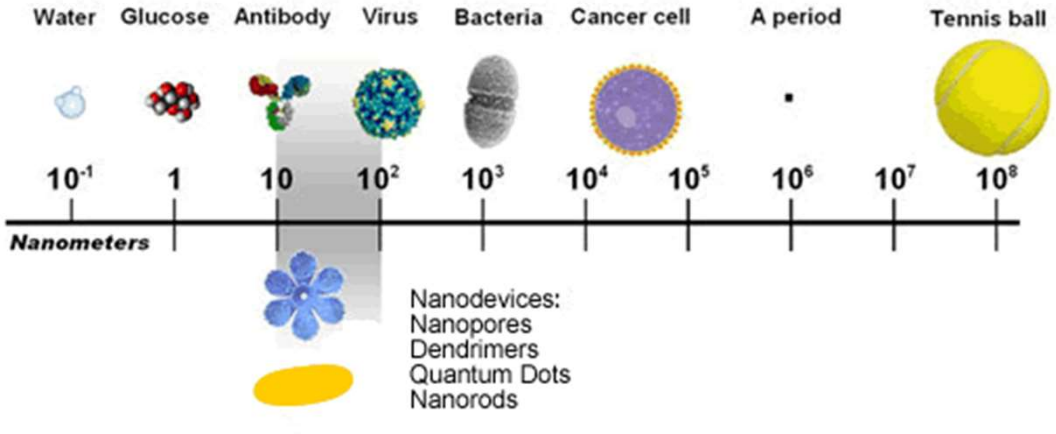
The Synthesis and The Catalytic Reaction of Gold Nanoparticles

Group members: Jiangchao, Moe, Tianxiang

09/08/2019

- **Nanoscience:** is the study of structures and materials on the scale of nanometers.
- It studies systems and manipulates matter on atomic, molecular and supramolecular scales.



- Why do we go Nano?

- All sciences converge when taken to the nanoscale.
- They have new properties and so new uses and benefits.
- Understanding the building blocks of the macromaterials enhances our control of these materials.

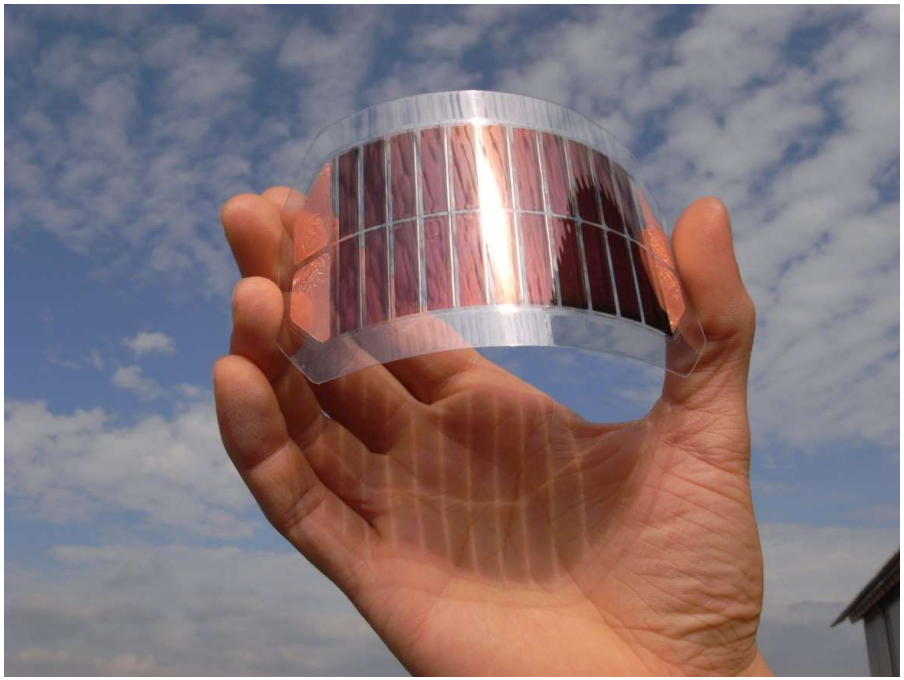
Size dependent optical property for Gold

Gold Metal

Smaller Au-NPs

Larger Au-NPs

- Nanomaterials have many applications;
  - Medical applications.
  - Solar cells.
  - Great Catalysts.

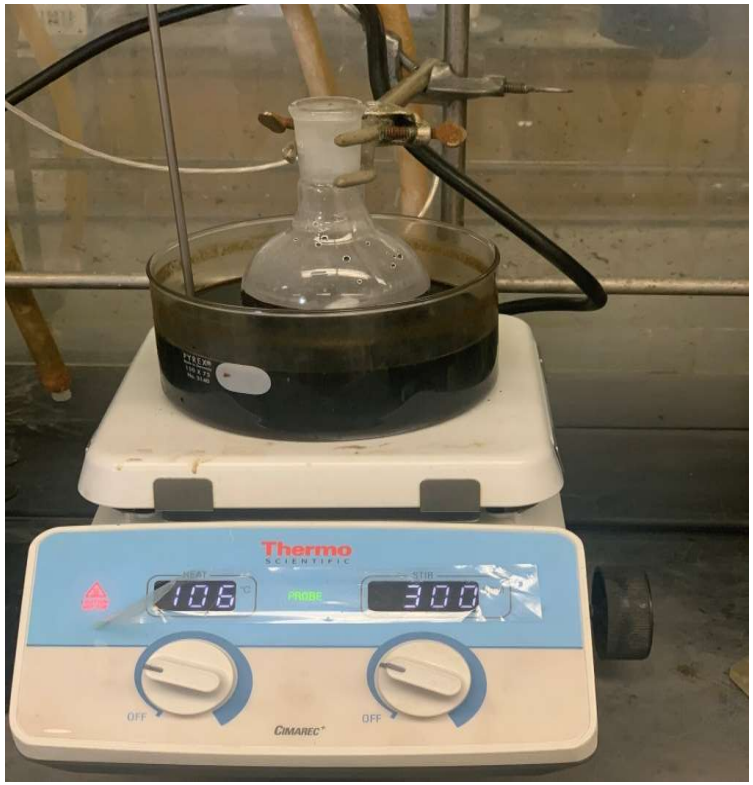


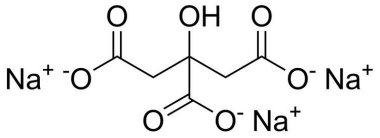
Nanocrystal Solar Cell

- Size controlled aqueous synthesis of Au-NPs.

➢Experimental Procedure:

❖ 150 mL of 2.2 M of trisodium citrate ($Na_3C_6H_5O_7$) aqueous solution in a 250 mL RBF. Then it was heated at 100 °C for 15 minutes with vigorous stirring.

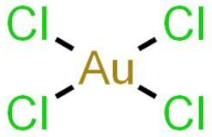




❖ 3 Sizes were prepared;

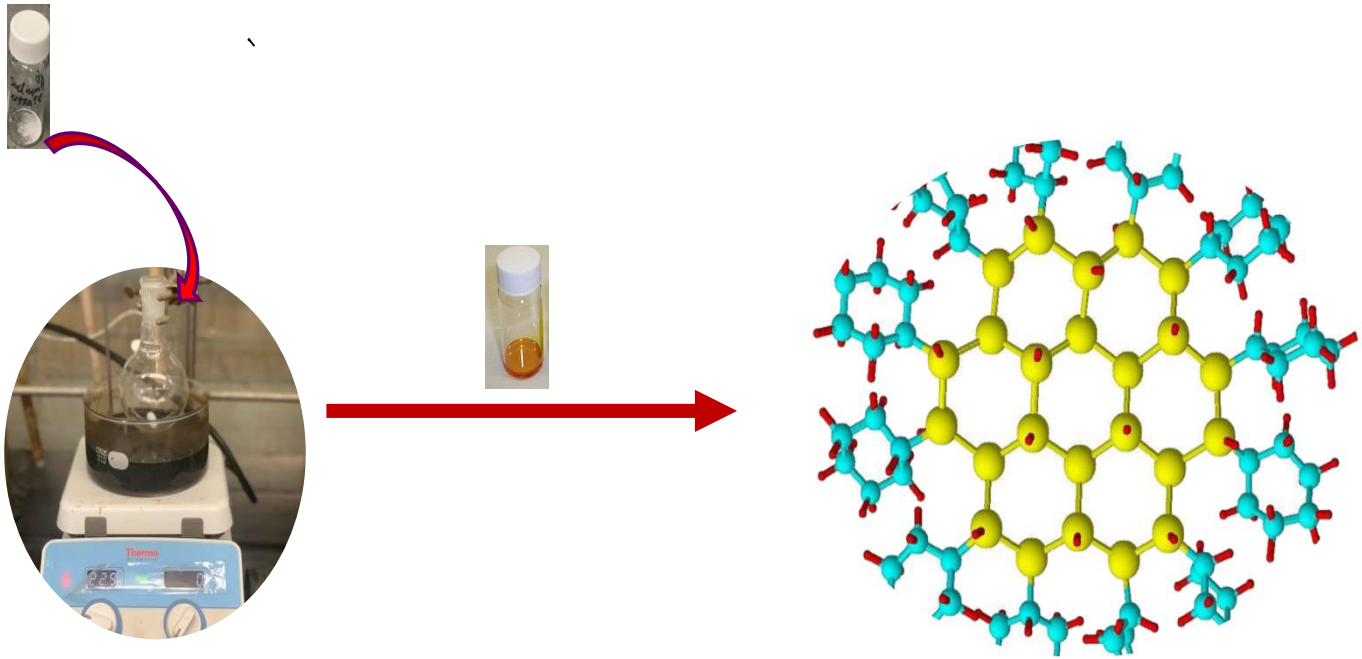
- Size #1: Seeds.

➢ 1 mL of 25 mM solution of $AuCl_4^-$ (prepared by Sheena) was added to the of trisodium citrate hot solution and kept at 100 °C for another 30 minutes and stirring.



Aqueous Synthesis of Au Nanoparticles

A. Seeds Preparation (Size#1)

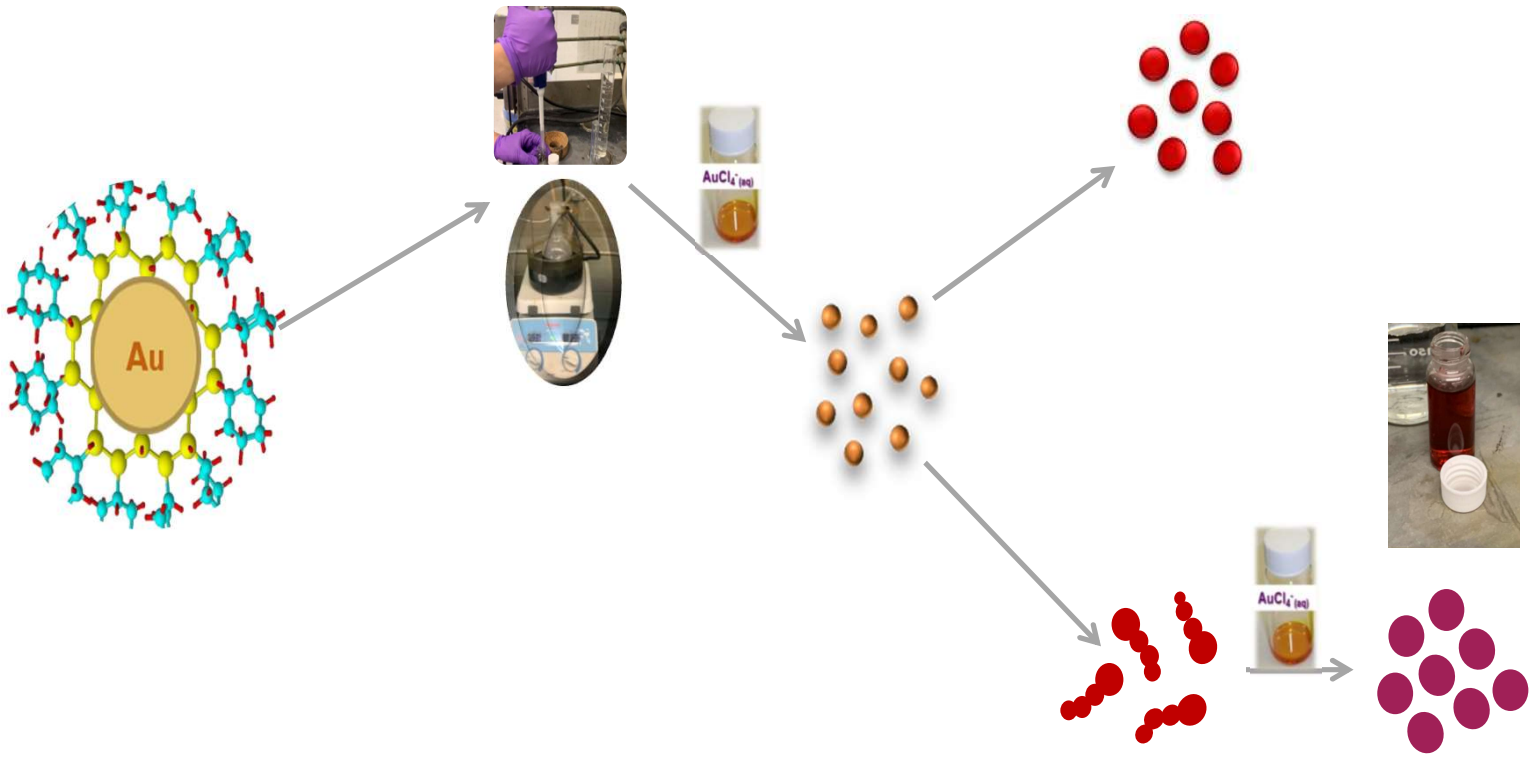


- <u>Size #2: First Injection.</u>

  1 mL 60 mM sodium citrate solution was added to the seeds and kept under the same conditions for 5 minutes. Then 1 mL of 25 mM solution of $AuCl_4^-$ (aq) was added and kept for 30 minutes.

1st injection

B. First Deposition (Size #2)

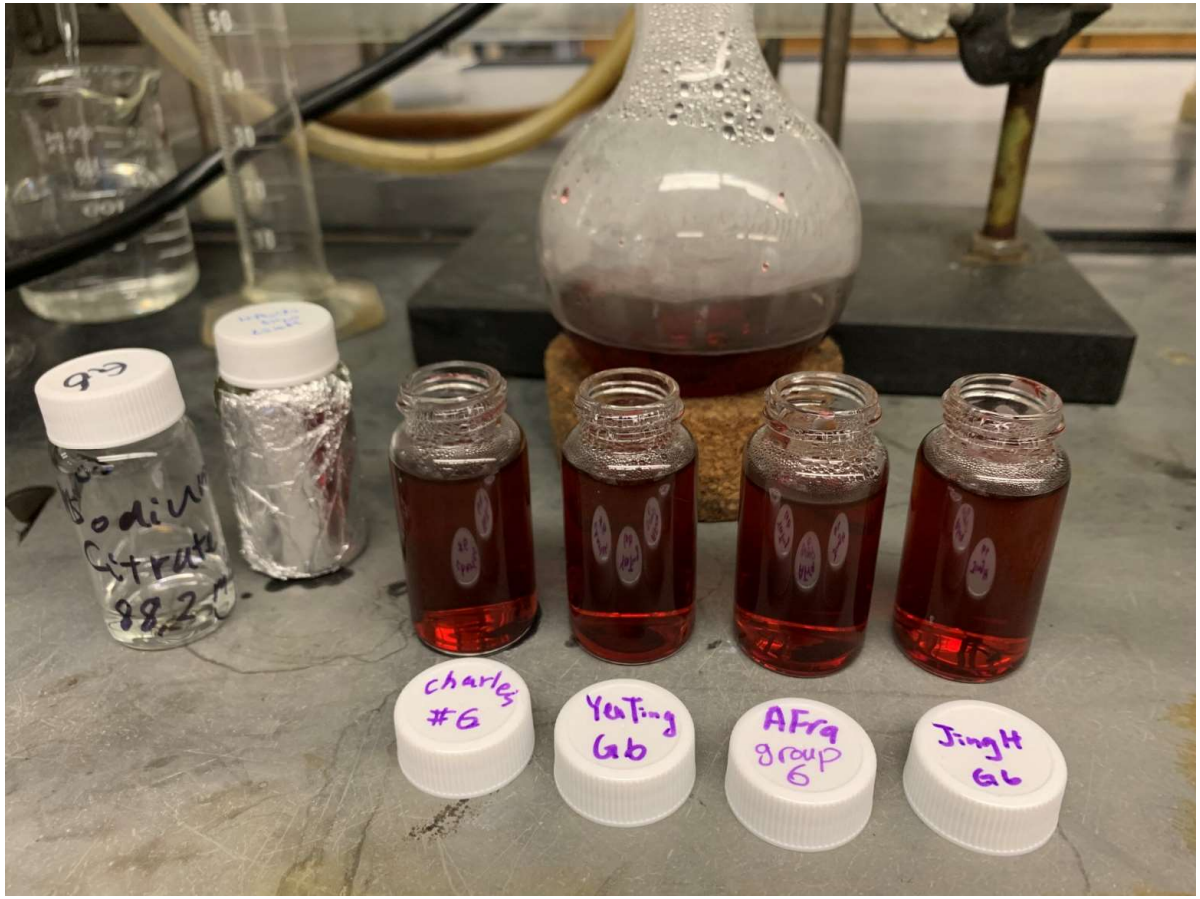


All reactions are under 100°C, 300rpm
(Vigorous stirring)

C. Second Deposition (Size #3)

- Size #3: Second Injection.

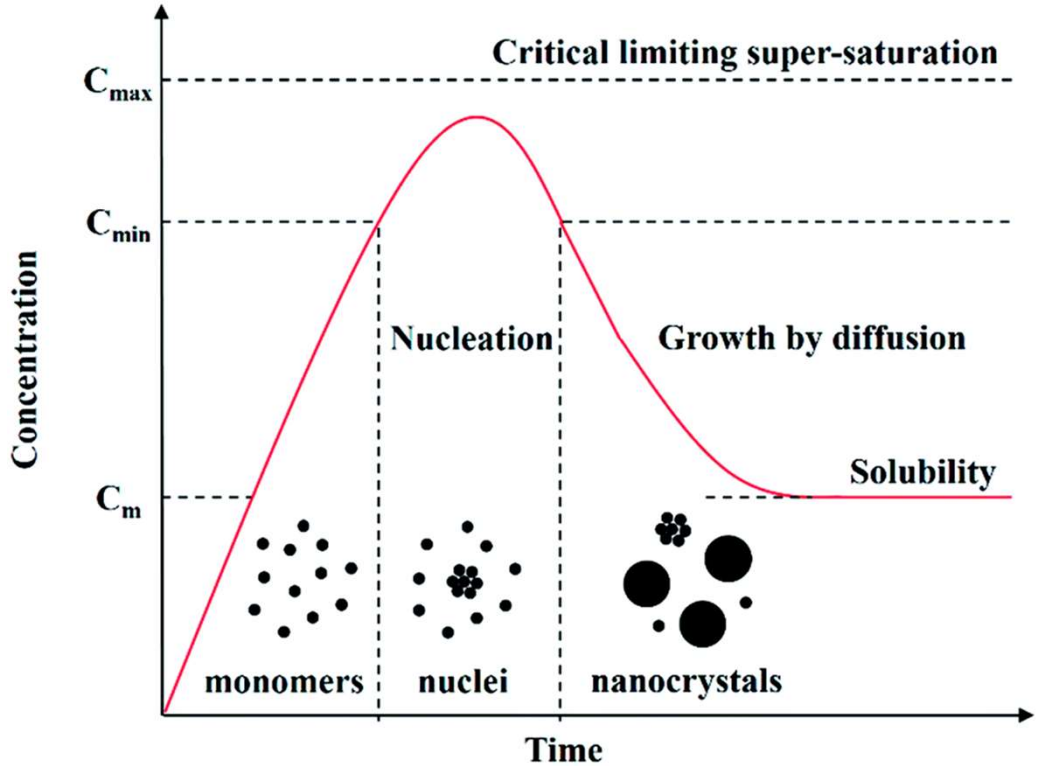
➢The same steps of the first injection was repeated.




0min
1min
20min
0min

- What is the mechanism of nucleation?

➢ **LaMer mechanism**: burst nucleation until extreme consumption of monomers, that drop significantly. Following nucleation growth occurs under the control of the diffusion of monomer through the solution.



- Characterization of the Au-NPs.

➢ Transmission electron microscopy (**TEM**).

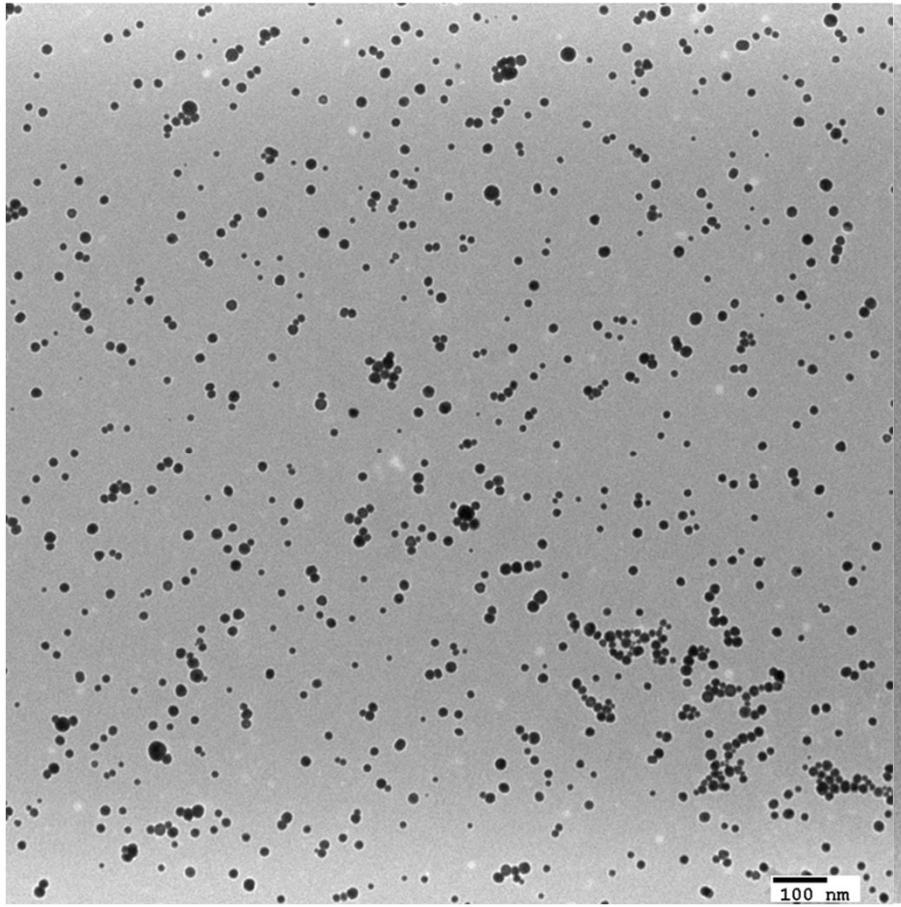
➢ X-Ray diffraction (**XRD**).

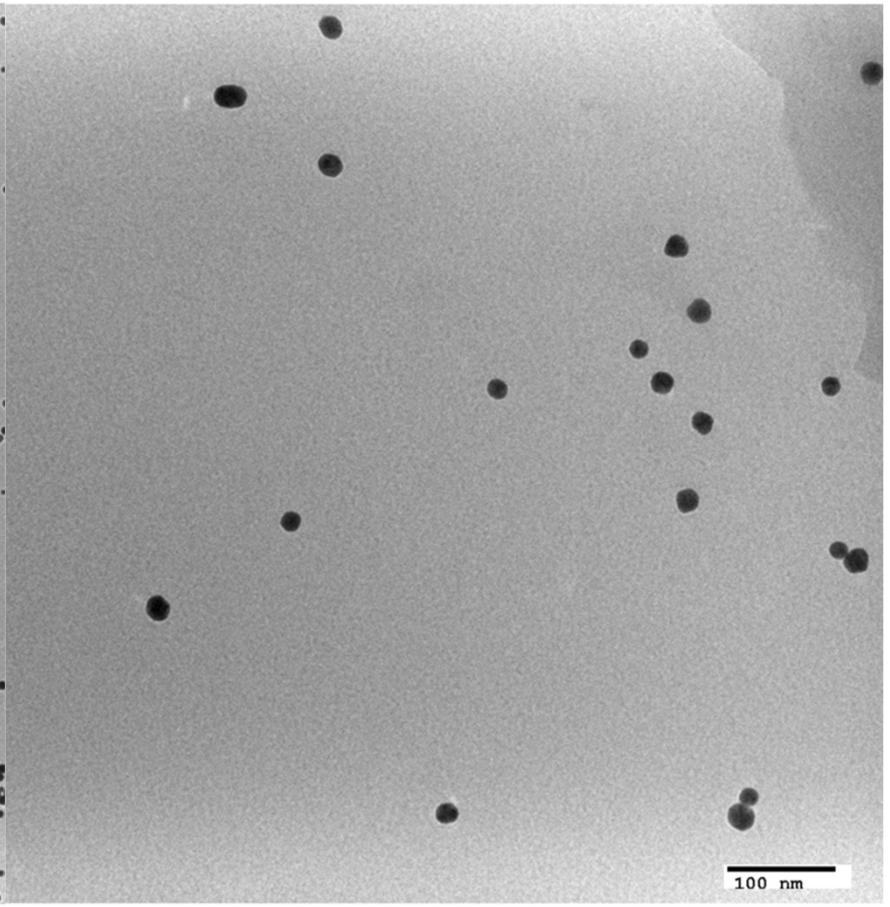
➢ Scanning electron microscopy (**SEM**).

➢ X-Ray absorption spectroscopy (**XAS**).

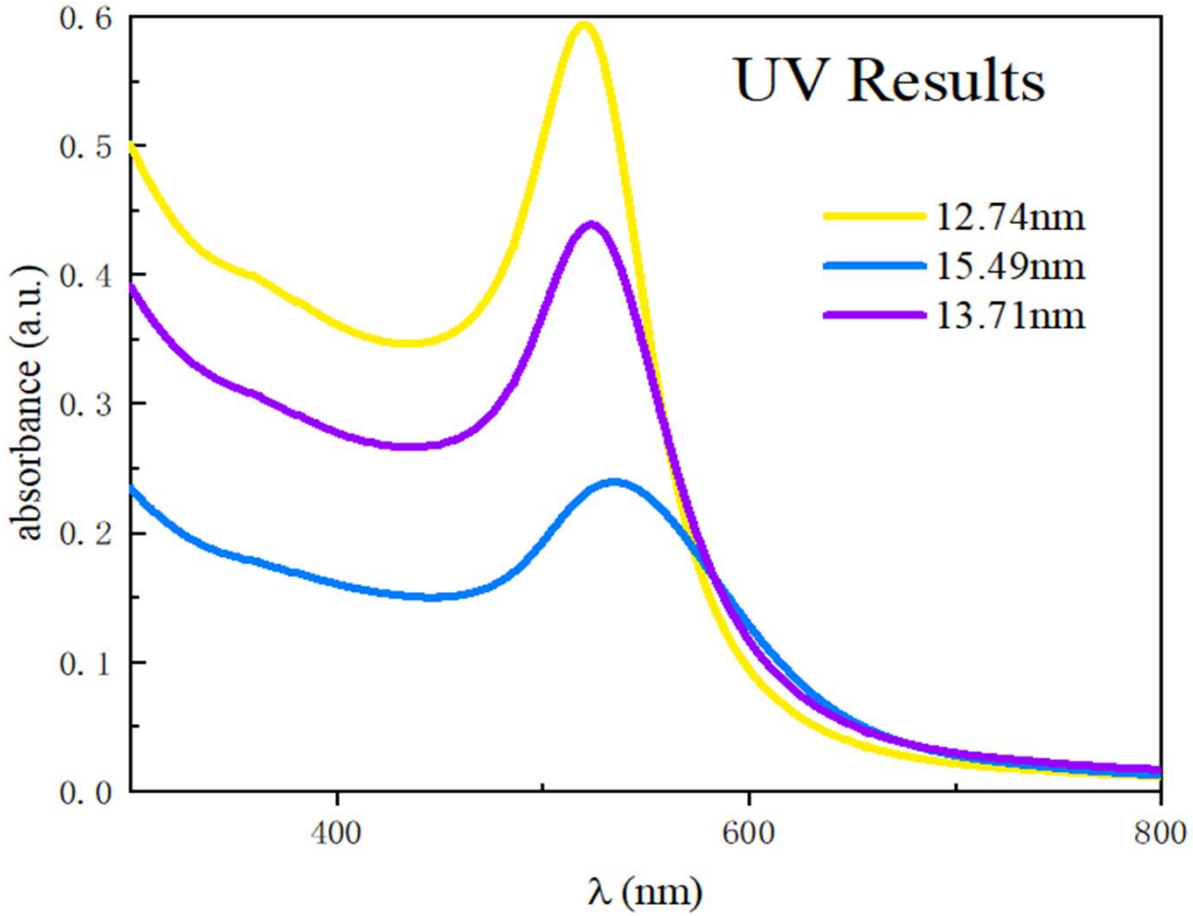
❖ In this experiment only TEM was used.


HITACHI
H-7650
EDAX
CAUTION
X-RAY
HITACHI





Size	Seeds	First Injection	Second Injection
Trial #1	8.83 nm	24.60 nm	12.74 nm
Trial #2	13.71 nm	15.49 nm	21.41 nm
Average	11.27 nm	20.04 nm	17.08 nm


UV Results
12.74nm
15.49nm
13.71nm
absorbance (a.u.)
0. 6
0. 5
0. 4
0. 3
0. 2
0. 1
0. 0
400
600
800
λ (nm)

Catalytic Activity

TOF – turn over frequency

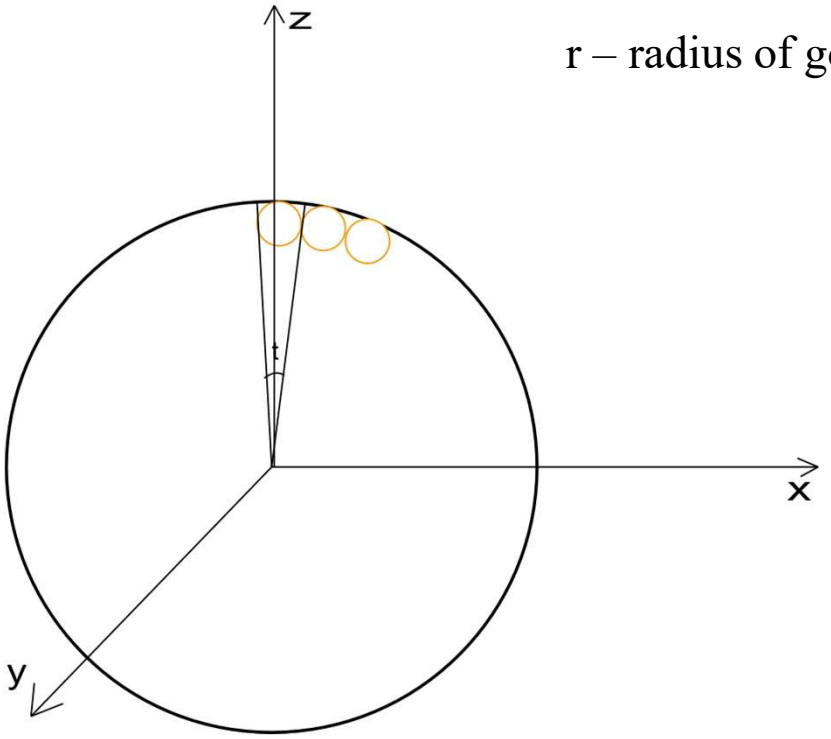
$$TOF(s^{-1}) = \frac{\#molecules\ reacted}{\#active\ sites \cdot time}$$

The reduction of 4-nitrophenol is a pseudo-first order reaction, so k can be determined using

$$\ln(C_t/C_0) = -k\,t$$

Catalytic Activity

To calculate the activate sites, we build the following model:



R – radius of the NP

r – radius of gold atom(72pm)

Function of sphere: $z = \sqrt{R^2 - x^2 - y^2}$

Area of each one projection of gold atom:

$$A = \iint_{\Omega} \sqrt{1 + {f_x}^2 + {f_y}^2}\, dxdy$$

Then change x, y into θ, φ while:

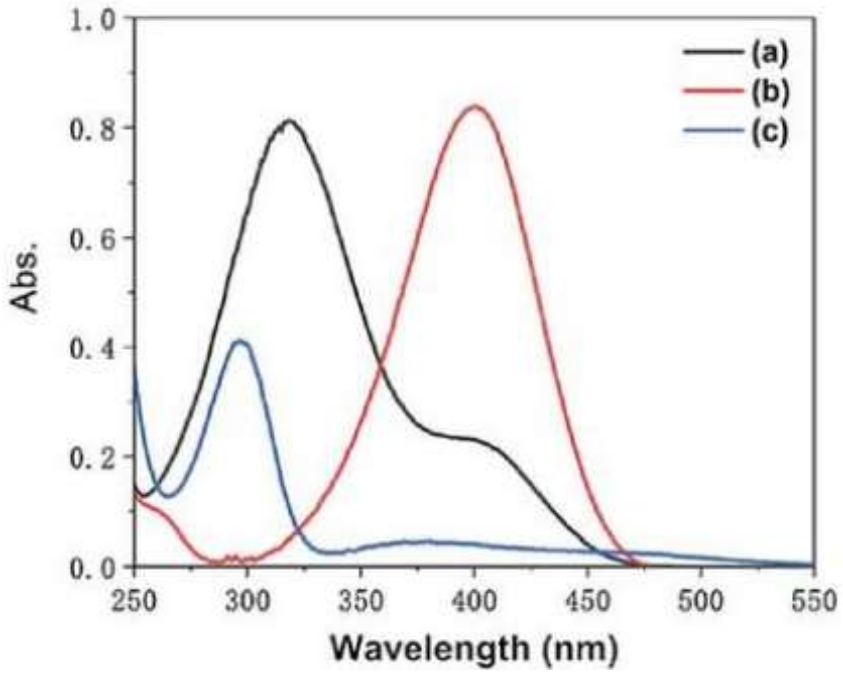
$$x = R\cos\theta\sin\phi$$
$$y = R\sin\theta\sin\phi$$

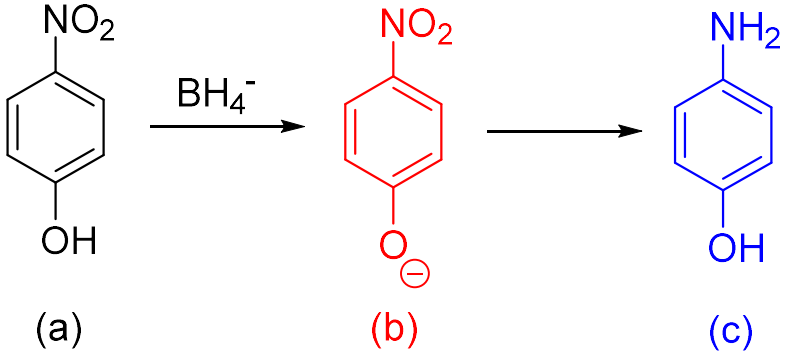
$$A = 4R^2 \int_0^{\pi/2} d\theta \int_0^{t/2} \sin\phi d\phi = 2\pi R^2 \left(1 - \cos(\frac{t}{2})\right)$$

$$\sin\left(\frac{t}{2}\right) = \frac{r}{R - r}$$

$$active\ sites \approx \frac{4\pi R^2}{2\pi R^2 \left(1 - \cos(\frac{t}{2})\right)}$$

The Reduction of 4-Nitrophenol

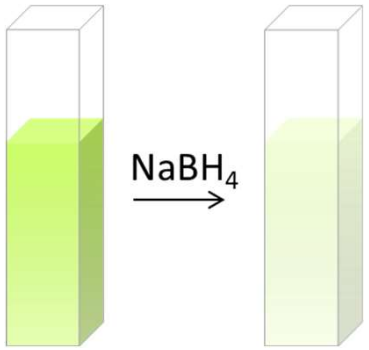




Use UV-vis to monitor the reaction!

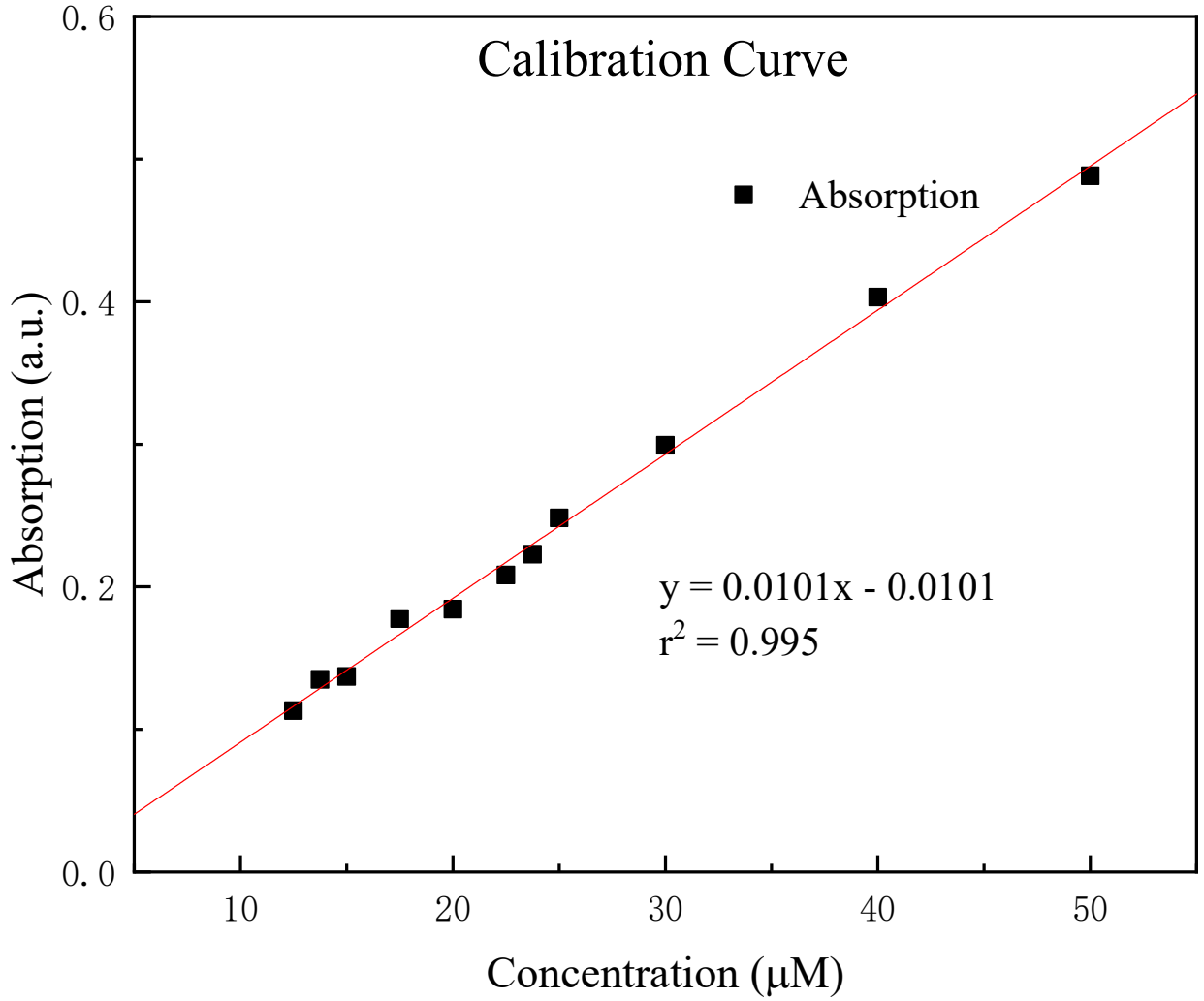
The Reduction of 4-Nitrophenol

1. Mix 0.3 mL of 0.14 mM 4-nitrophenol with 2 mL 42 mM sodium borohydride solution in a 2 mL cuvette.

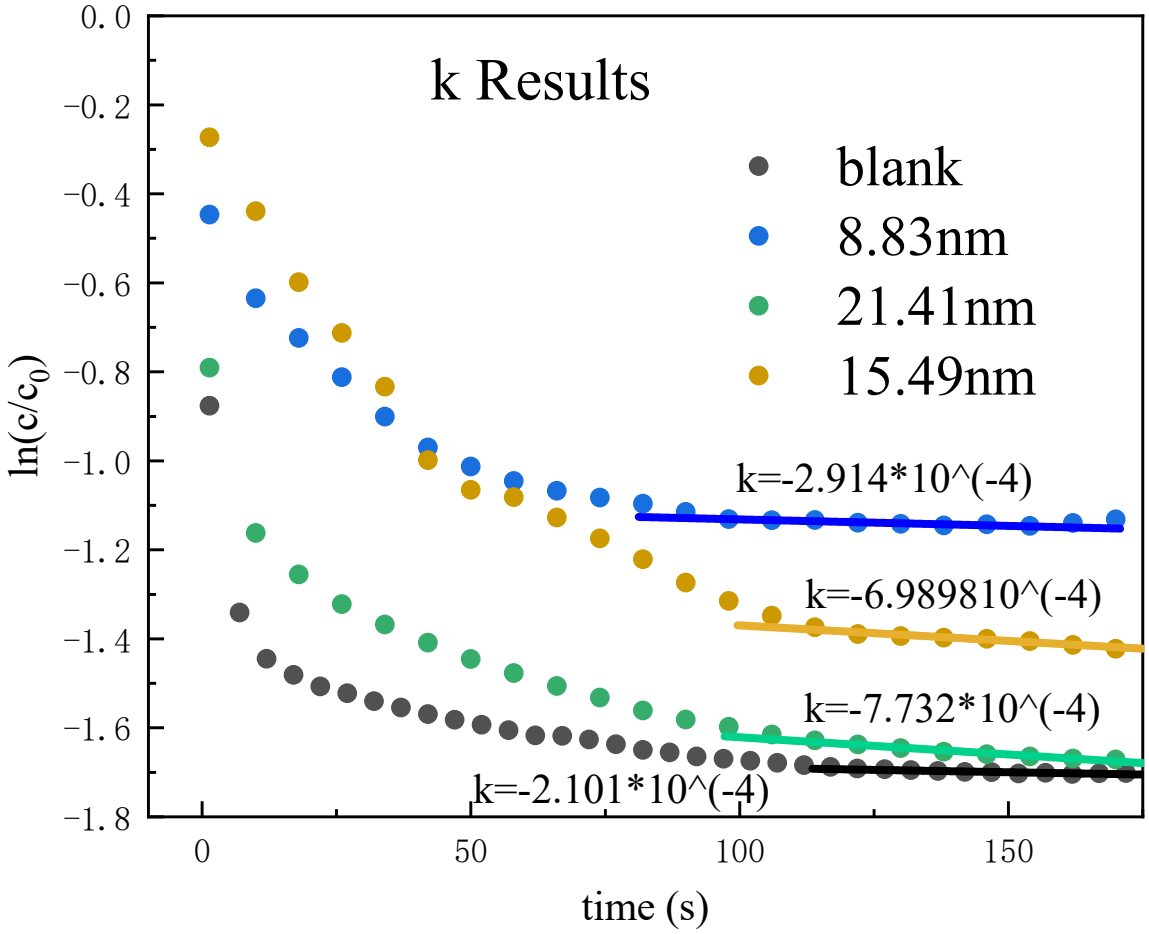


2. Add gold nanoparticles (based on $1.64*10^{-6}$ mol gold atoms) and record the absorbance change at 400nm every 10 seconds.

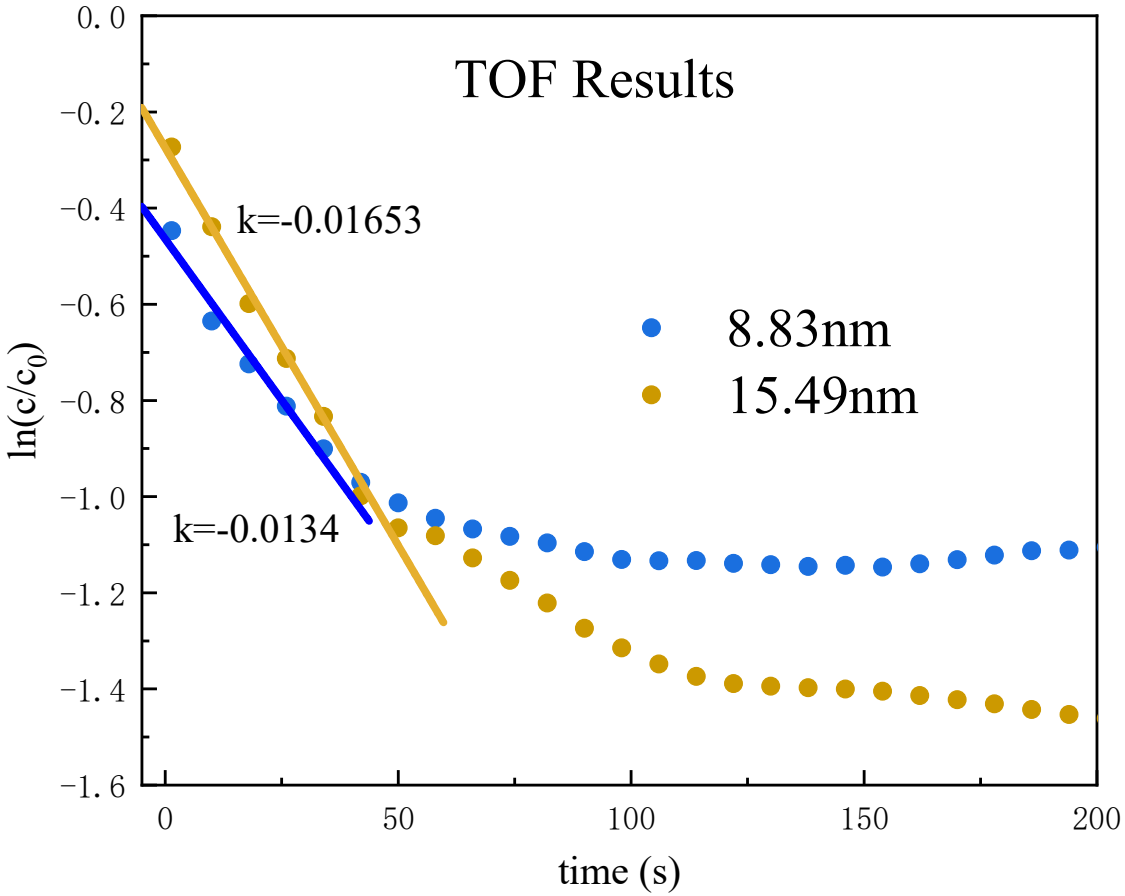
The Reduction of 4-Nitrophenol



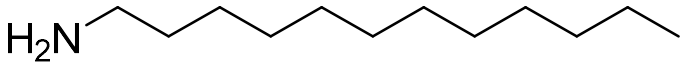
The Reduction of 4-Nitrophenol



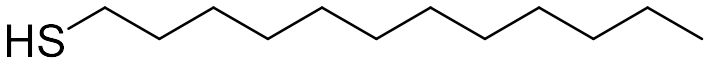
The Reduction of 4-Nitrophenol



Ligands of NPs



dodecylamine

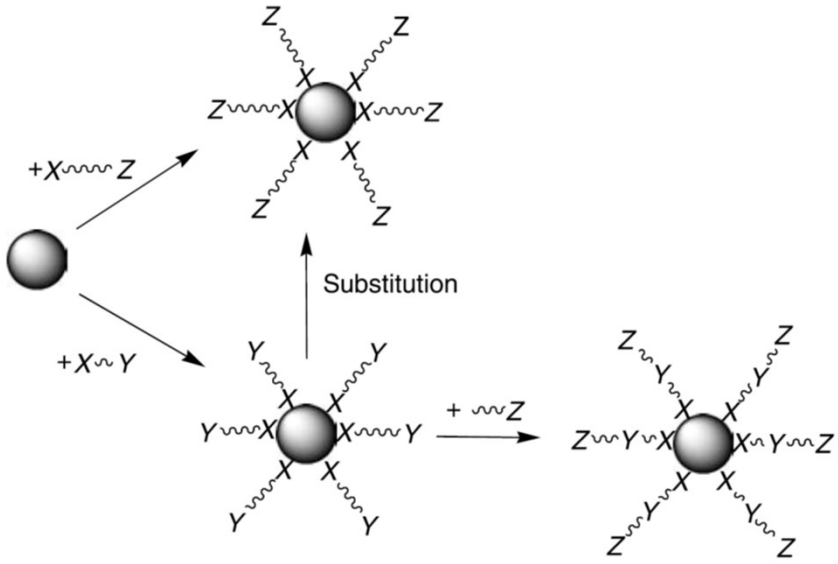


1-dodecanethiol

◆ Why use ligands?

1. To change the surface property of nanoparticles.

2. To protect the nanoparticles from collapsing.

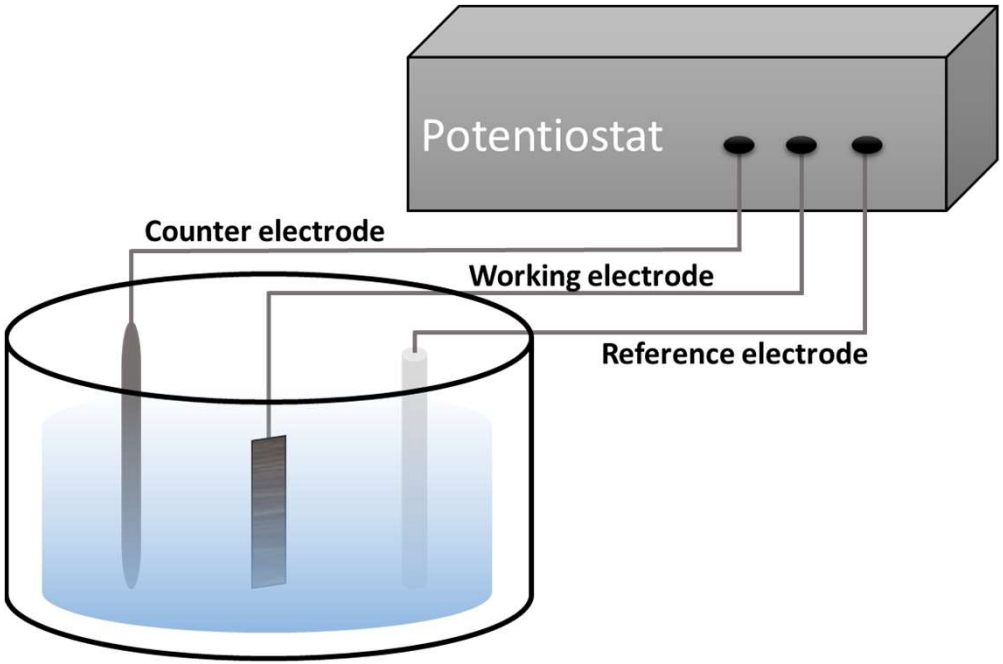


Ligands of NPs

Ligand Change Reaction:

1. Use nitrogen to dry the gold NPs (prepared by Sheena)
2. Get about 4 mg dried NPs into a 50mL RBF
3. Add 2 mL toluene then follow with 10 equiv. ligand
4. Add 5 mL more toluene to wash the gold NPs
5. Heat the RBF and boil it for 5min(oil bath)
6. Cool it down and wash it with toluene (use rotary evaporator)
7. Disperse the gold NPs in hexane

MeOH Oxidation



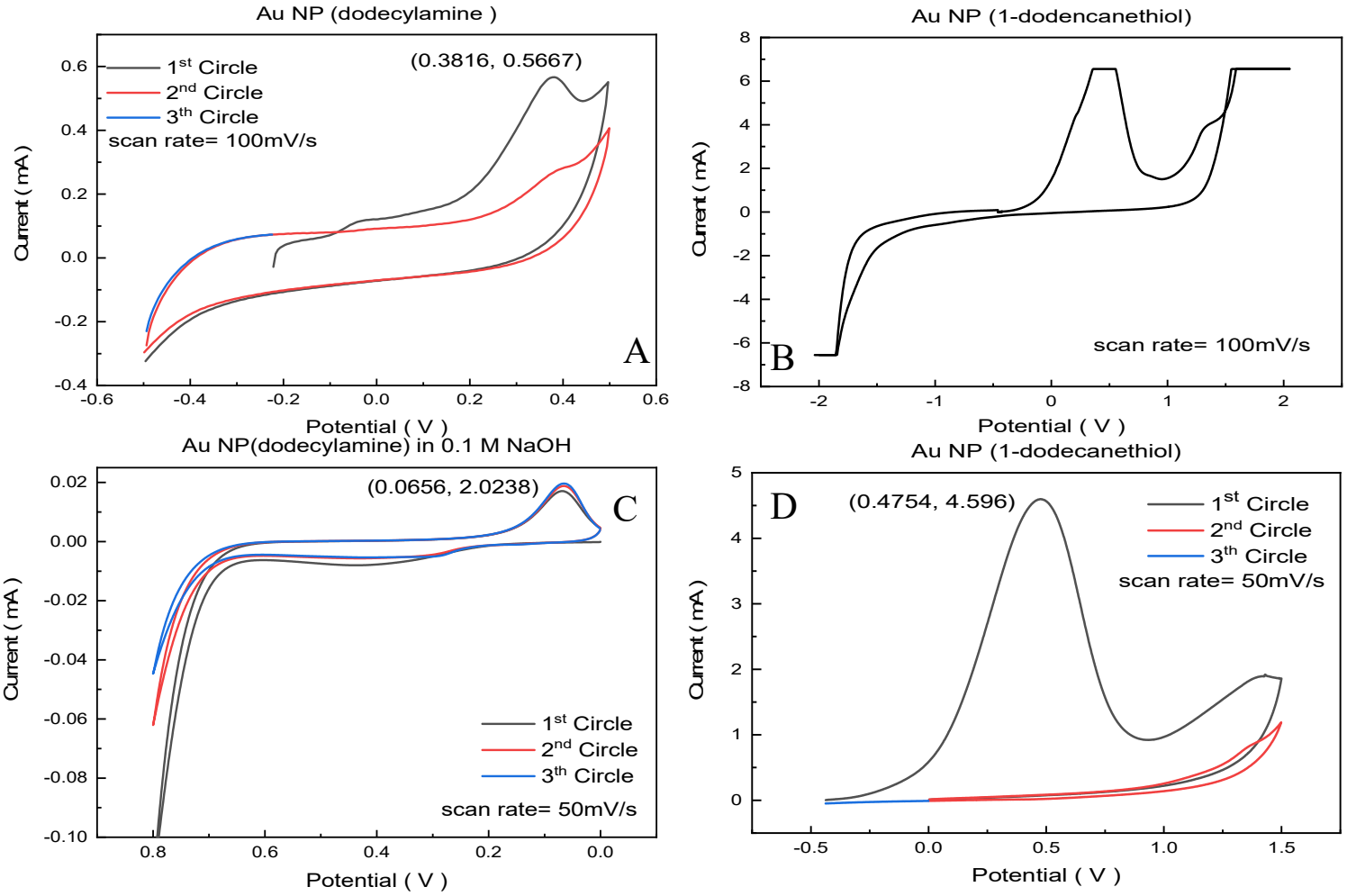
Electrolyte: 0.1 M NaOH and 0.1 M MeOH
Couter electrode: Pt
Working electrode: 40 μg Au layer on a 1cm*1cm carbon paper
Reference electrode: AgCl/Ag

$$CH_3OH \rightarrow (CH_3OH)_{ads}$$

$$(CH_3OH)_{ads} \rightarrow CO_{ads} + 4H^+ + 4e^-$$

$$CO_{ads} + H_2O \rightarrow CO_2$$

CV study of Au NPs with different ligands



CV study of Au NPs with different ligands

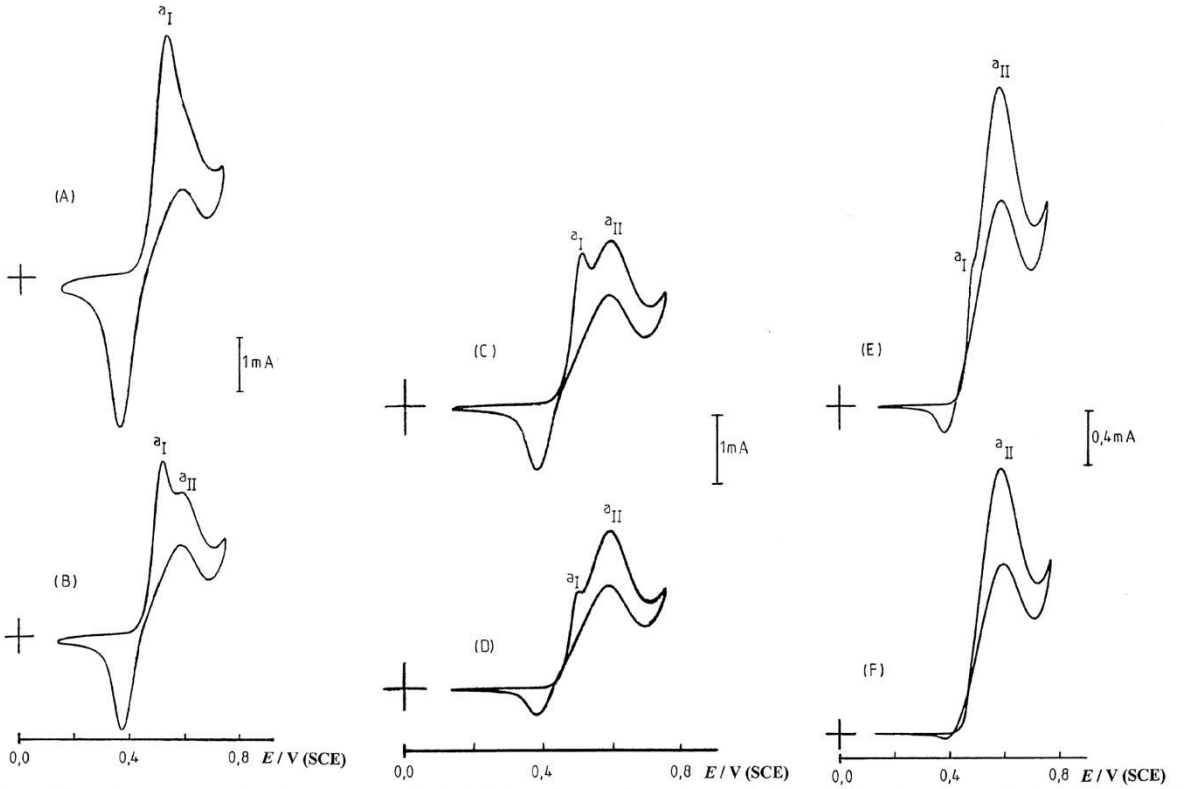
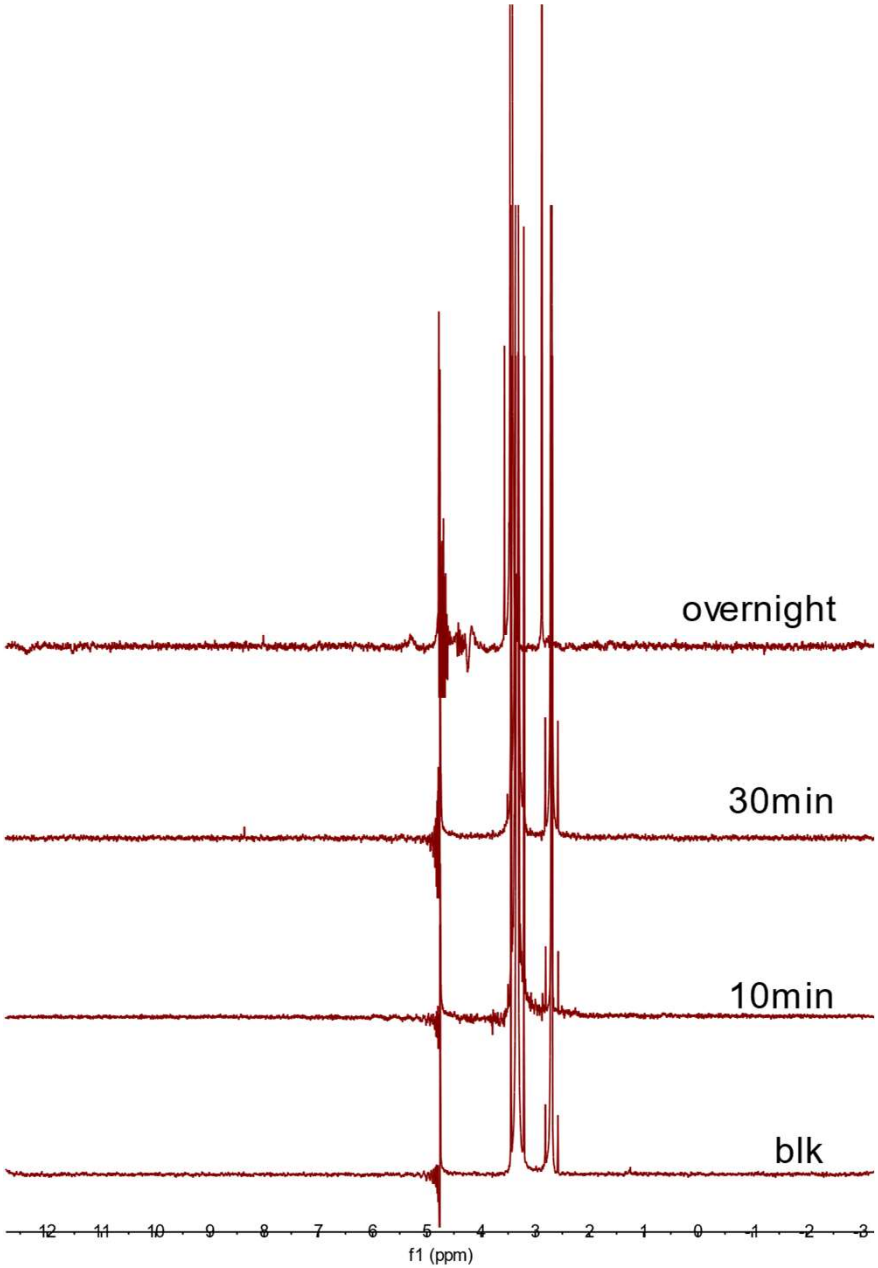
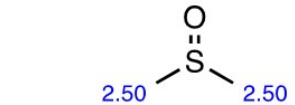


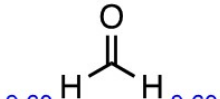
Fig. 5. Effect of scan rate on the voltammograms of MNGC electrode recorded in 0.1 M NaOH + 0.1 M methanol. (A) 200; (B) 100; (C) 50; (D) 20; (E) 10 and (F) 2 mV s^{-1}.

Elshafei A A . Journal of Electroanalytical Chemistry, 1999, 471(2):89-95.

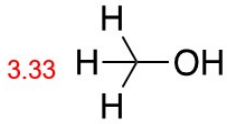




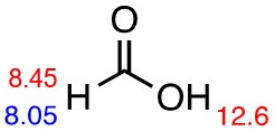
Dimethyl sulfoxide (DMSO)



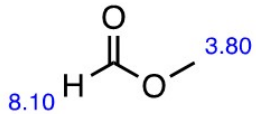
formaldehyde



methanol



formic acid



methyl formate

Summarization

1. What influenced the synthesis of gold NPs is various, including temperature, environment of the flask, the spin rate of the stir bar, etc. Little difference may cause totally new results.

2. Bigger size of nanoparticles usually means less active sites per nanoparticle, thus tof is lower and the catalytic activity is worse.

3. Different ligands change the surface property of the nanoparticles, thus it may influence the overpotential of the whole reaction, the stability. Only by experiments can we find the best one.

4. Many ligands didn’t got a good result due to different reasons. Given more time, we would like to find which condition is best for this nanoparticle, and then test CV of NPs with different ligands to get better catalyst.

Thanks

Group members: Jiangchao, Moe, Tianxiang

Thanks for the help of Sheena

09/08/2019