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Metal nano-particle synthesis By proton beam irradiation

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Contents

I. Introduction

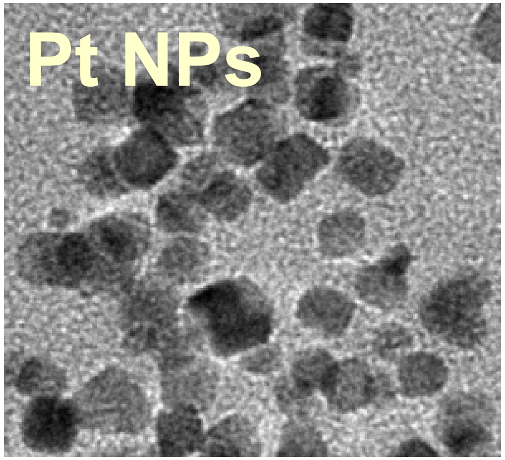
II. Experimental set up

III. Synthesis of metal NPs by proton beam irradiation

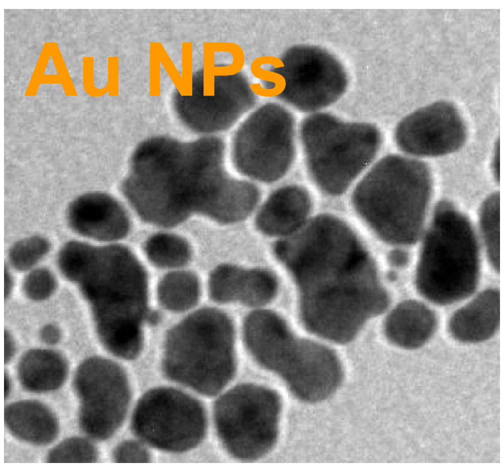
IV. Summary

1. **Introduction**
2. Experimental set up
3. Synthesis of metal NPs by proton beam irradiation
4. Summary

Applications of metal nanoparticles



★ Widely used as a catalyst in diverse application
- In catalytic converters, a device found in the exhaust system of most cars
- In fuel cell, used as a catalyst to combine hydrogen and oxygen to produce electricity and water



★ Au NPs represent excellent biocompatibility
- Drug delivery ; Polymeric NPs engineered to carry antitumor drug
- Luminescent biomarkers ; Semiconductor quantum dots with amine or carboxyl groups on the surface.
- MRI shielding ; Nano-magnetic/carbon composite materials to shield medical devices from RF fields.

Methods of nanoparticles synthesis

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- Physical & chemical
  - Electrochemical method (Mulvaney et al. 1993)
  - Sol-gel method (Catalando et al, 1997; Matsuoka et al, 1997)
  - Evaporation method (Lamber et al, 1995)
  - Microemulsion method, Reverse micelle method (Marignier et al, 1985; Petit et al, 1990)

- Radiation
  - E-beam (Belloni et al. 1998)
  - Gamma-ray
  - Proton beam (Song et al. 2005)

Mechanism of metal nanoparticles using irradiation

1. Formation of hydrated electron by irradiation.

$$H_2O \xrightarrow{\gamma\text{-irradiation}} e_{aq}^-,\ H_3O^+,\ H\cdot,\ H_2,\ OH\cdot,\ H_2O_2$$

$$(CH_3)_2CHOH + OH\bullet(H\bullet) \rightarrow (CH_3)_2C\bullet OH + H_2O(H_2)$$

2. Reduction of metal ion by hydrated electron

$$e_{aq}^- + M_1^+ \rightarrow M_1^0$$

$$e_{aq}^- + M_1^{n+} \rightarrow M_1^{(n-1)+}$$

$$(CH_3)_2C\bullet OH + M^{n+} \rightarrow (CH_3)_2CO + M^{(n-1)+} + H^+$$

$$nM_1^0 \rightarrow\rightarrow\rightarrow M_{agg}$$

In case of proton beam, + α ??

Weak point of chemical reduction method

★ Require complicated chemical processing

★ Generate unwanted toxic byproducts,
such as reagent and oxidant.

★ Require reducing agent.

★ Require delicate temperature control

Materials & Methods

★ Pt solution

- 0.5% H_2PtCl_6 in DW
- 6% Iso-propyl alcohol : Radical scavenger
- 1mM CTAB or 15mM SDS : Surfactant
- Proton beam irradiation condition

  Beam current ; 10nA to 2μA

★ Au

- 0.5mM to 2mM of H_2AuCl_4
- 0.5mM NaOH : Radical scavenger
- 0.25mM to 2mM CTAB : Surfactant
- Proton beam irradiation condition

  Beam current ; 10nA

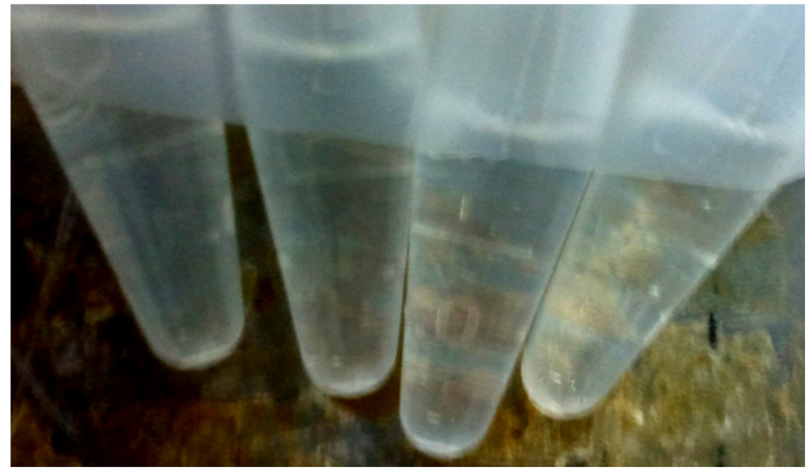
★ **Parameters**

- **Energy, LET, conc. of surfactant, conc. of metal ion, etc..**

Synthesized metal nanoparticles by proton beam irradiation

Platinum aqueous solution

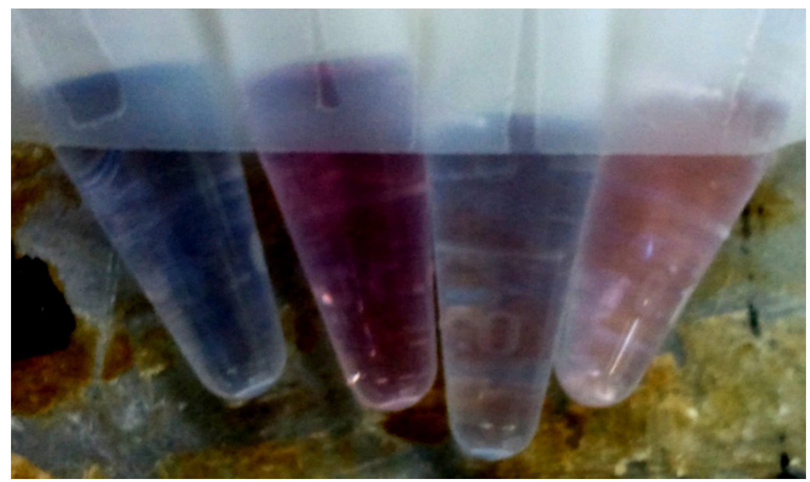
Gold aqueous solution



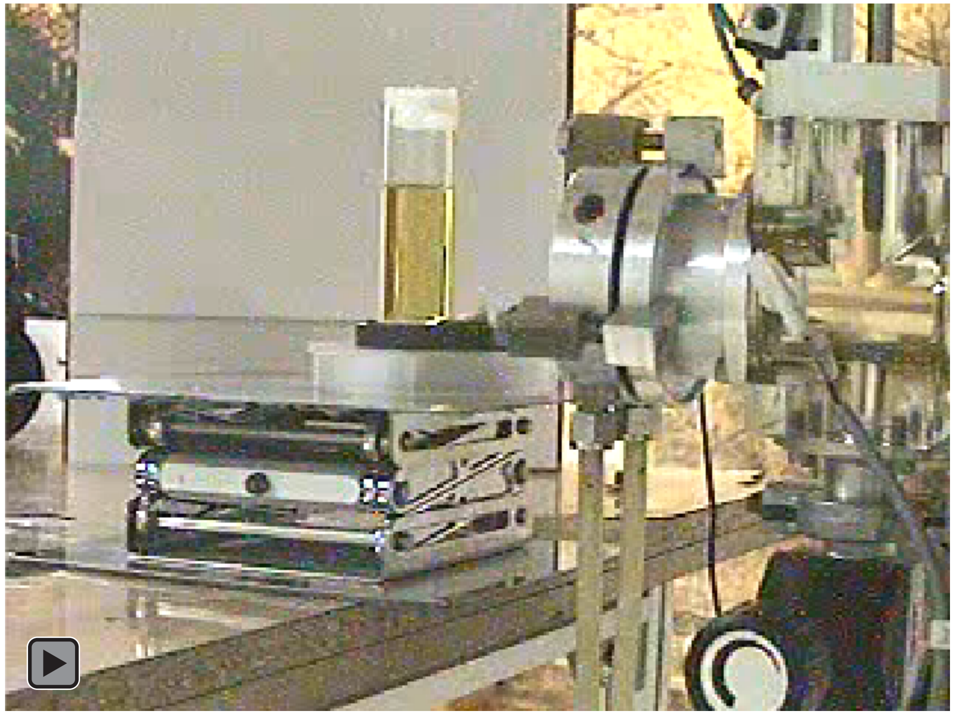
Before

Proton beam irradiation

After

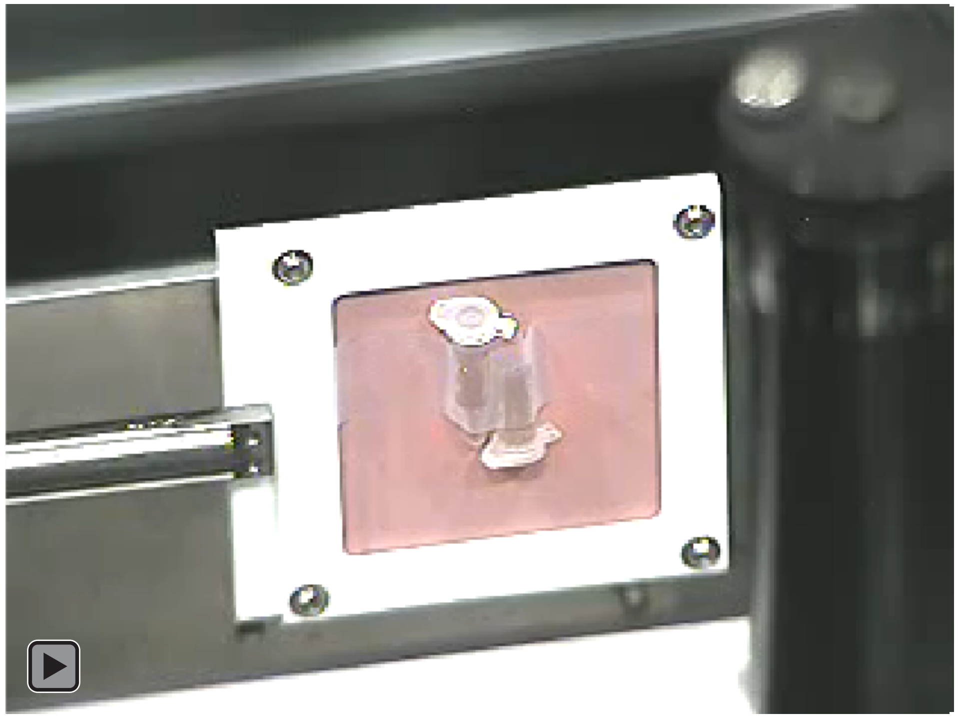


Platinum



45 MeV CW beam
Beam current : 1μA

Gold



20MeV pulsed beam
Peak current : 1mA
Repetition rate : 1Hz

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Pt NPs - Effect of LET and energy gap (△E)

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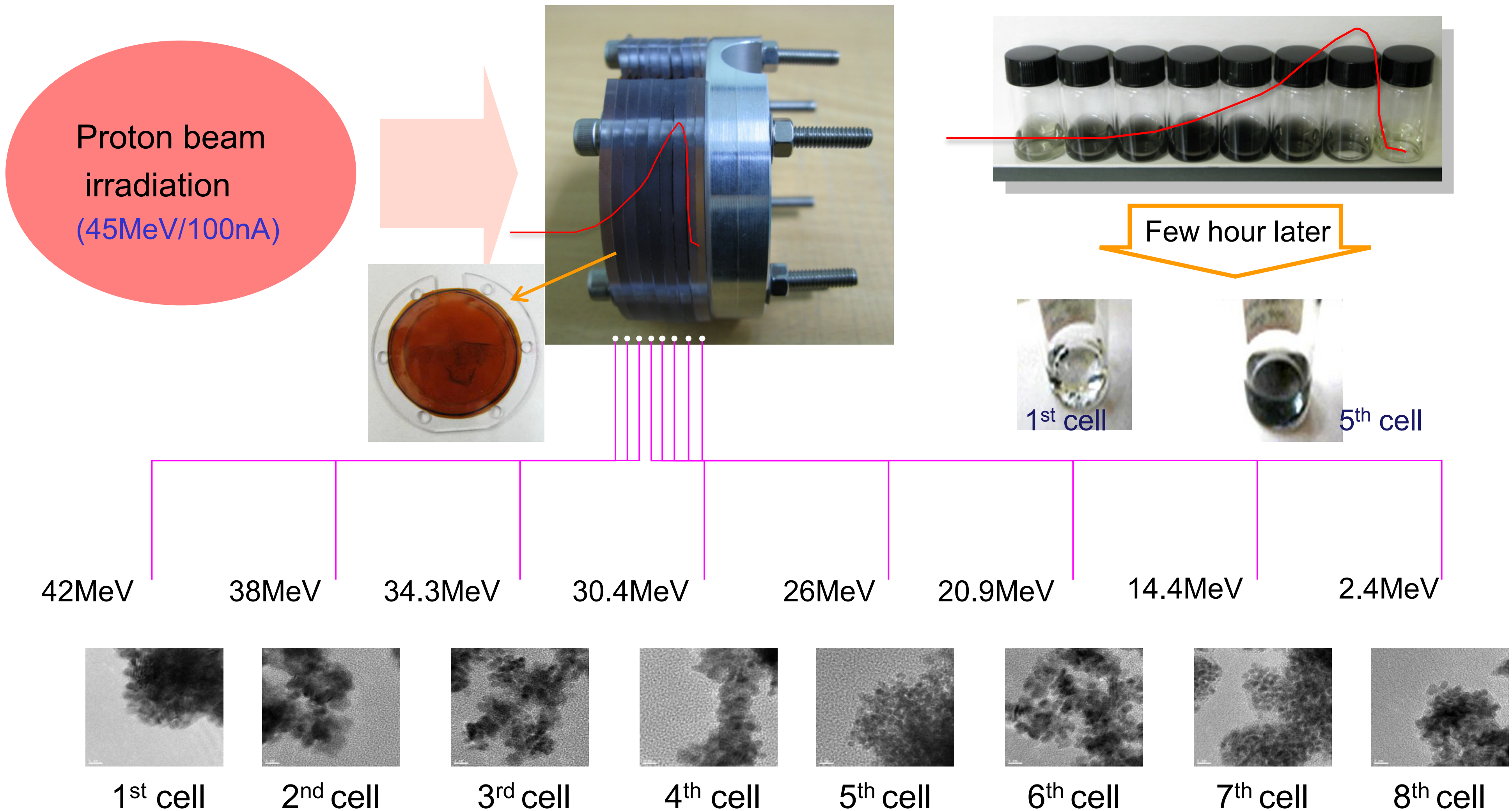

TEM images and photograph of Pt nanoparticles synthesized by proton beam irradiation – *45MeV/100nA – (H_2PtCl_6 ; 0.5%), 60sec* with using Slice Sample stack

Pt NPs - Effect of LET and energy gap (△E)

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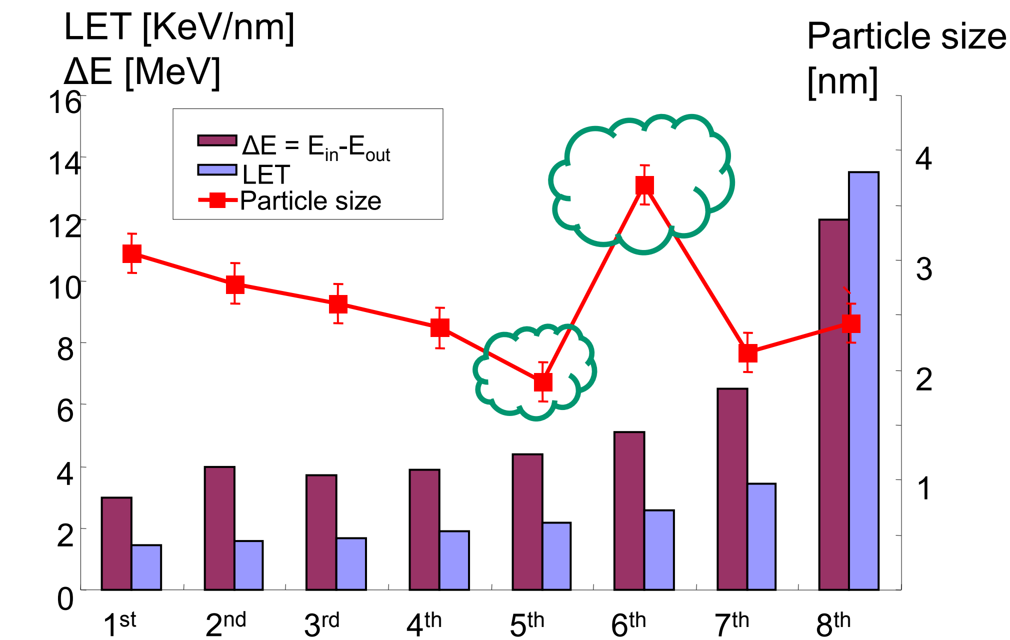
Experimental condition

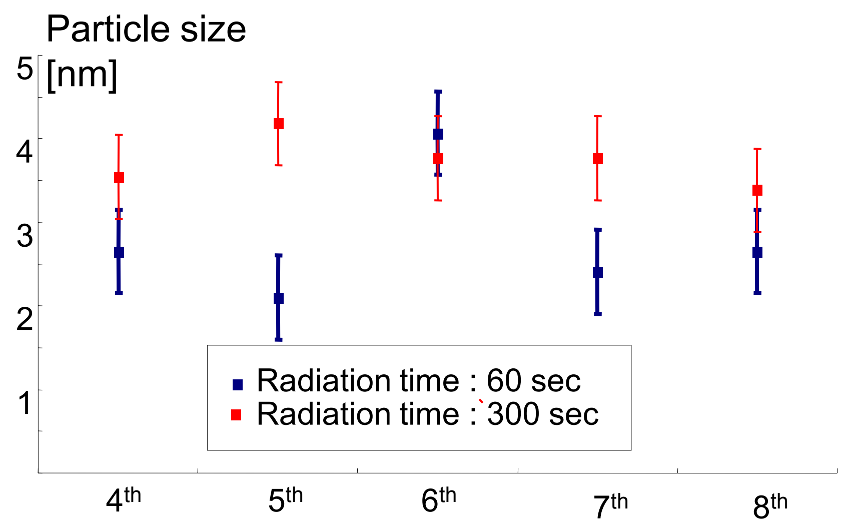
- *45MeV/100nA - (H_2PtCl_6 ; 0.5%), 60sec*



cell	1st	2nd	3rd	4th	5th	6th	7th	8th
Energy (MeV)	42	38	34.3	30.4	26	20.9	14.4	2.4
size(㎚)	3.4	3.1	2.9	2.65	**2.1**	**4.1**	2.4	2.7

Experimental condition

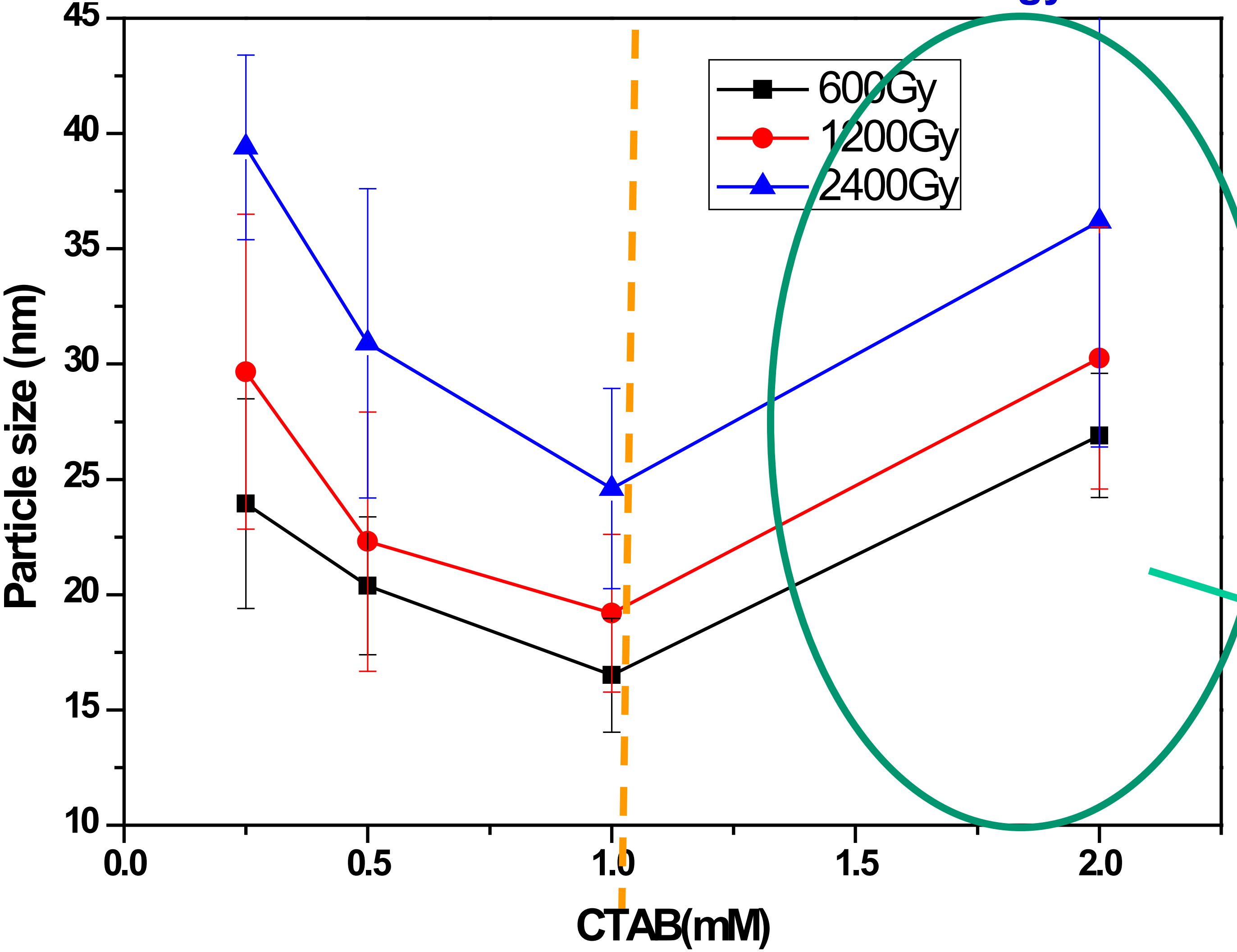
- *45MeV/100nA - (H_2PtCl_6 ; 0.5%), 60sec*
- *45MeV/100nA - (H_2PtCl_6 ; 0.5%), 300sec*



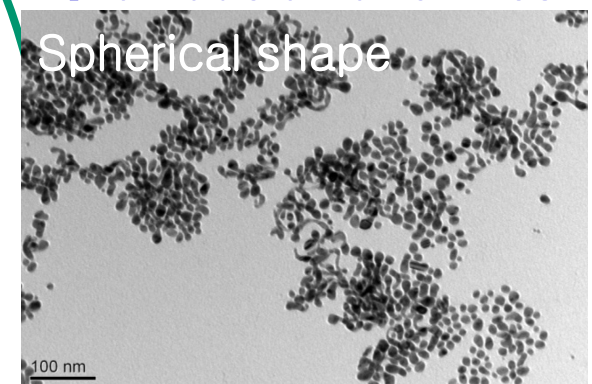
Au NPs – Total dose & Conc. of surfactant

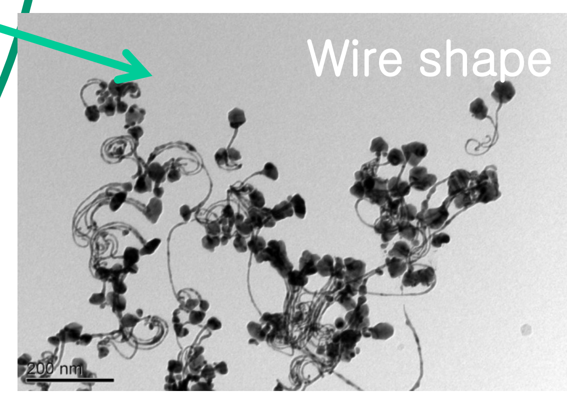
Experimental conditions

- Beam current : 10nA
- $HAuCl_4$ conc. : 0.5mM
- CTAB conc. : 0.25 to 2mM
- Dose : 0.6 to 2.4 Kgy
- Dose rate : 0.7Gy/s



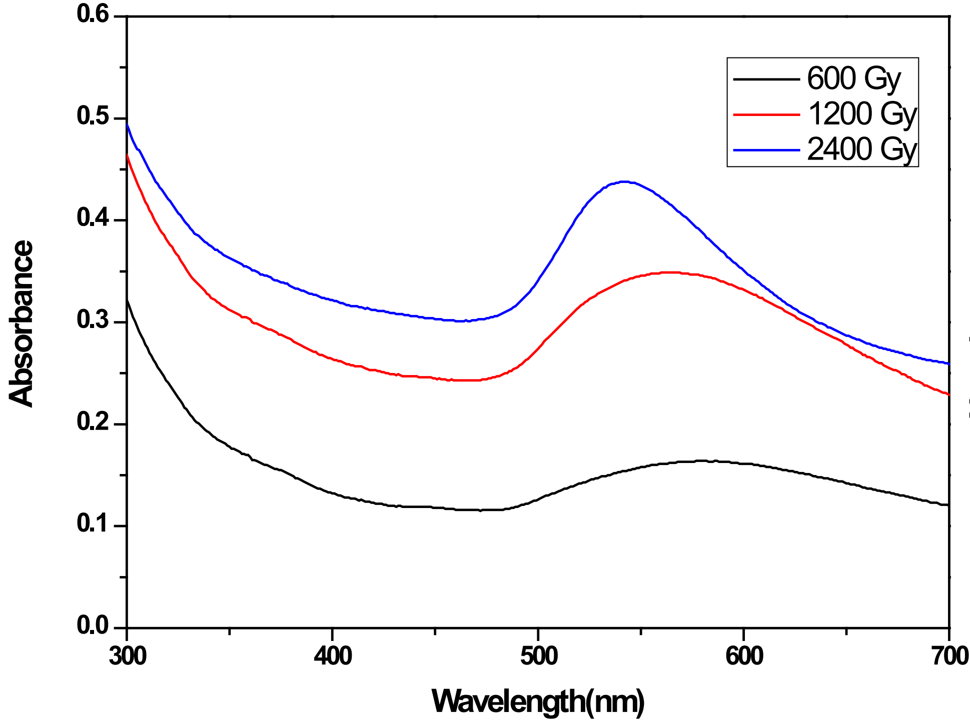
Below of 1mM CTAB conc.
→NPs size is decreased
2mM CTAB conc.
→It made a nanowires



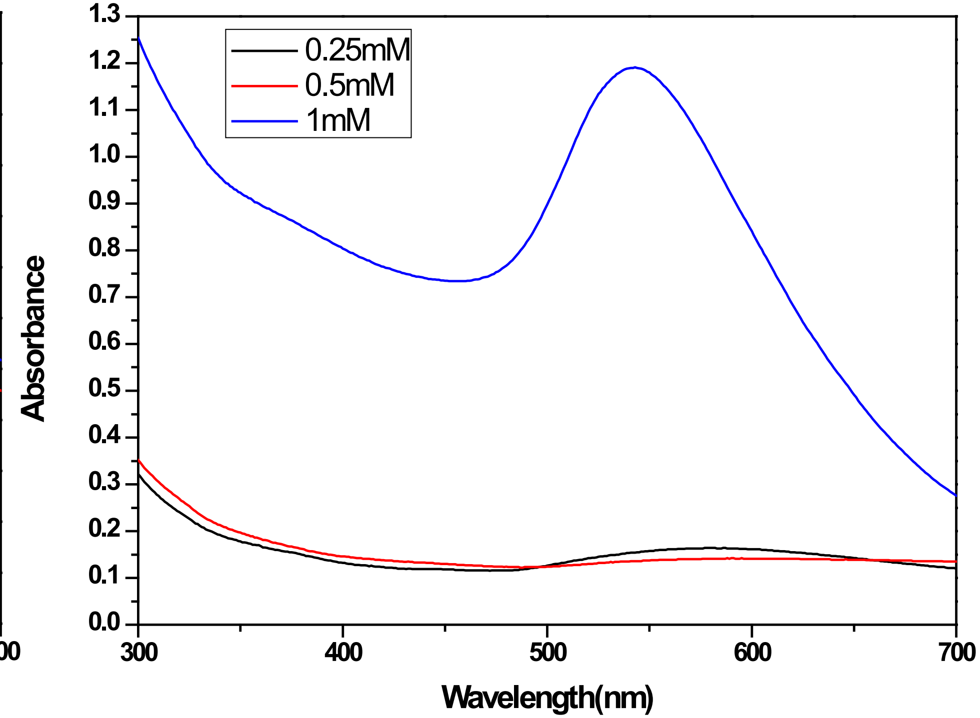


Au NPs – Total dose & Conc. of surfactant

CTAB : 0.25mM

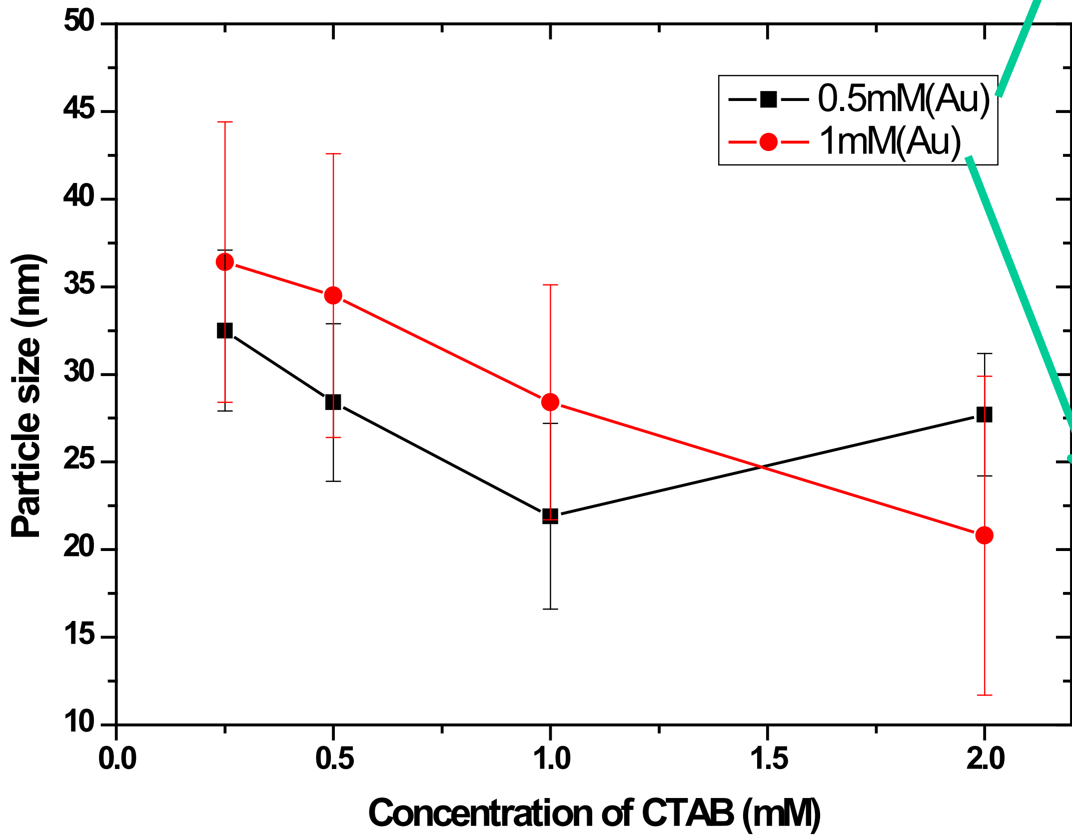


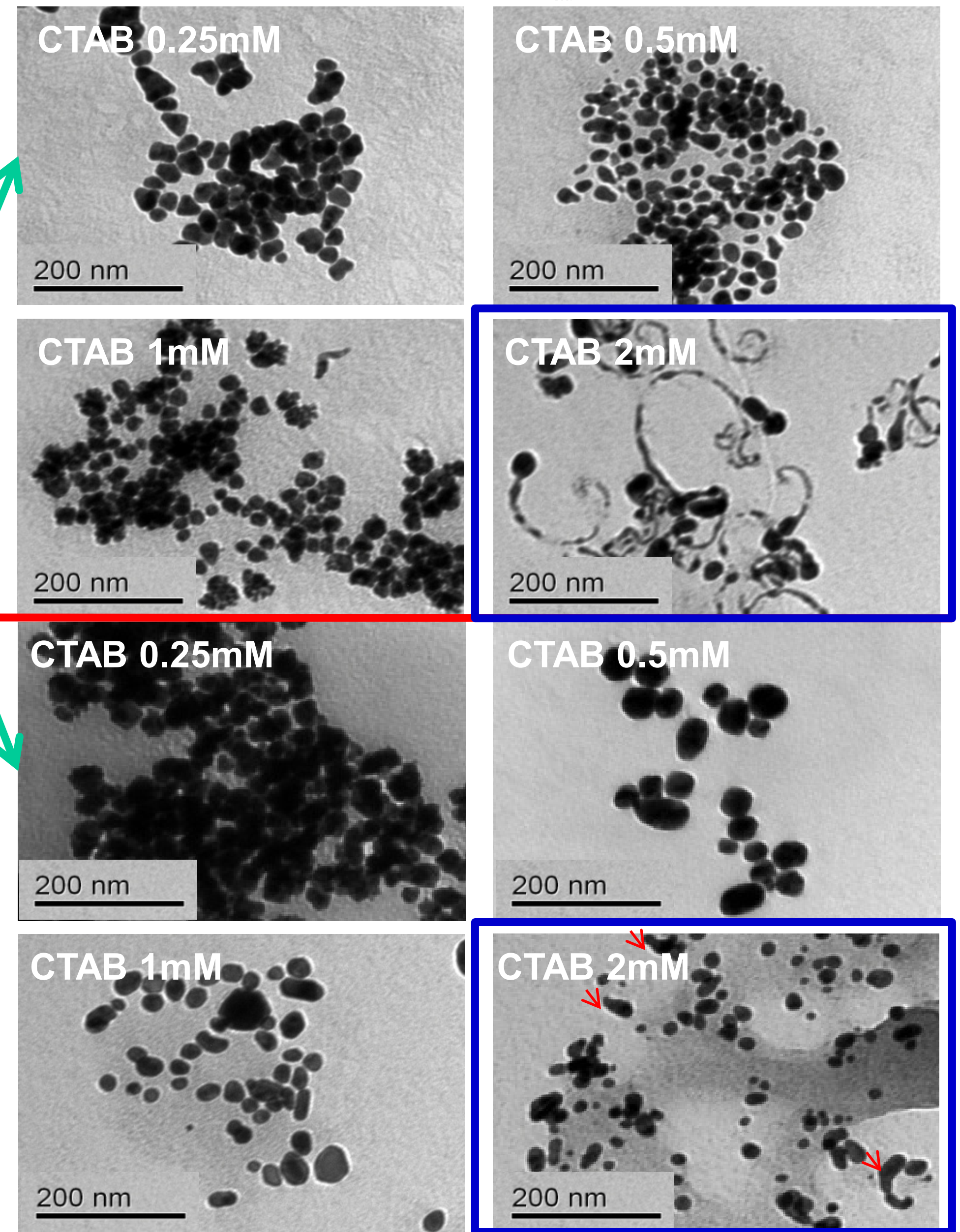
Total dose : 600Gy



Au NPs – Effect of metal ion & surfactant conc.

Experimental condition
- Beam current : 10nA
- $HAuCl_4$ conc. : 0.5mM or 1mM
- CTAB conc. : 0.25 to 2mM

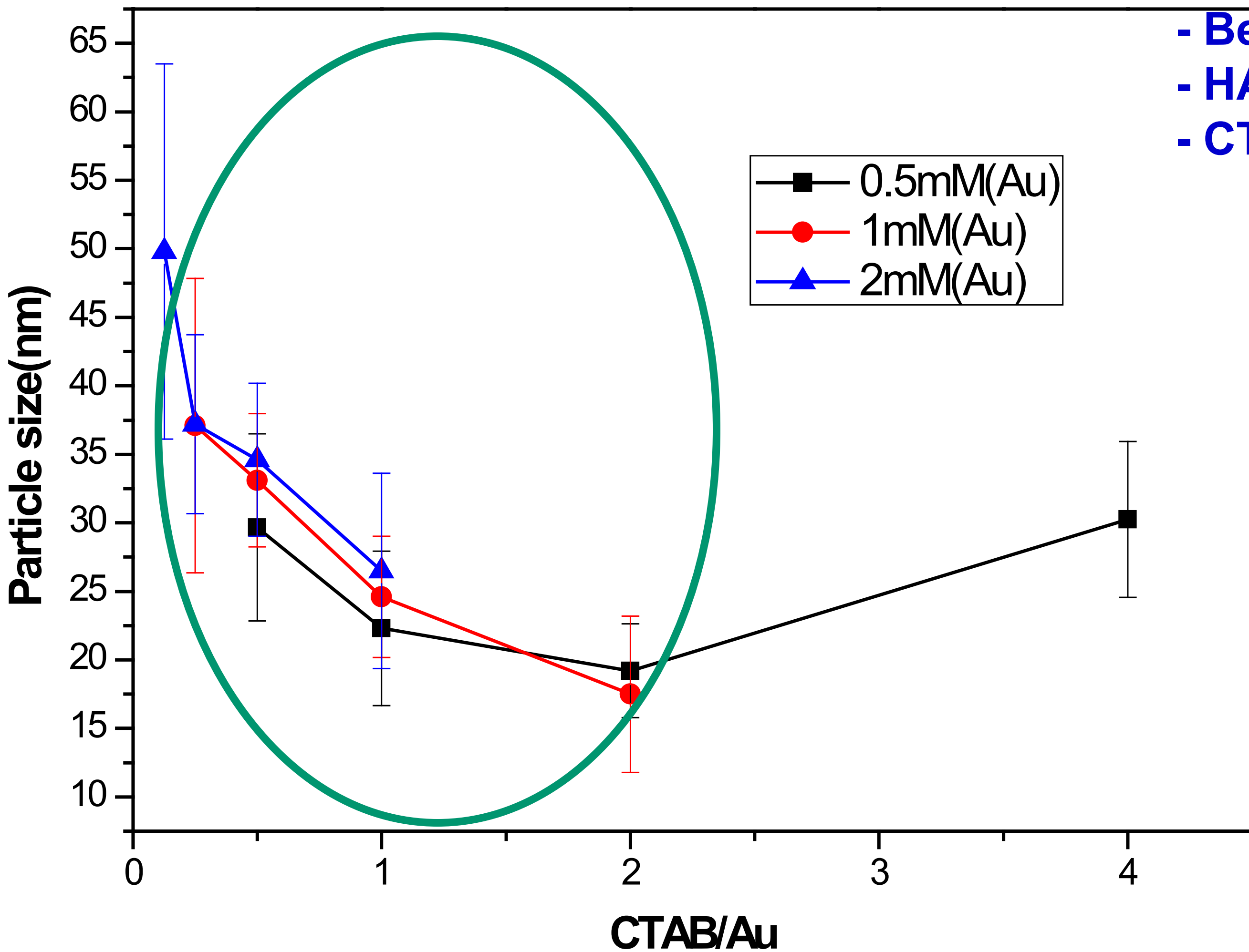




Au NPs – Ratio of CTAB & Au ion

Experimental condition

- **Beam current : 10nA**
- **$HAuCl_4$ conc. : 0.5mM or 1mM**
- **CTAB conc. : 0.25 to 2mM**

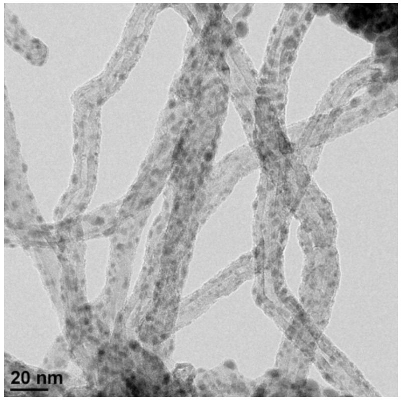


CTAB : Gold ion = 1:1
→Particle size is similar

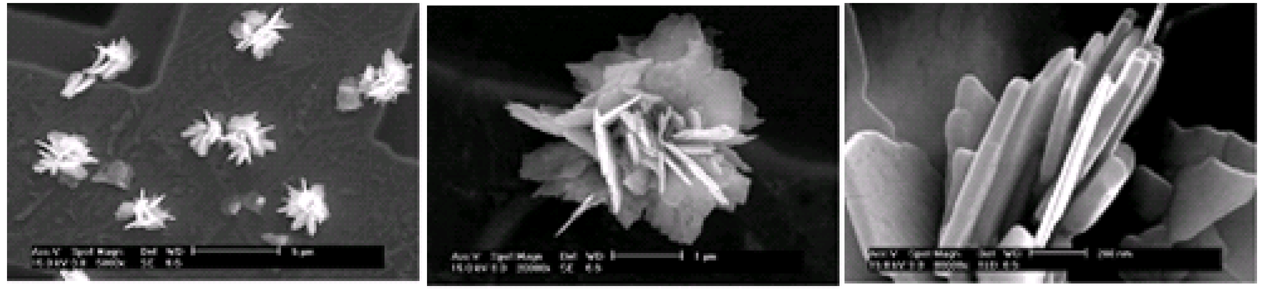
CTAB > Gold ion
→Particle size is decreased

CTAB<Goid ion
→ Particle size is increaed

Others

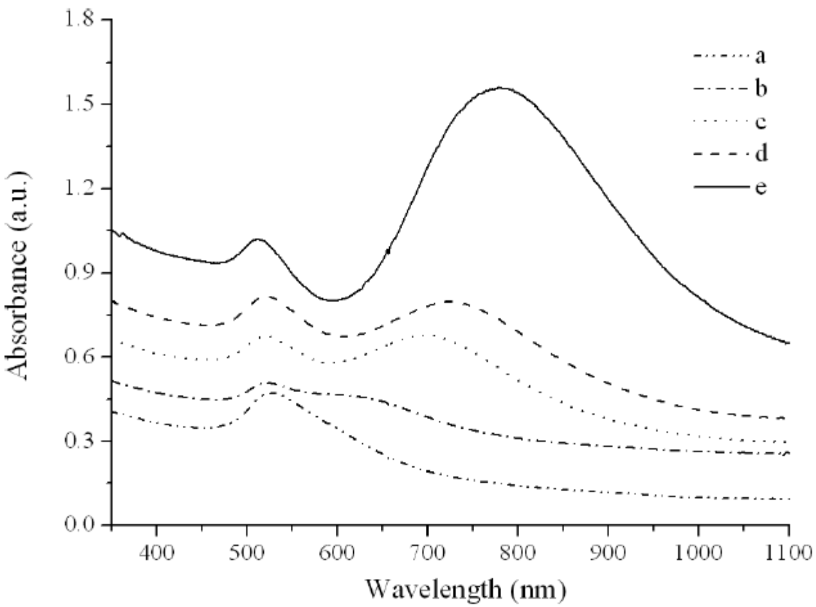


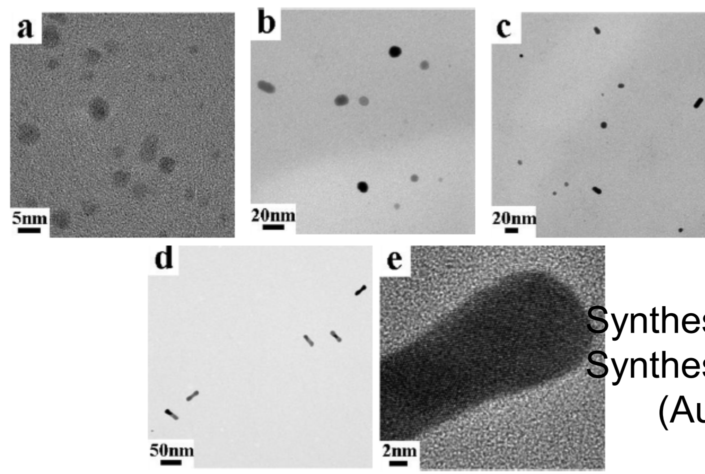
Ag-CNT nano complex



Flower-shape Ag nanomaterials
- Pulse beam irradiation.

J.H. Song, J. Kor. Phys. Soc. 56 (2010) 2072-6





Synthesis of Au nanorod
Synthesis Au-Ag alloy
(Au:Ag=9:1)

(a) 0 μl (b) 25 μl (c) 35μl
(d) 75 μl (e) 100 μl of 0.001M $AgNO_3$
2.73Gy/sec, 120min

Summary

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- ❖ Nanoparticle synthesis by proton beam irradiation is environmentally friendly because proton beam irradiation method not use a toxic reducing agent.
- ❖ We studied metallic nanoparticles synthesized by proton beam irraidaiton
- ❖ Investigated shape and size nano particles with different conditions; beam energy, total dose, dose rate, surfactant concentration and ratio of metallic ion and surfactant.
- ❖ We can be controlled shapes and size of nanoparticles.

- ❖ Future study
  - As the adjust the precisely experimental conditions, we will to narrow down the error.

Thank you for your attention