 mL PAH and 3 mL NaHPO4 aggregates)

Encapsulated Au NC response to Cr(VI)



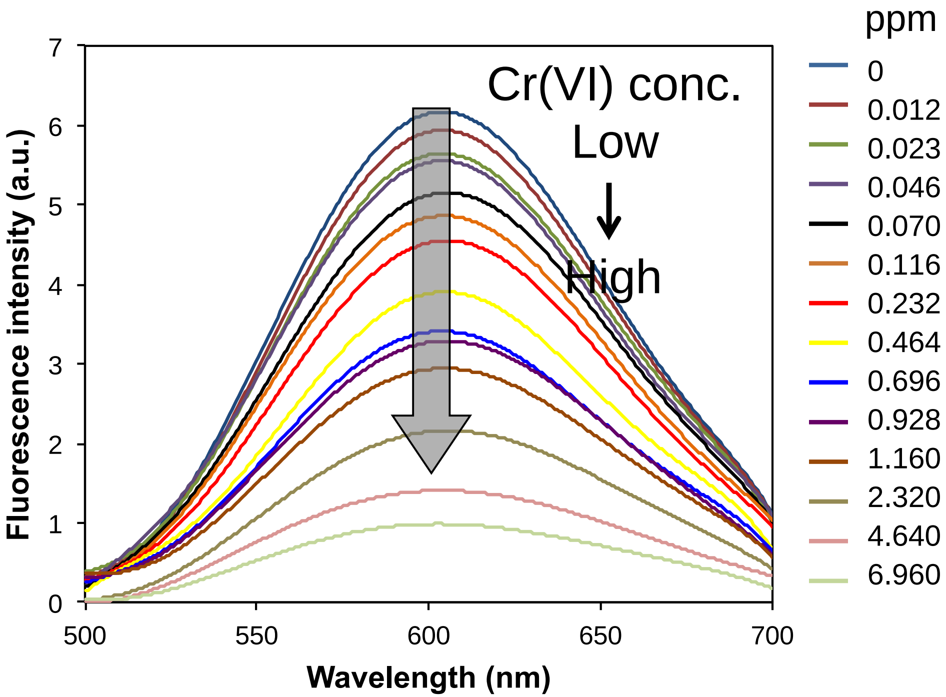


Fluorescence measurements carried at pH 7

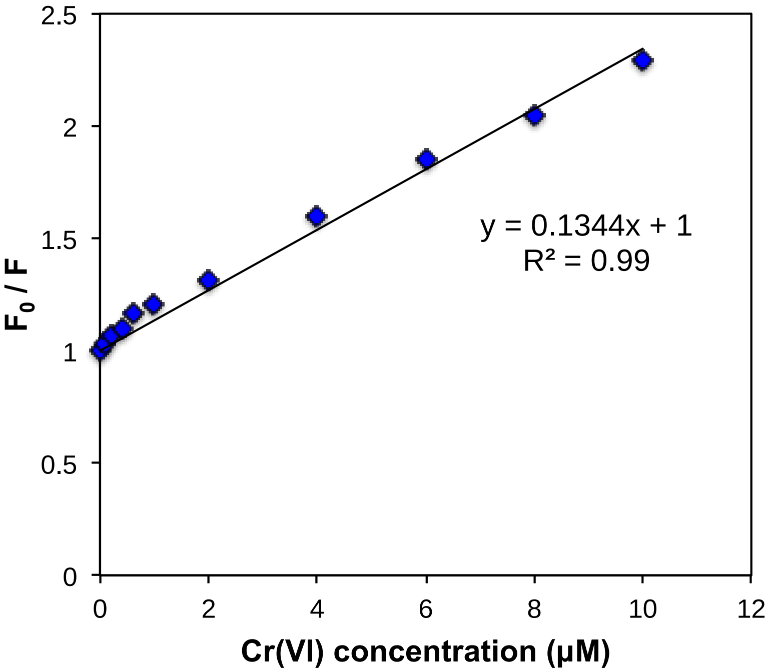
K_{SV} increase indicates higher sensitivity

LOD is 0.006 ppm(!) < 0.1 ppm MCL

Sensing Cr(VI) in simulated drinking water



Fluorescence measurements carried at pH 7.5 in simulated drinking water



K_{SV} still higher than free Au NCs case, but lower than Au-NACs in DI water case

LOD is 0.012 ppm → 8x lower MCL

The takeaways

- Catalytic function of ENPs can be understood and exploited through materials design
  - Reductive degradation of NO_3^-, NO_2^-, others
  - Control of indium metal structure supported on palladium NP surface

- Sensing function of ENPs can be understood and exploited through materials design
  - Fluorescence properties of metal nanoclusters
  - Redox chemistry of CrO_4^{2-} can "turn off" fluorescence
  - Encapsulation of Au nanoclusters increases quantum yield and sensitivity

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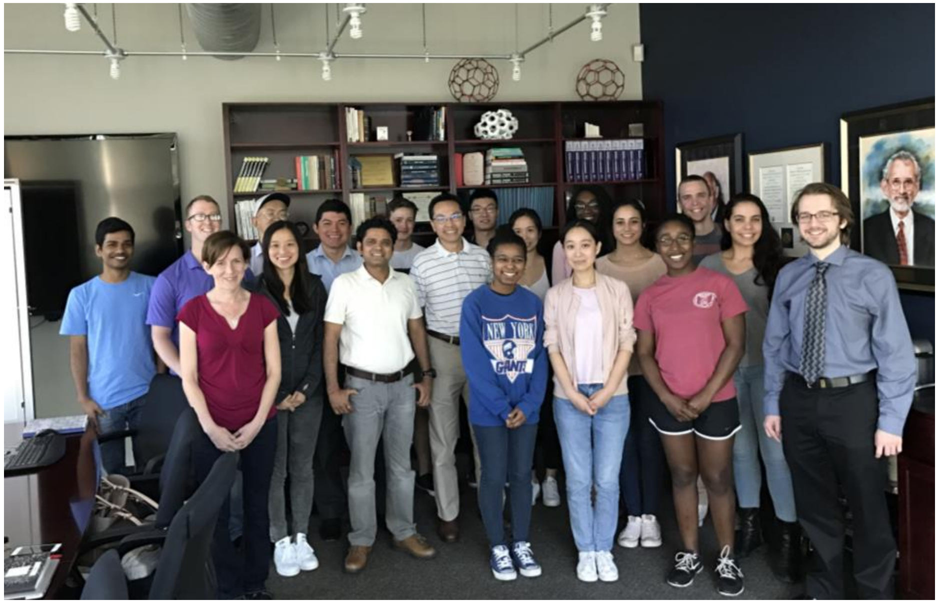
- National Energy Research Scientific Computing (NERSC) Center
- Center for Nanoscale Materials
- Argonne National Laboratory
- Catalysis and Nanomaterials Group

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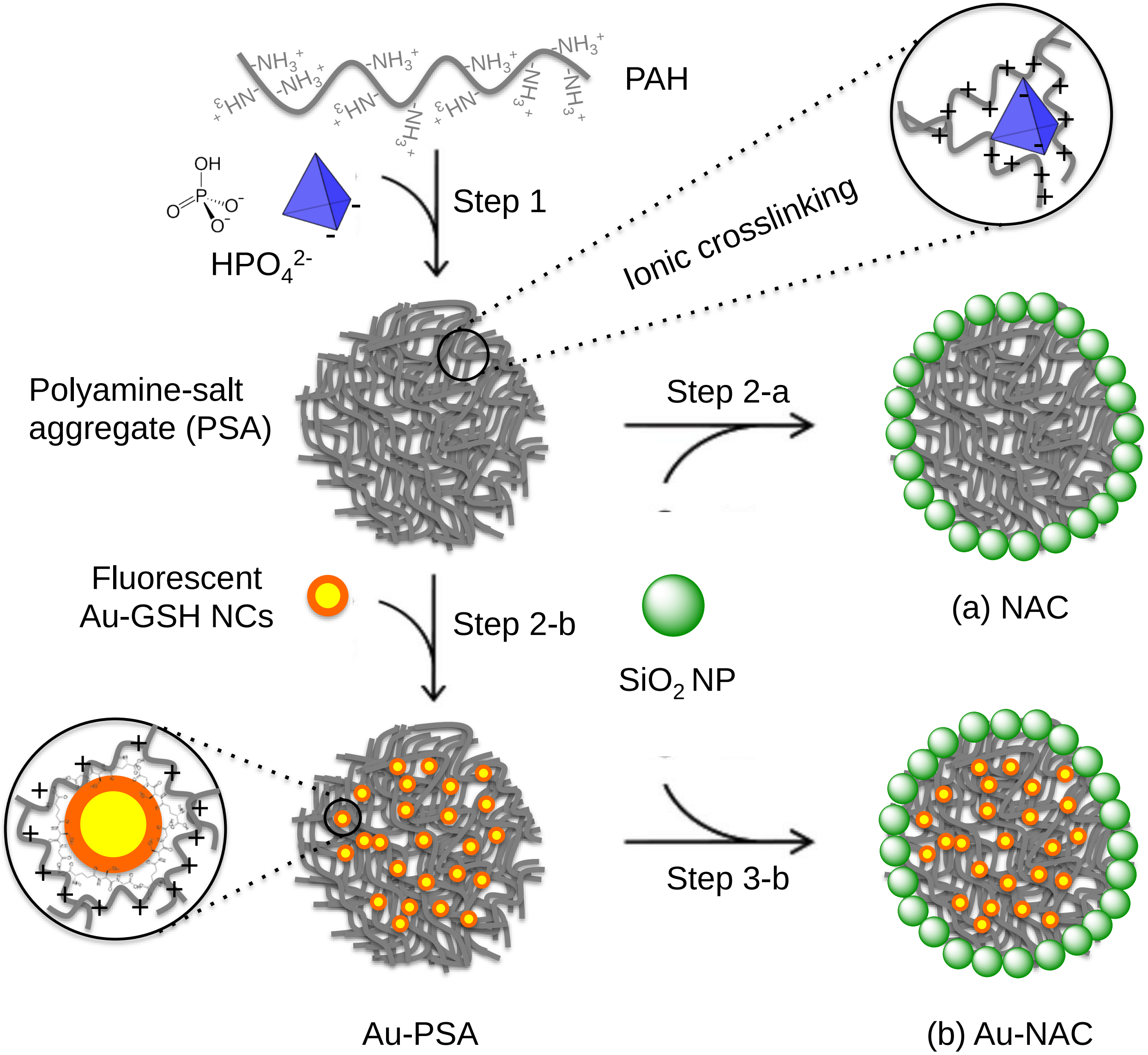
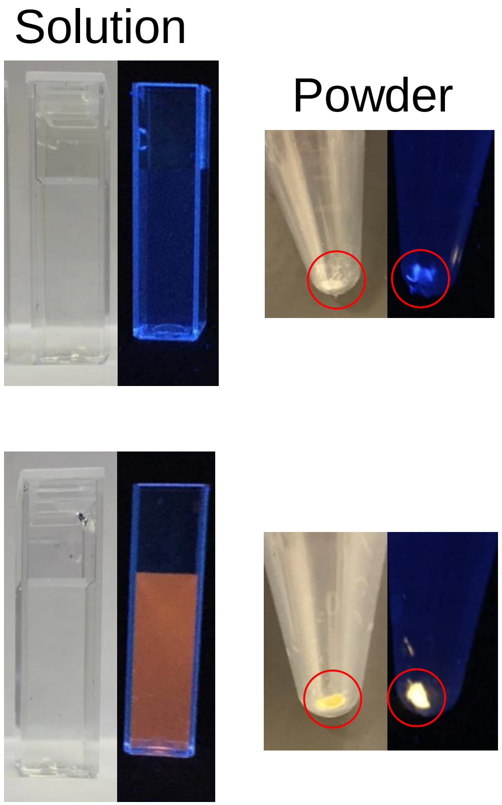
Encapsulate NCs to improve LOD?

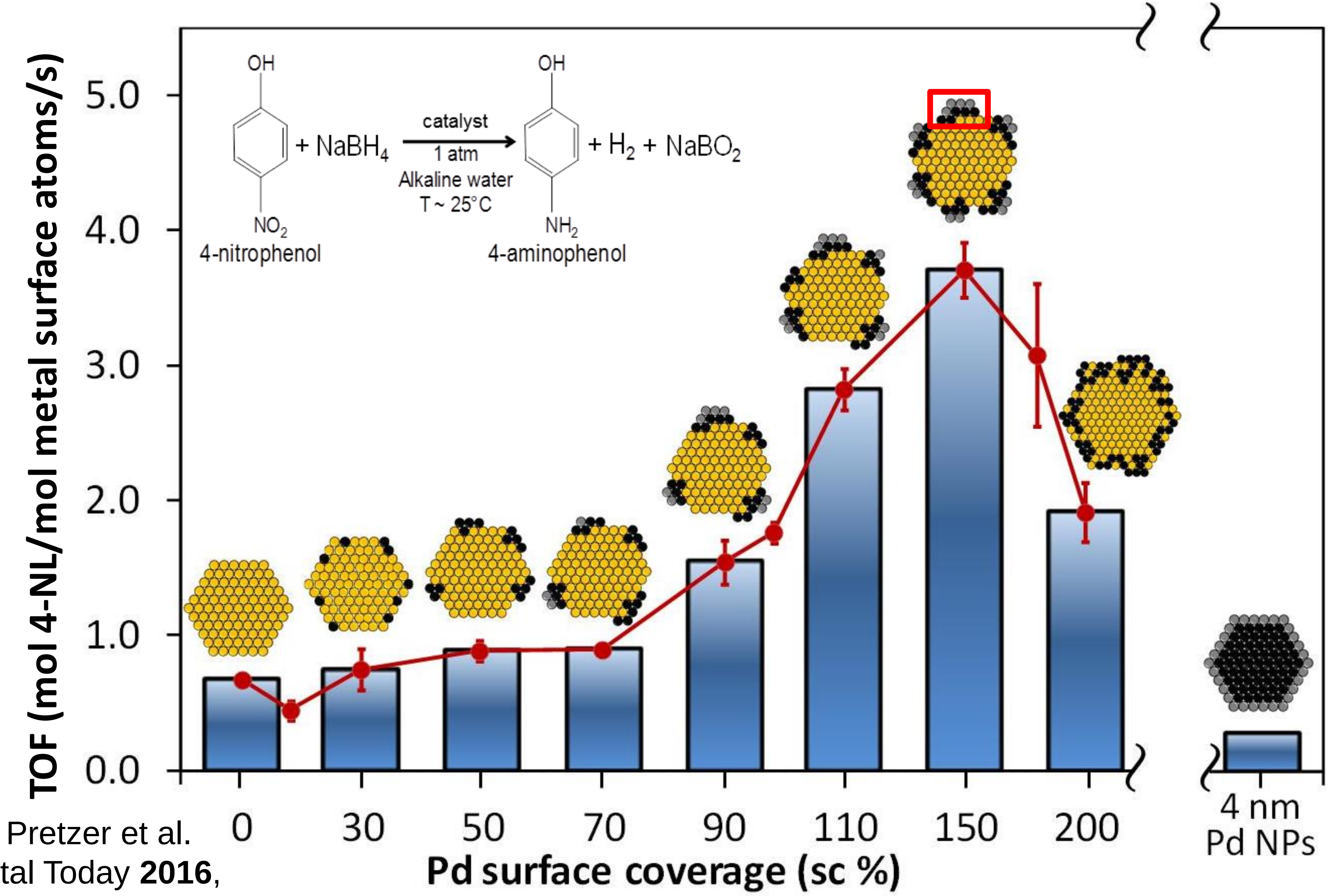


Nanoparticle-assembled capsule (NAC) synthesis chemistry

(Ref: Wong and co-workers, J. Mater. Chem., 2011, 21, 9454-9466)



Catalytic reduction of nitrophenol



(L. Pretzer et al. Catal Today **2016**, 264, 31-36)

Simulated drinking water composition

General Parameters	*Specification*	
Water Source	De-ionized water (conductivity < 1 µS/cm)	
pH adjusted with HCl	7.5±0.25	
Temperature	20±2.5 C	
Constituents	*Concentration (mg/L)*	*Concentration (mM)*
Bicarbonate (HCO_3^-, initial)	183	3.0
Calcium (Ca^{2+})	40	1.0
Chloride (Cl^-)	71	2.0
Fluoride (F^-)	1.0	0.053
Magnesium (Mg^{2+})	12	0.50
Nitrate (NO_3^-)	8.9 (2.0 as N)	0.14
Phosphate (PO_4^{3-})	0.12 (0.04 as P)	0.0013
Silica (SiO_2)	20 as SiO_2	0.33
Sodium (Na^+)	89	3.86
Sulfate (SO_4^{2-})	48	0.50
Total Diss. Solids (TDS)	*478*	-
Ionic Strength	-	*8.5*

NEWT General test water (fresh)

Cost Analysis

- 1 g gold chloride trihydrate ($HAuCl_4$) costs \$122 @Sigma-Aldrich
- 0.00197 mg gold per filter paper
- The gold on one filter paper costs \$0.0005
- Per filter paper costs ~\$0.1
- Total cost per fluorescent paper ~\$0.1 !
- Less than the cost of the commercialized Hach Cr(VI) test kit, ~\$0.7 per test.