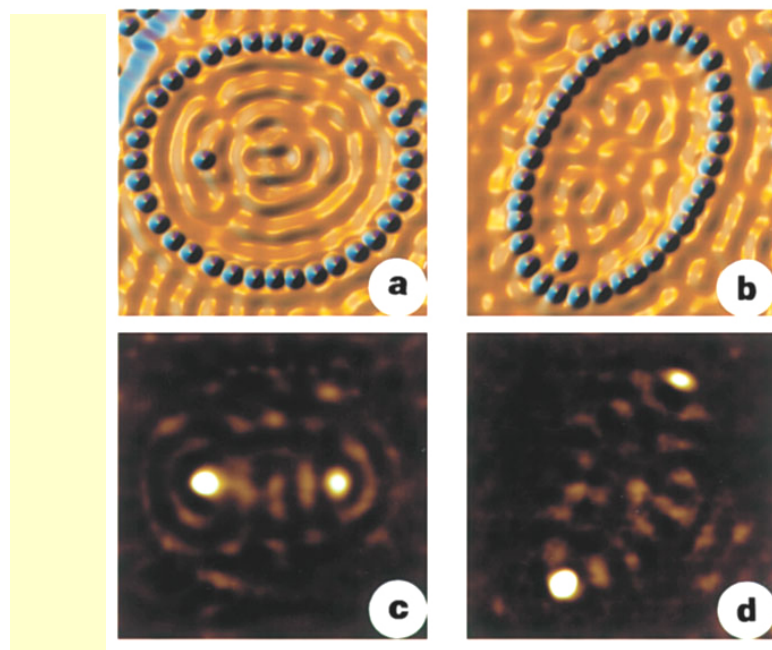


# 奈米粒子之合成、特性與應用



劉如熹  
台灣大學化學系

[rsliu@ntu.edu.tw](mailto:rsliu@ntu.edu.tw)

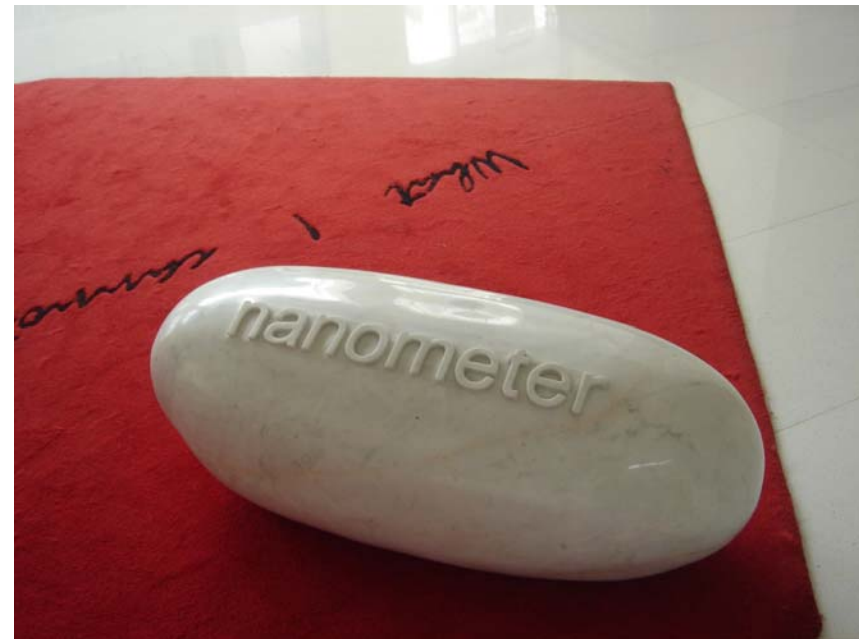






# Nanometer

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## 奈(納)米(nanometer)

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奈(納)米(nanometer)為一個長度單位，簡寫為 nm

$$1\text{nm} = 10^{-3} \mu\text{m} = 10^{-6}\text{mm} = 10^{-9}\text{m} \circ$$

(奈米為一米的十億分之一)

在原子物理中仍常使用埃作單位 ( $\text{\AA}$ )， $1\text{\AA} = 10^{-10}\text{m}$   
所以  $1\text{nm} = 10\text{\AA}$ 。

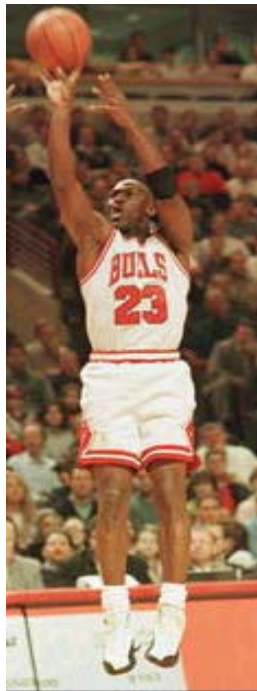
氫原子之直徑為  $1\text{\AA}$ ，所以  $1\text{nm}$  等於 10 個氫原子一個挨一個排起來的長度。



# Nanoworld

1 奈米 (nanometer) = 十億分之1 米 ( $10^{-9}$  m)

人高



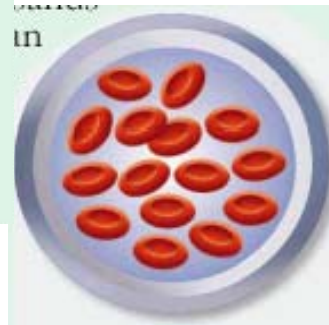
20億 奈米

針頭



100萬 奈米

紅血球



1千 奈米

分子及DNA



1 奈米

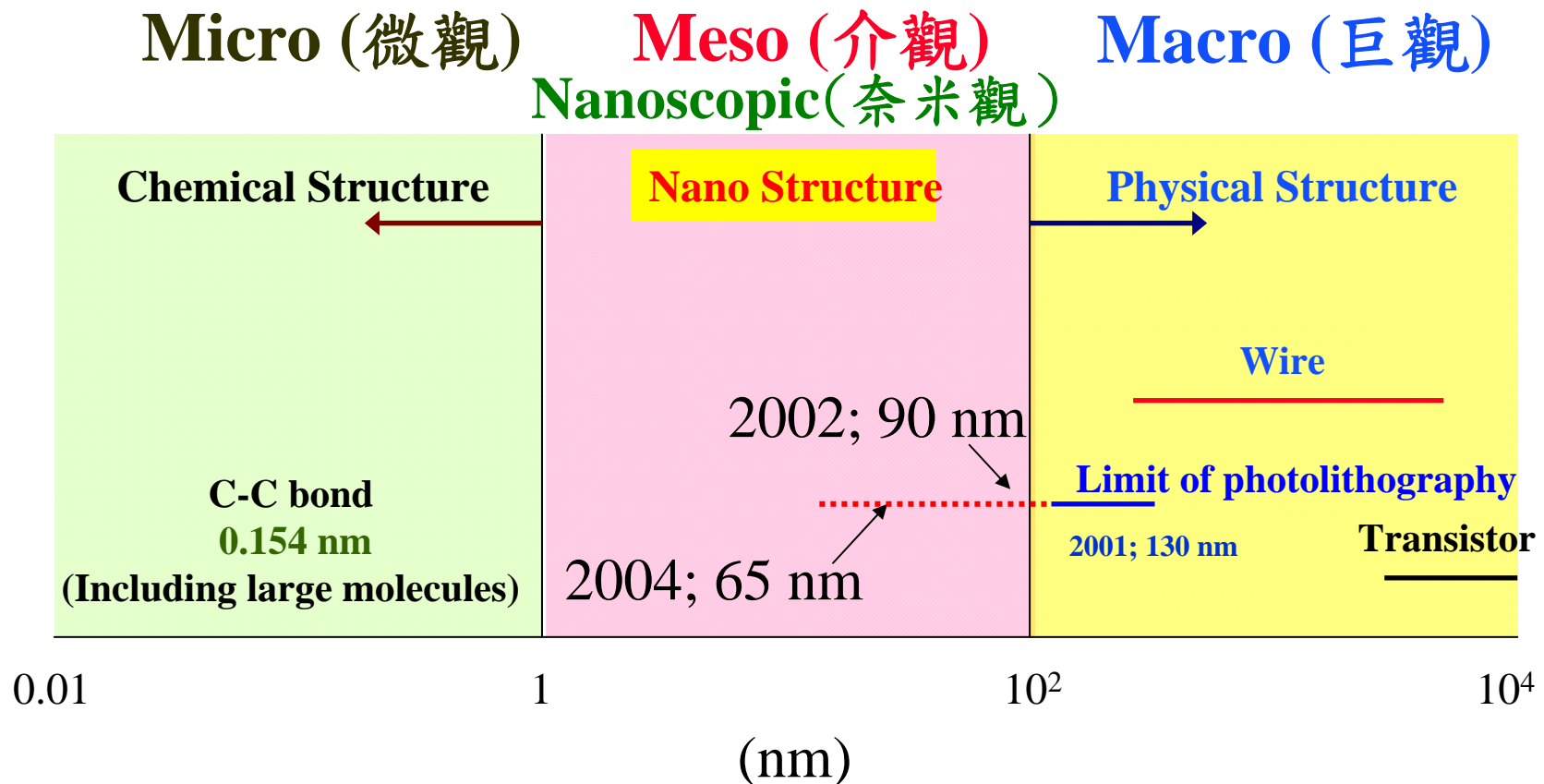
氫原子



0.1 奈米



## Definition





奈米

<http://www.google.com>

Keywords:

納米: 91,900 項

奈米: 15,600 項

(10/18/2001)

[http://home.kimo.com.tw/nano\\_china/01.htm](http://home.kimo.com.tw/nano_china/01.htm)

(納米資訊網)

納米



## 佛經

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《維摩詰經》裡有「芥子納須彌」文。

納須彌於芥子意近一粒沙一世界。「芥子」、「須彌」是佛教裡常見的名詞。

「芥子」是芥菜的種子，體積很小；「須彌」指須彌山，也叫妙高山；

古代印度的宇宙觀，須彌山是世界的中心，也是最高的一座山。

這兩個名相，通常被用來譬喻極小和極大。

以須彌山之高大、廣寬能納入微小的芥子，而無所增減；

「芥子納須彌」，芥子如是細小，空間有限，竟能容納無限大的須彌山，而不會產生擠壓及變形。須彌體積這麼大，與它相對應的芥子，則是極微細的種子，

一般人的觀念是「大的可以納小」，「小的不可以納大」。

以佛學的般若智慧來觀察諸法平等，否定了空間體積。

這種「大小無礙」的論點，用於華嚴經中來顯示華嚴境界，

這個不可思議的法界，意在說明法界的體性廣大，無所不包而大小無礙，

所以有云：「心容妙理虛空小，道契真如法界寬」。





分 厘 毛 絲 忽 微 纖 沙 塵 埃 渺 漠 模糊 逡巡

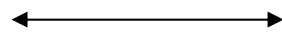
$10^{-1}$   $10^{-2}$   $10^{-3}$   $10^{-4}$   $10^{-5}$   $10^{-6}$   $10^{-7}$   $10^{-8}$   $10^{-9}$   $10^{-10}$   $10^{-11}$   $10^{-12}$   $10^{-13}$   $10^{-14}$

m

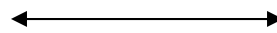
$\mu$

n

(納, 奈)



Macroscopic



Nanoscopic

須臾 瞬息 彈指 刹那 六德 虛空 清淨

$10^{-15}$

$10^{-16}$

$10^{-17}$

$10^{-18}$

$10^{-19}$

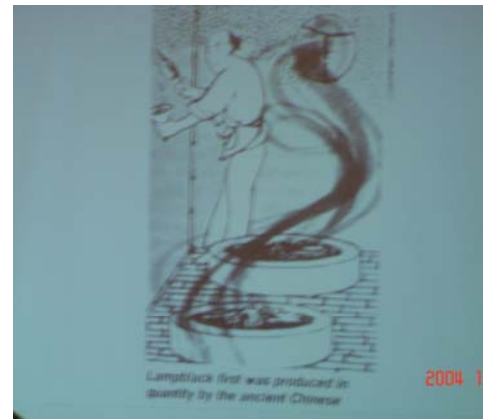
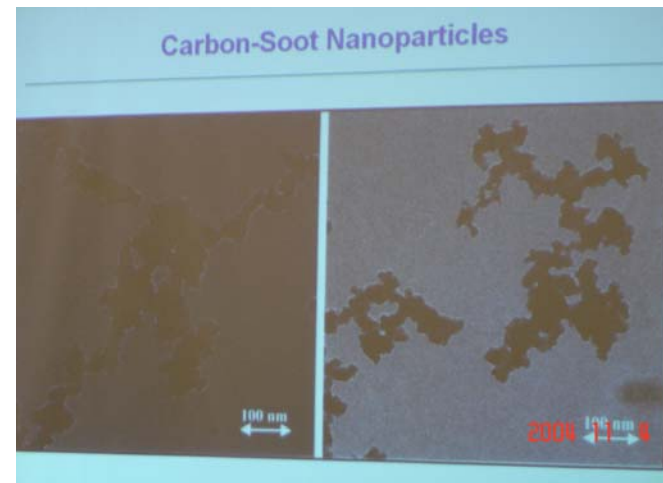
$10^{-20}$

$10^{-21}$

「算法統宗」(1592年刊)



## 老祖宗的奈米材料





## The Lycurgus Cup (賴庫爾 戈斯杯)



第四世紀羅馬產物，斯巴達國王被所安普洛西亞所變成的藤曼纏繞，拉往冥府。

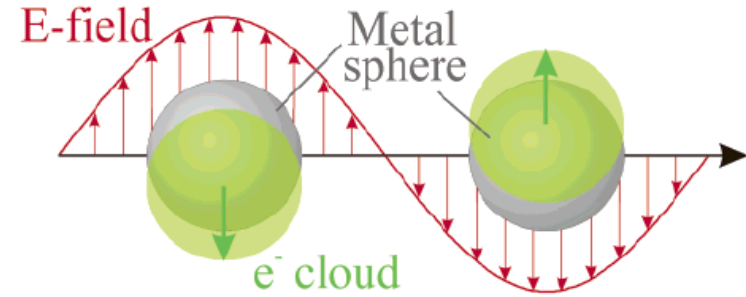
白天在光線照射下，酒杯的顏色是綠色。

晚上若燈光由酒杯內透射過來，則呈洋紅色。

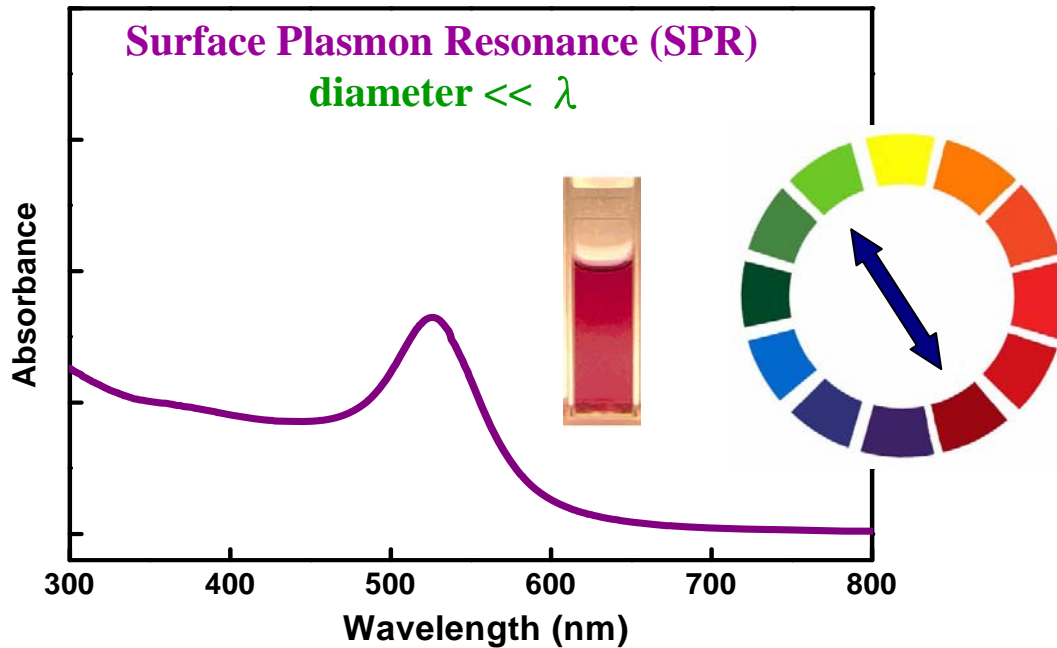
化學成分與現代玻璃相近。但含少量70奈米之金屬金(40 ppm)與銀粒子(300 ppm)，其於白天對綠光有很強的散射(即白光照射，酒杯只反射綠光)。而燈光由酒杯之透射光，只有紅光和藍光能穿透出來，混合後形成洋紅色光。

<http://www.thebritishmuseum.ac.uk/science/lycurguscup/sr-lycugus-p1.html>

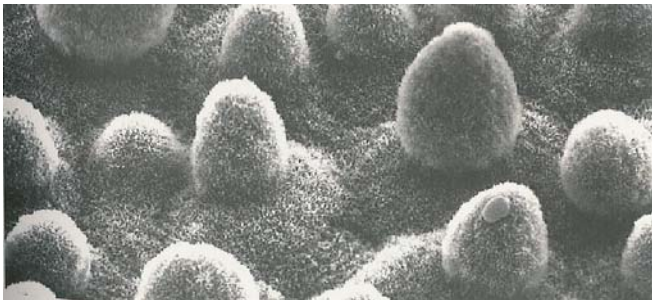
# Color of Nano Gold



Lycurgus Cup



## Lotus Effect

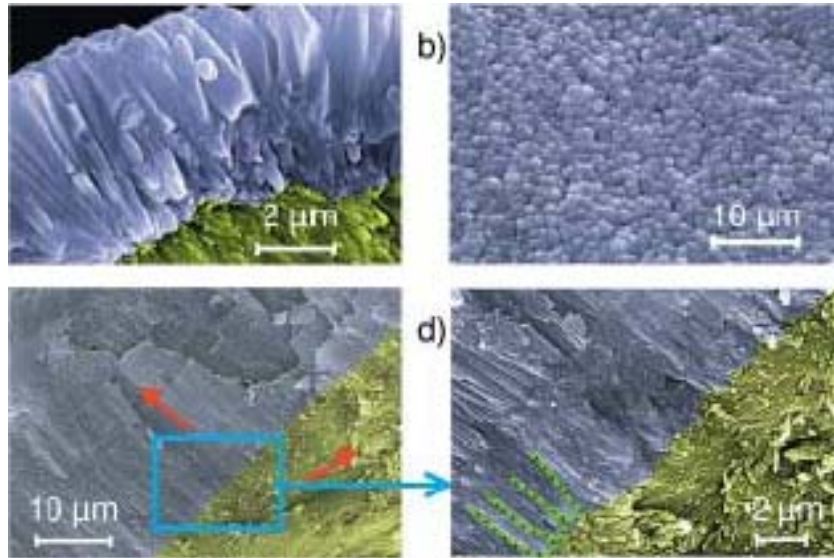


我們常吃的藕，生長於池塘的淤泥中，但它露在水面上亭亭玉立的蓮花荷葉卻出污泥而不染，美麗聖潔。荷葉的基本化學成分是葉綠素、纖維素、澱粉等多糖類的碳水化合物，有豐富的羥基（-OH）、（-NH）等極性基團，在自然環境中很容易吸附水分或污漬。而荷葉葉面都具有極強的疏水性，灑在葉面上的水會自動聚集成水珠，水珠的滾動把落在葉面上的塵土污泥粘吸滾出葉面，使葉面始終保持乾淨，這就是著名的“荷葉自潔效應”。為什麼會有這種“荷葉效應”，以傳統的化學分子極性理論來解釋，不僅解釋不通，恰恰是相反。從機械學的光潔度（粗糙度）角度來解釋也不行，因為它的表面光潔度根本達不到機械學意義上的光潔度（粗糙度），用手觸摸就可以感到它的粗糙程度。經過兩位德國科學家的長期觀察研究，即上世紀九十年代初終於揭開了荷葉葉面的奧妙。原來在荷葉葉面上存在著非常複雜的多重奈米和微米級的超微結構。在超高解析度顯微鏡下可以清晰看到，在荷葉葉面上佈滿著一個挨一個隆起的“小山包”，它上面長滿絨毛，在“山包”頂又長出一個饅頭狀的“碉堡”凸頂。因此，在“山包”間的凹陷部份充滿著空氣，這樣就在緊貼葉面上形成一層極薄，只有奈米級厚的空氣層。這就使得在尺寸上遠大於這種結構的灰塵、雨水等降落在葉面上後，隔著一層極薄的空氣，只能同葉面上“山包”的凸頂形成幾個點接觸。雨點在自身的表面張力作用下形成球狀，水球在滾動中吸附灰塵，並滾出葉面，這就是“荷葉效應”能自潔葉面的奧妙所在。

研究表明，這種具有自潔效應的表面超微納米結構形貌，不僅存在於荷葉中，也普遍存在於其他植物中。某些動物的皮毛中也存在這種結構。

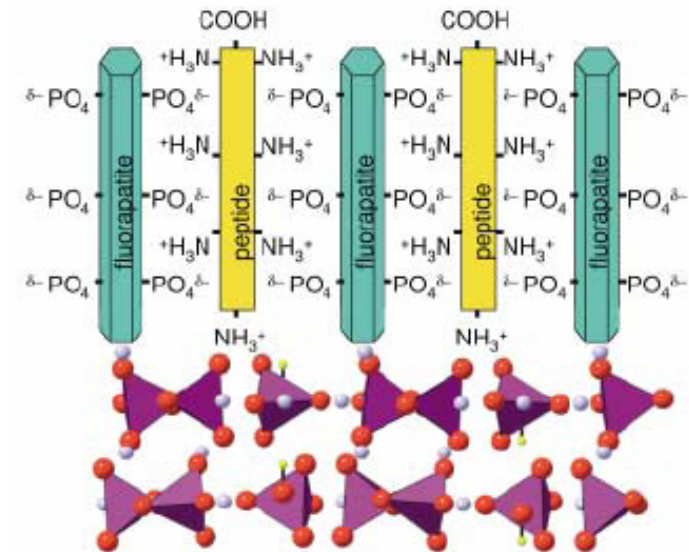
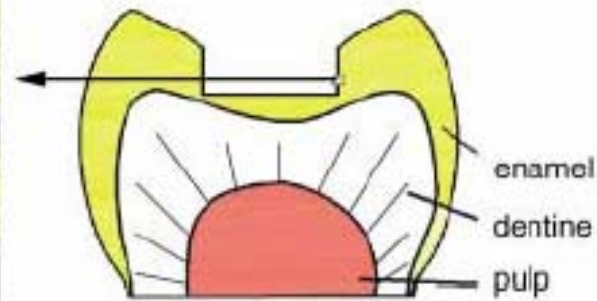
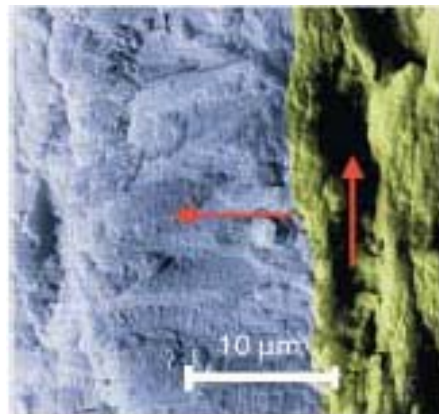
Ref: <http://www.casnano.ac.cn/gb/kepu/cailiao/cl025.html>

## Application – regeneration of human tooth enamel



growth rate : 500nm / day

The formed fluorapatite shows the Knoop hardness ( $400 \pm 100$ ) similar to enamel hardness.



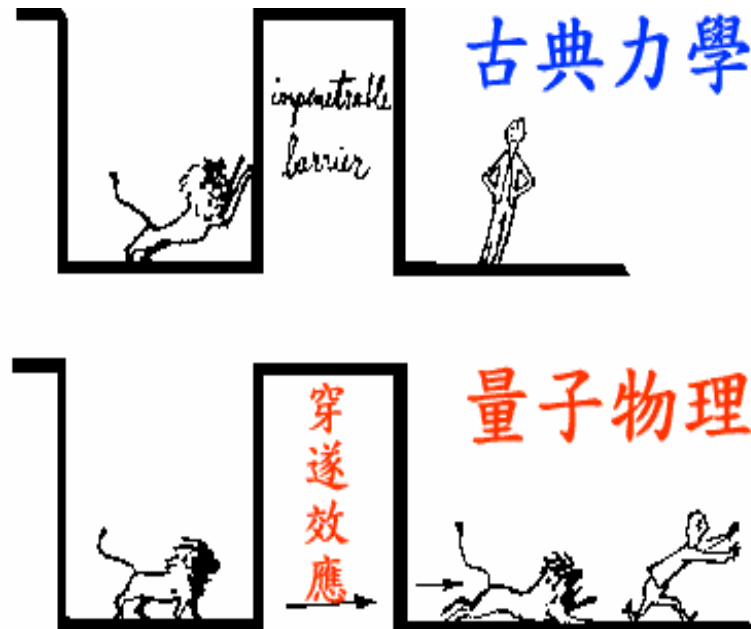


## 奈米科技的誕生

以掃描隧道電子顯微鏡和原子力顯微鏡的發明為先導的。1981年美國IBM公司在瑞士的蘇黎世實驗室的教授G.Binnig和H.Rohrer博士發明了掃描穿隧電子顯微鏡,(Scanning Tunneling Microscopy),簡稱為STM。其可直接觀察到原子。它的橫向解析度達0.1nm,縱向解析度達0.01nm。兩位博士因發明STM而於1986年獲得諾貝爾物理獎。由於STM及原子力顯微鏡的發明,不僅可以直接觀察原子、分子,而且能夠利用STM直接操縱和安排原子和分子,這就實現了人們由來已久的兩個幻想,一是直接看到原子,二是按人們的意願去安排原子、分子、這在人類科學史上是一個巨大的進步。



## 量子穿隧效應

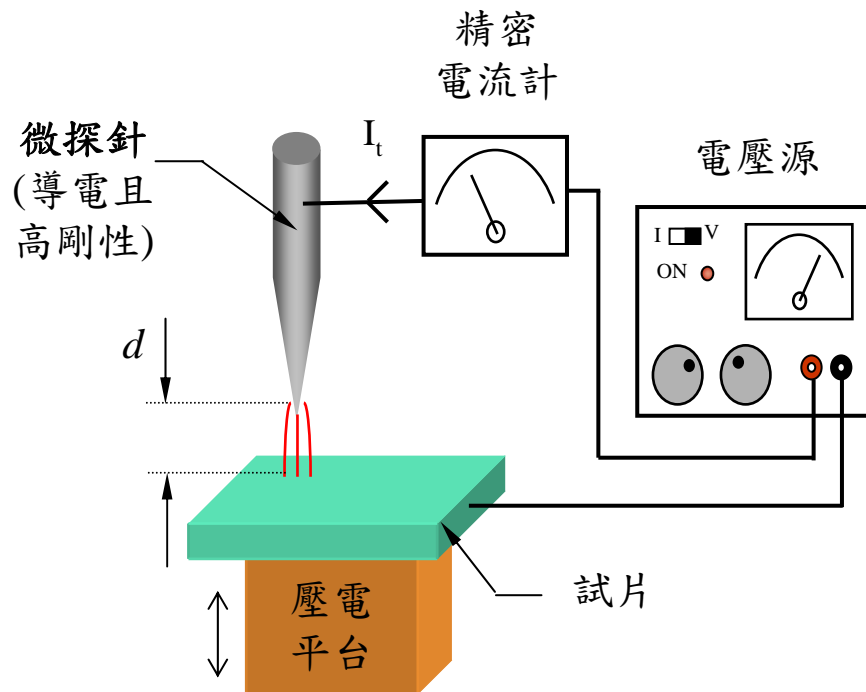


The difference between classical theory and quantum theory, illustrating tunneling through potential barrier. This illustration was used by Van Vleck in his last publication, the Julian E. Mack Lecture at his Alma Mater, the University of Wisconsin, in 1979. (After B. Bleaney, *Contemp. Phys.* 25 (1984) 320.)



# Scanning Tunneling Microscopy

## 穿隧電流感測器示意圖



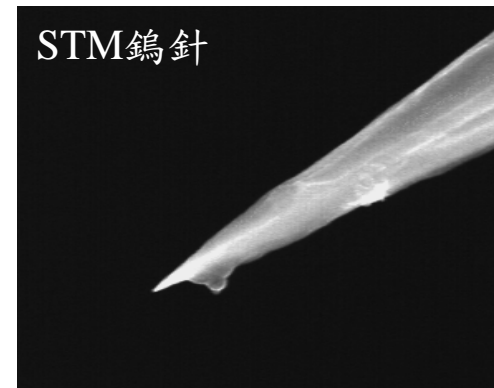
$$I_t \cong V e^{-Cd}$$

$I_t$ ：穿隧電流(量測時保持為定值)

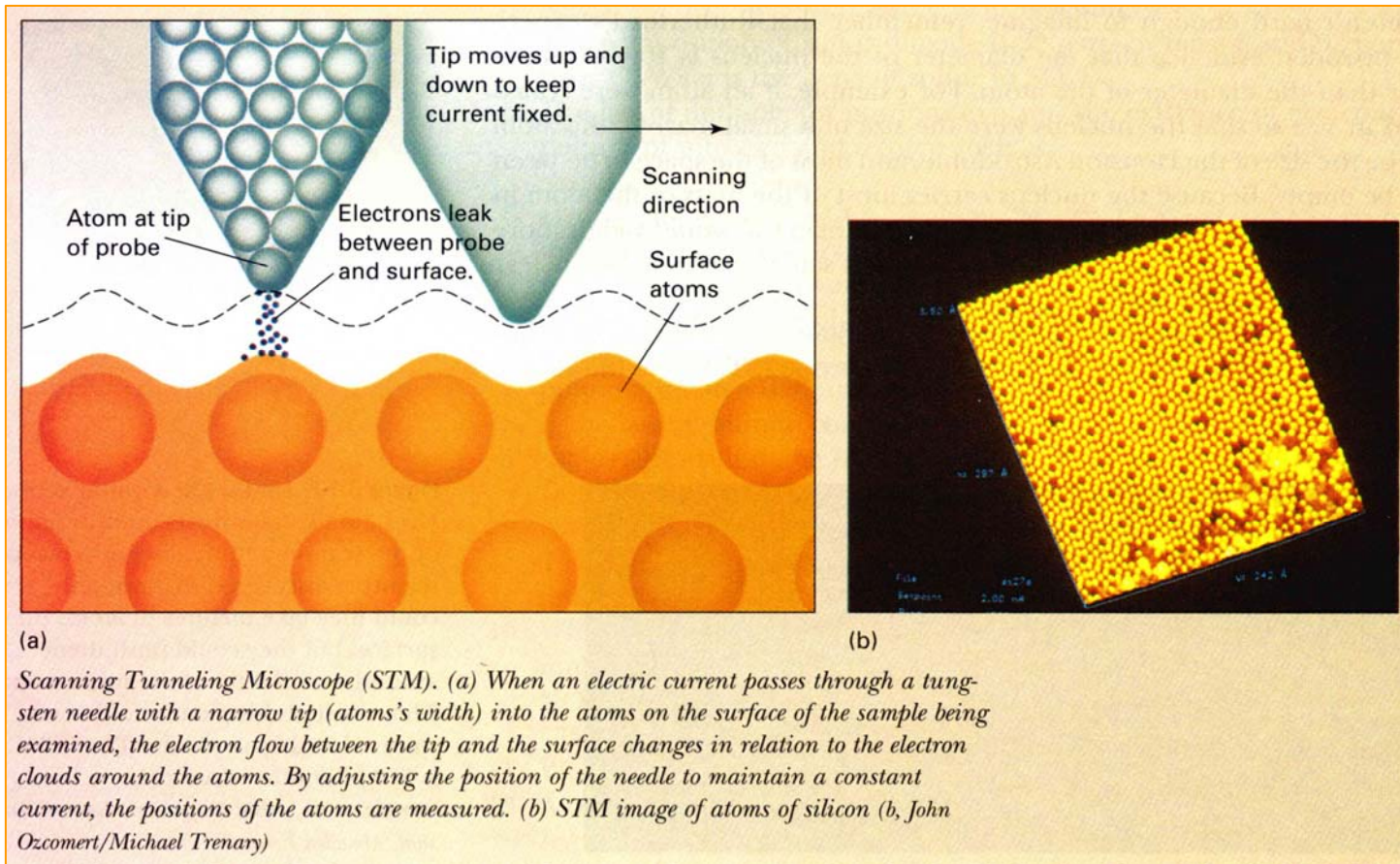
$V$ ：施加於探針和試片間的偏壓

$C$ ：材料常數

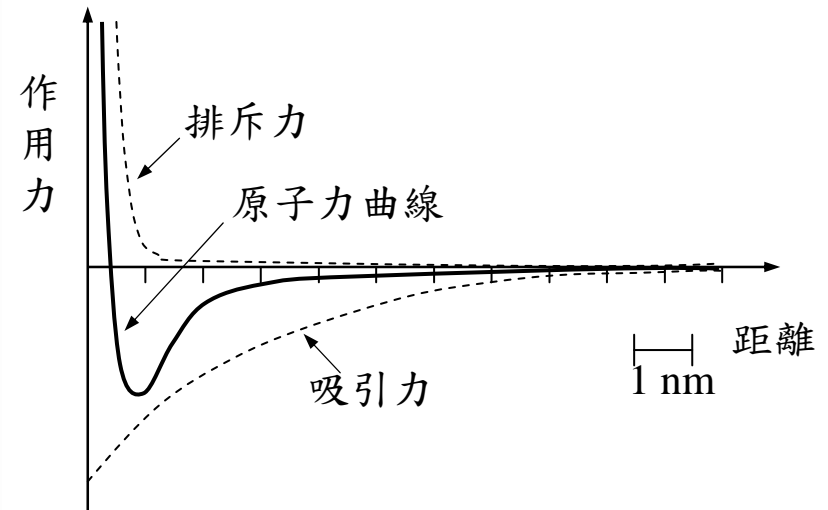
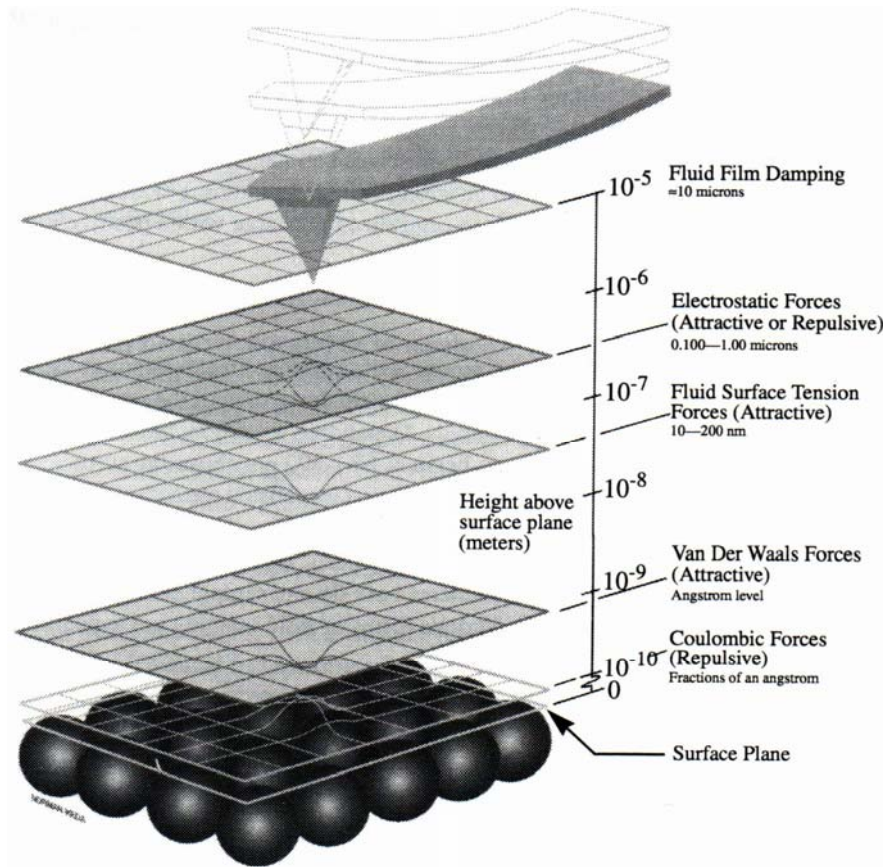
$d$ ：探針和試片間的間距



# Scanning Tunneling Microscopy



# Atomic Force Microscopy

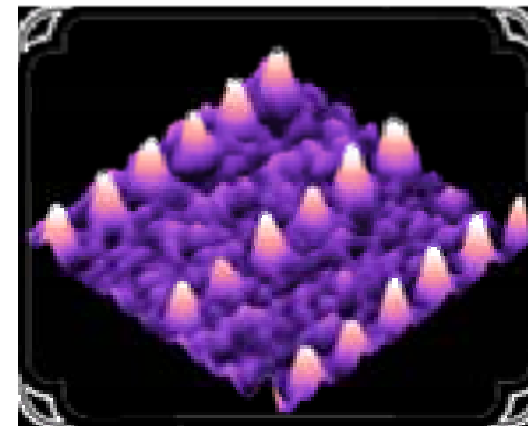
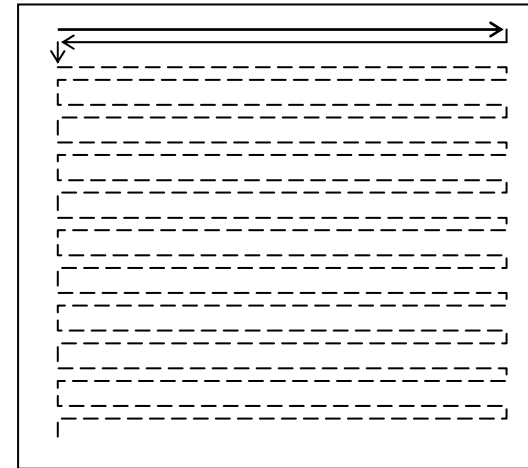
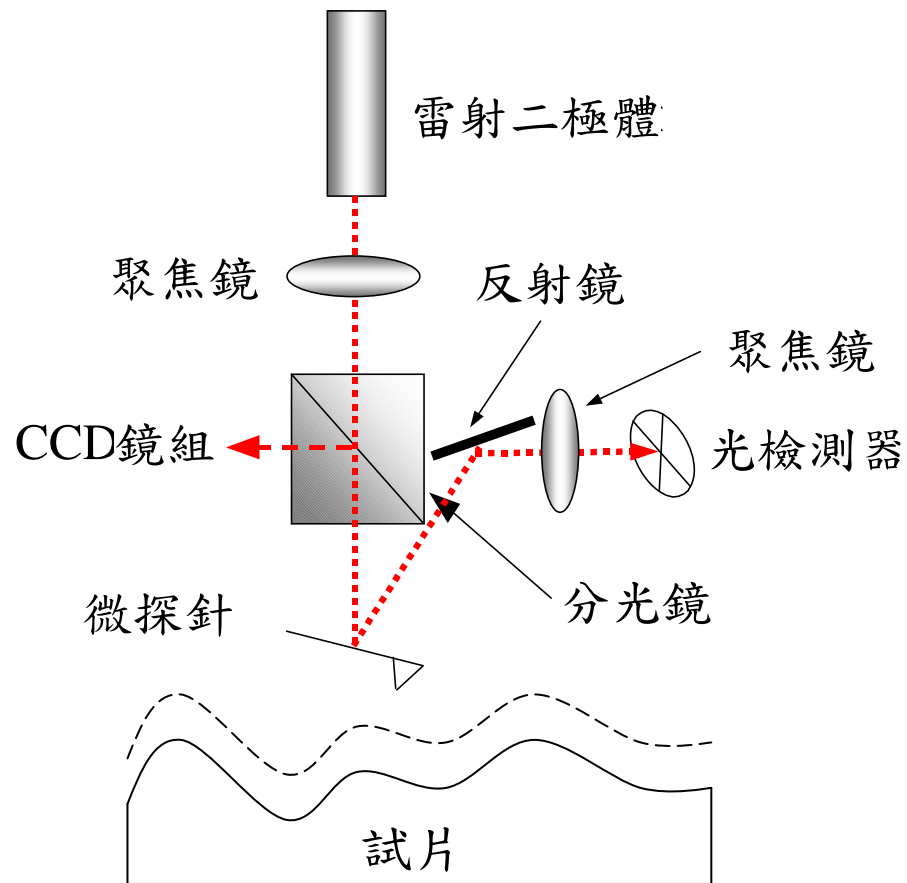


原子力與距離關係圖



# Atomic Force Microscopy

掃描方式





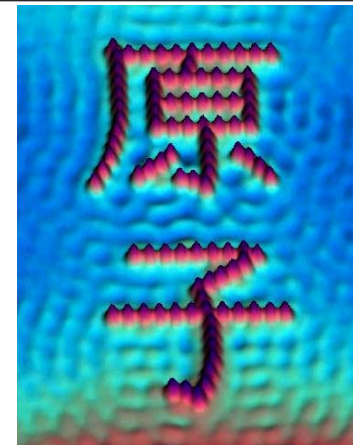
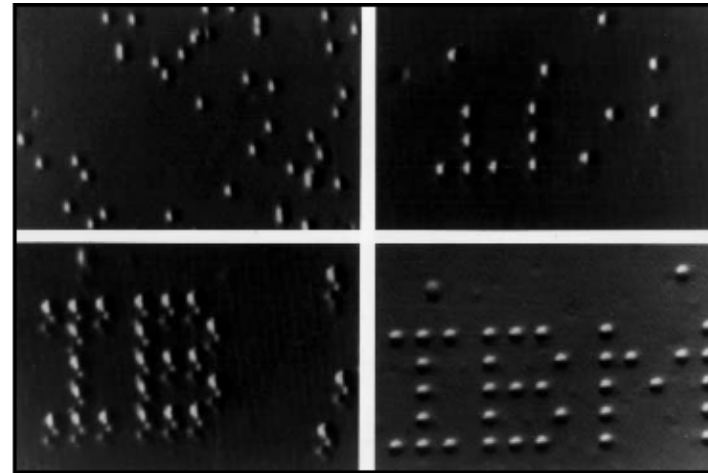
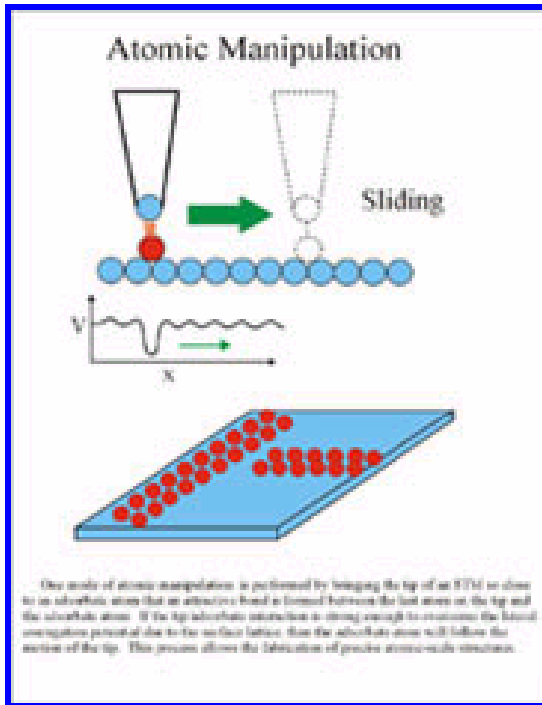
# The Art of Atom Manipulation: from *IBM* to Quantum Corral and Quantum Mirage

**Xe/Ni(111)**  
D.M. Eigler  
E.K. Schweizer  
Nature 344  
(1990) 524

**Fe/Cu(111)**  
M.F. Crommie, C.P. Lutz, D.M. Eigler, Science 262 (1993) 218

**Co/Cu(111)**  
H.C. Monoharan, C.P. Lutz, D.M. Eigler  
Nature 403 (2000) 512

# 平移原子操縱術



D.M. Eigler  
IBM, Amaden

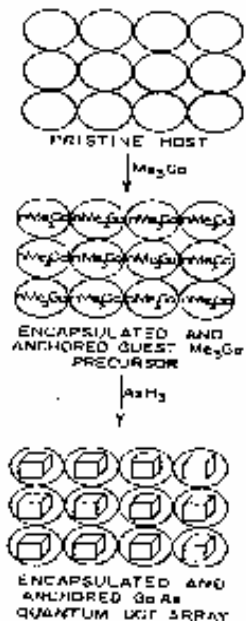


— 100 nm



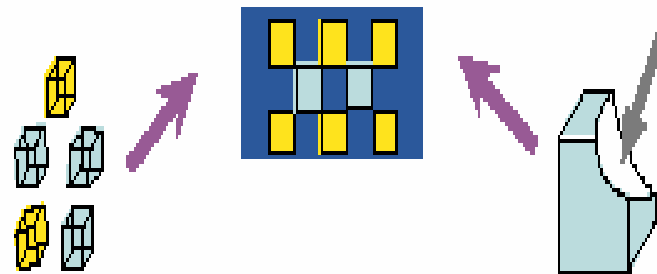
# “Bottom Up” or “Top Down”

## Bottom Up Approaching



Nanochemistry synthesis

## Nanostructured Material



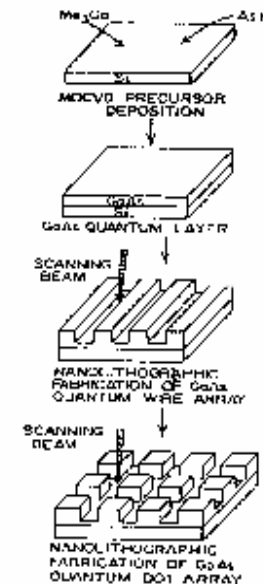
Assemble from Nano-building Blocks

- powder/aerosol compaction
- chemical synthesis

'Sculpt' from Bulk

- mechanical attrition (ball milling)
- lithography/etching...

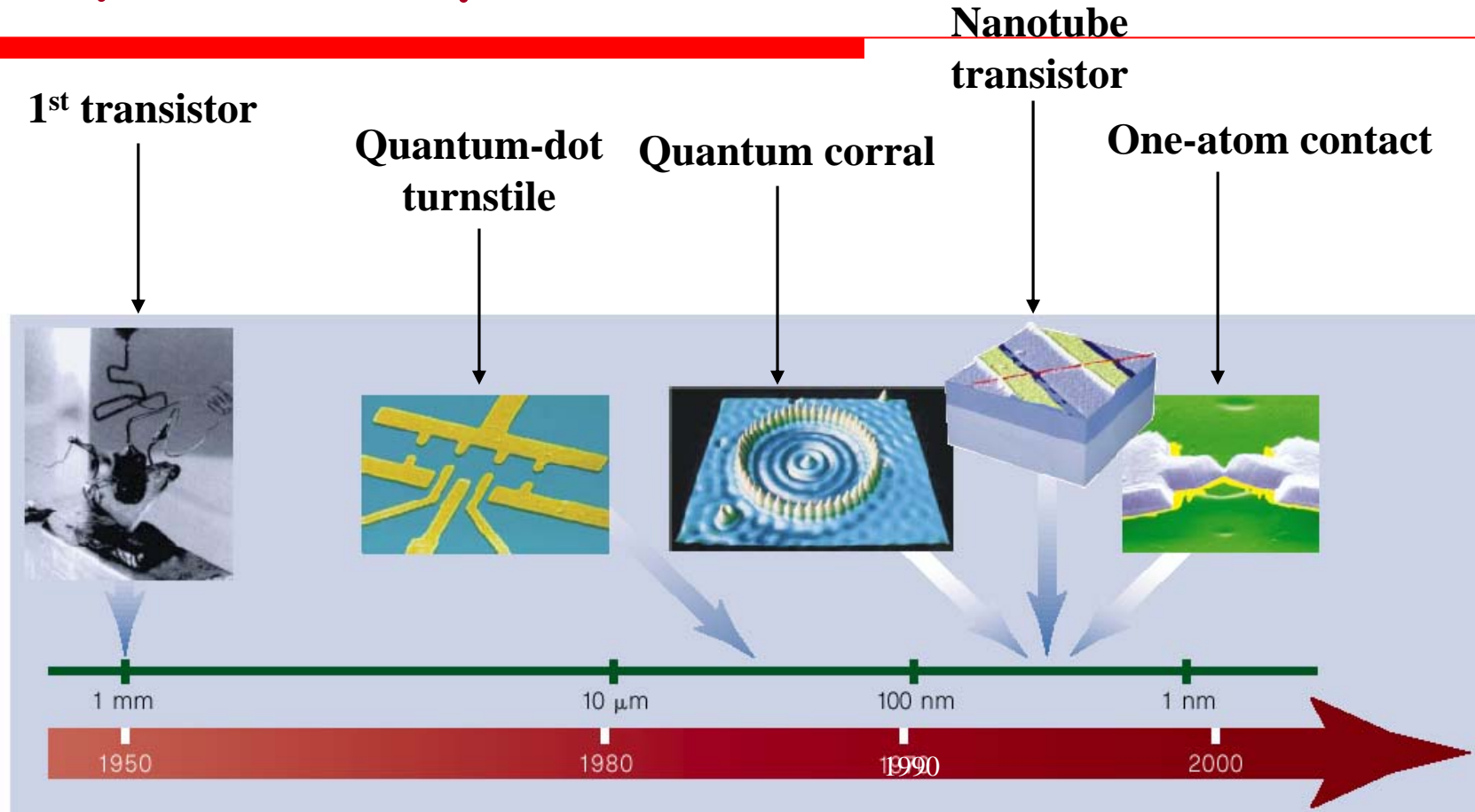
## Top Down Approaching



Nanophysics fabrication



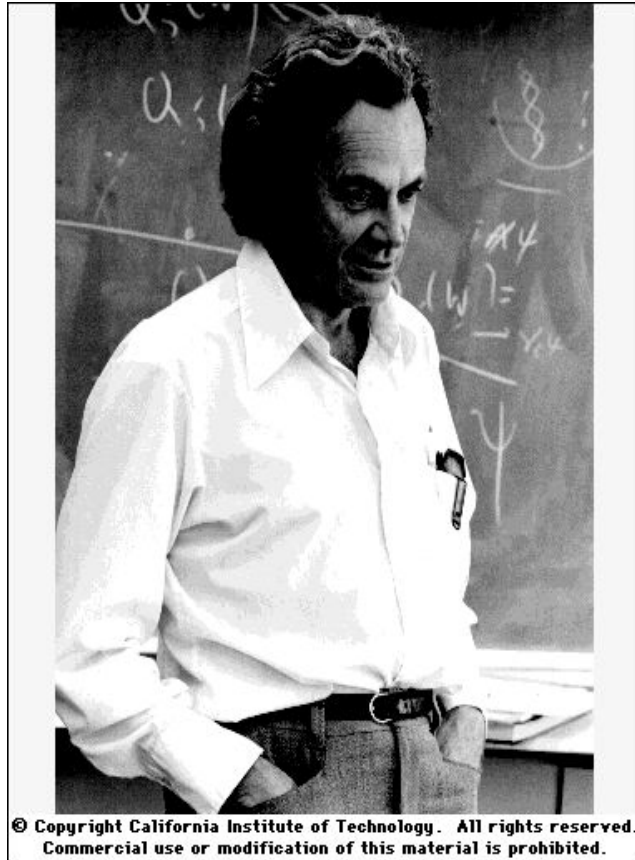
# A quantum leap for electronics



Ref: Nature **394**, 131 (1998).

# There's plenty of room at the bottom.

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*The father of nanotechnology*

*Richard Feynman*

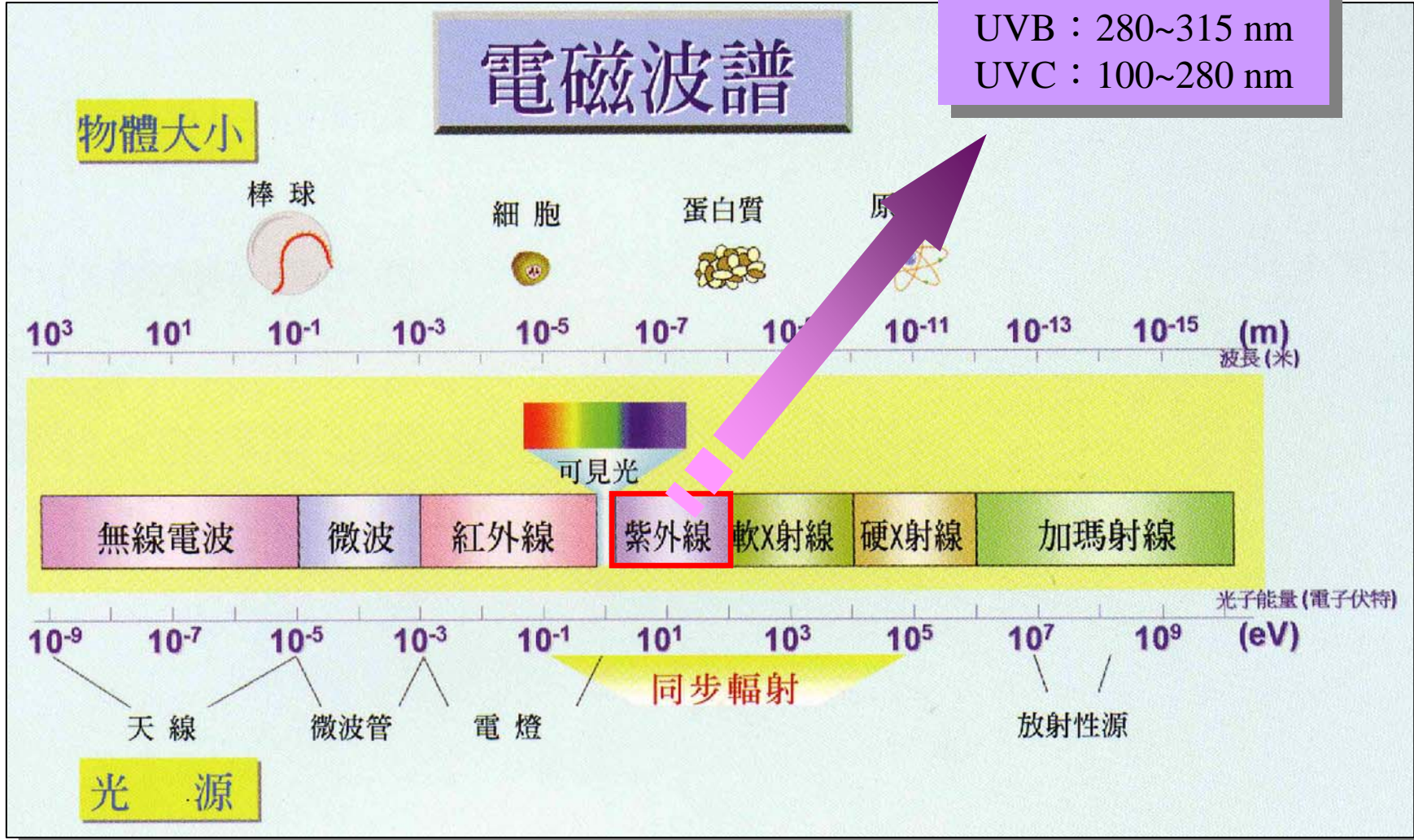
American Physical Society on Dec. 19, 1959  
at the Caltech.



# 含奈米粒子之防曬品



紫外線之分類  
 UVA : 315~400 nm  
 UVB : 280~315 nm  
 UVC : 100~280 nm





## 紫外線指數分類、曬傷時限與建議防護措施一覽表

紫外線指數	曝曬級數	曬傷時限	防護措施
0~2	微量級		
3~4	低量級		
5~6	中量級	30 分鐘內	使用帽子、洋傘、防曬液與太陽眼鏡並盡量待在陰涼處
7~9	過量級	20 分鐘內	使用帽子、洋傘、防曬液與太陽眼鏡，並著長袖衣物待在陰涼處，且上午十時至下午二時不外出為宜
10~15	危險級	15 分鐘內	使用帽子、洋傘、防曬液與太陽眼鏡並著長袖衣物待在陰涼處，且上午十時至下午二時不外出為宜



## 日光防護係數 (Sun Protective Factor, SPF) (僅適用於UVB)

定義：塗用防曬化妝品時皮膚產生最小紅斑量  
(minimal erythema dose, MED) 所需  
光能量與未塗防曬化妝品時皮膚產生  
MED所需光能量之比。

$$\text{SPF值} = \text{MED (塗用防曬化妝品)} / \text{MED (未塗用防曬化妝品)}$$

## 不同SPF等級防曬化妝品之防曬能力

SPF	防曬等級	要求	應用物件
2~6	最低	允許曬黑	黑膚色人
6~8	中等	允許有些曬黑	膚色偏深的人
8~12	高度	允許有限曬黑	一般皮膚的人
12~20	高強	允許少許曬黑	敏感皮膚的人
20~30	超強	不允許曬黑	野外作業、游泳
30 以上	高超強	更不允許曬黑	受強烈陽光暴曬



## 要求防曬型化妝品對於防護UVA之功效較UVB更重要原因如下：

### 紫外線之分類

UVA：315~400 nm

UVB：280~315 nm

UVC：100~280 nm

- 一. UVA占UV總量之97%。
- 二. UVA對皮膚之穿透力較深，其可達真皮使膠原蛋白變性。
- 三. UVA具累積作用，即終生所受UVA之劑量為累加的。
- 四. UVA可穿透較薄的衣服、玻璃窗及游泳池的水而作用於人的皮膚。
- 五. UVA是皮膚曬黑的主要UV波段。
- 六. UVA是致使皮膚老化與皮膚癌之主要元凶之一。



## 適用於UVA之日光防護係數

Protection Factor of UVA (PFA) :

PFA值 = MPPD (塗用防曬化妝品) / MPPD (未塗用防曬化妝品)

日本化妝品工業聯合會：protection grade of UVA (PA) PA+ =

PFA2~4：對黑色素之產生具低效防護作用。

PA++ = PFA6~8：對黑色素之產生具中效防護作用。

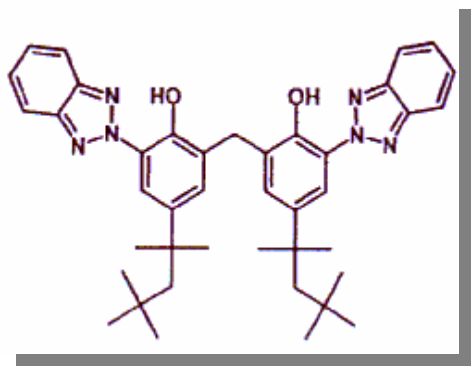
PA+++ = PFA>8：對黑色素之產生具高效防護作用。

(MPPD: **Minimum persistent pigment darkening dose**; 使持續色素致黑之最小劑量)

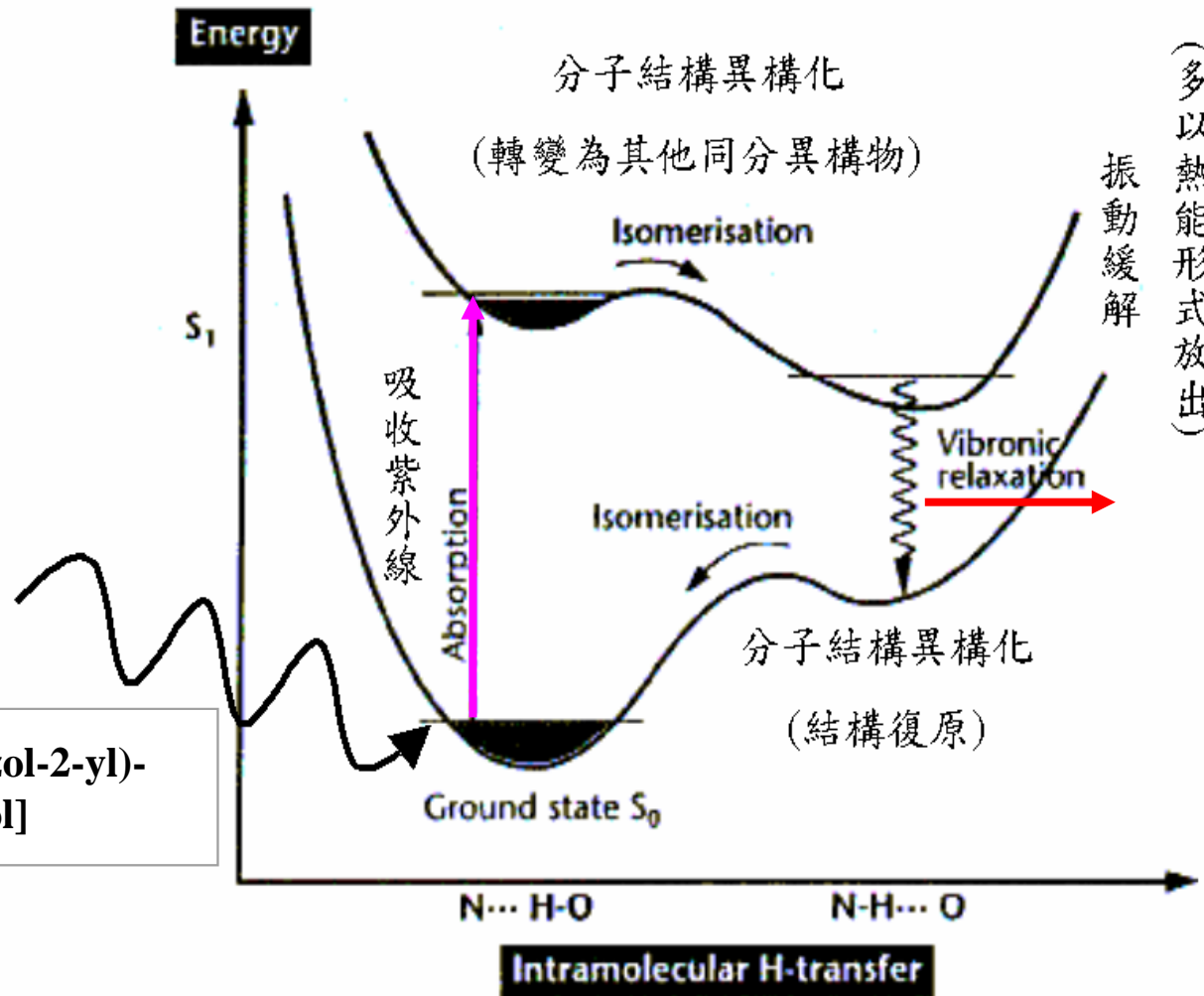


## 化學性吸收劑吸收紫外光之機制

### Tinosorb M之結構



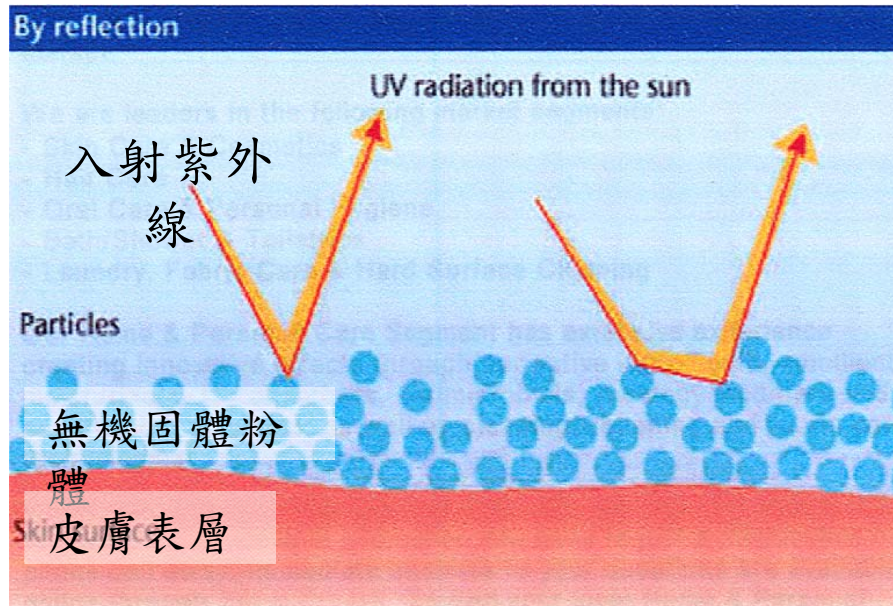
2,2'-Methylenbis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol]



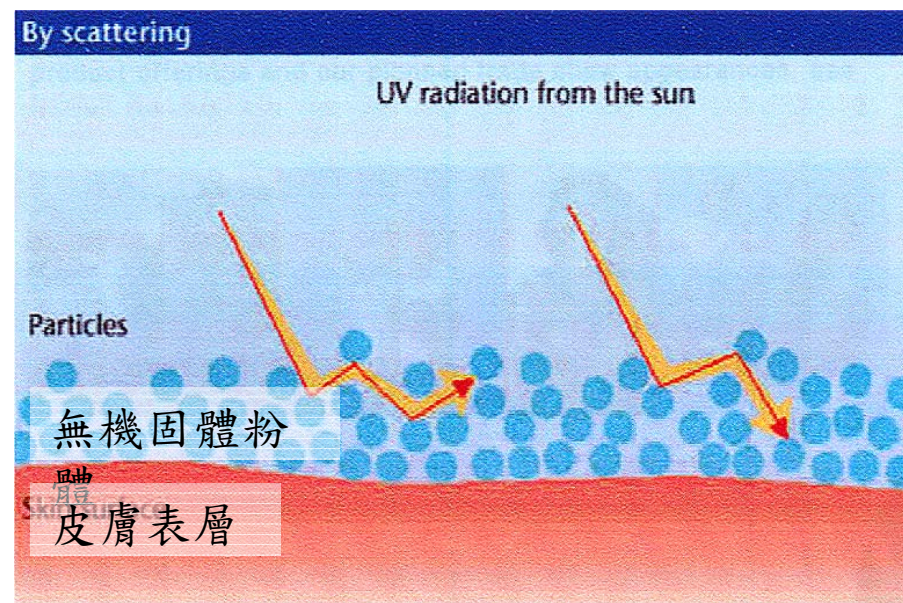


## 物理性屏蔽劑屏蔽紫外線機制示意圖

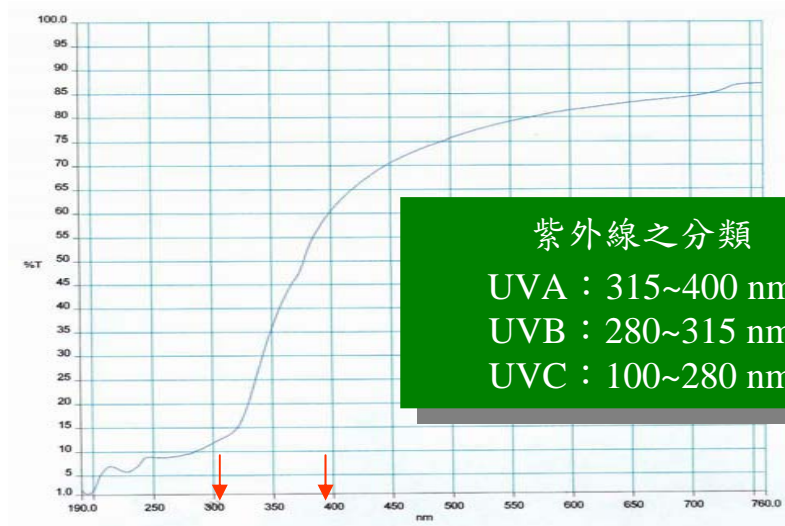
反射



散射



## 商用防曬用品之穿透率



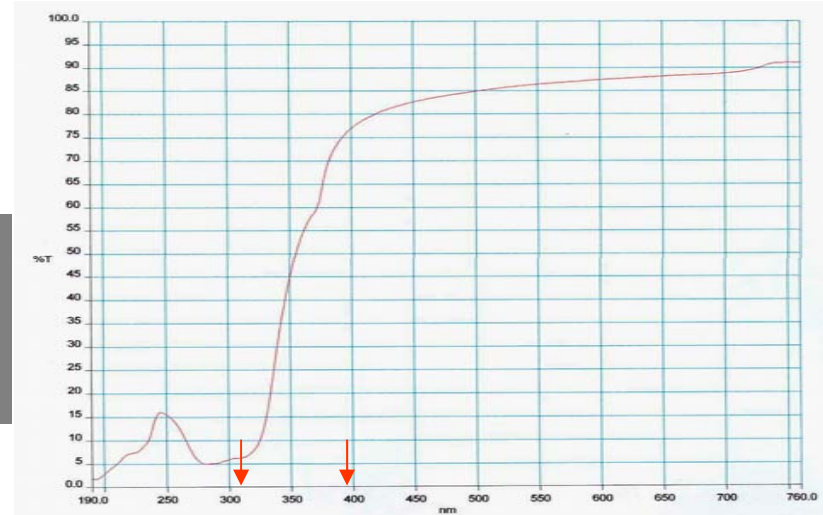
紫外線之分類

UVA : 315~400 nm

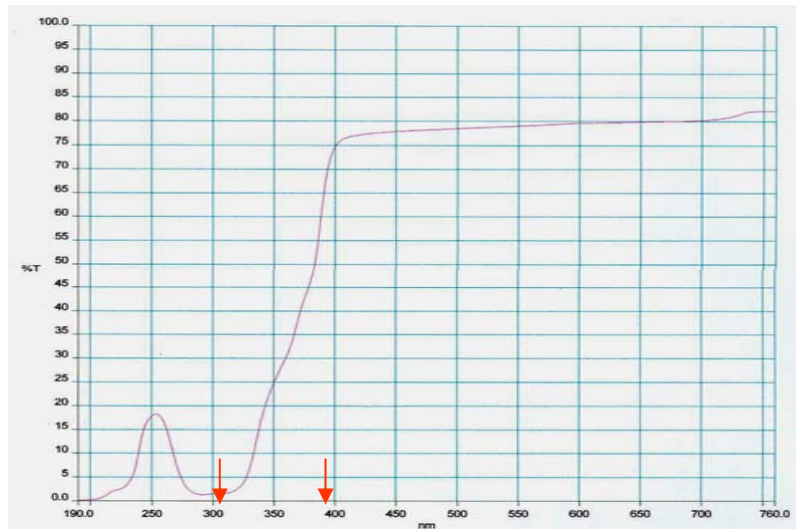
UVB : 280~315 nm

UVC : 100~280 nm

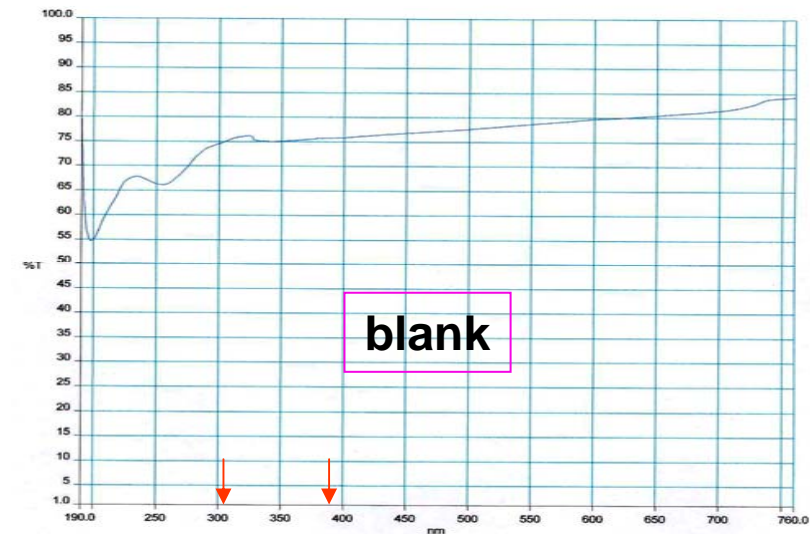
AVENE-SPF50/nano particles;化學防曬



ESTEE LAUDER-SPF30/ nano particles ;化學防曬

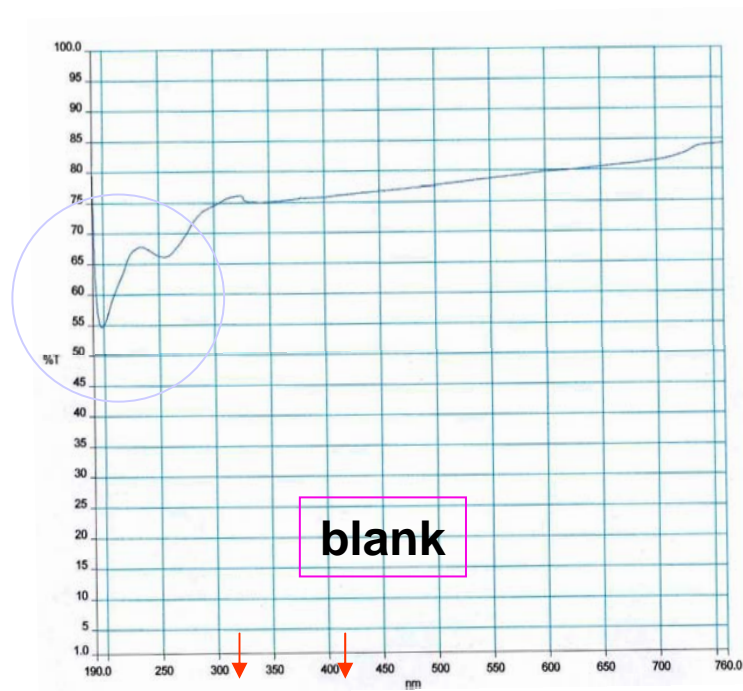


Lancaster-SPF15/化學防曬

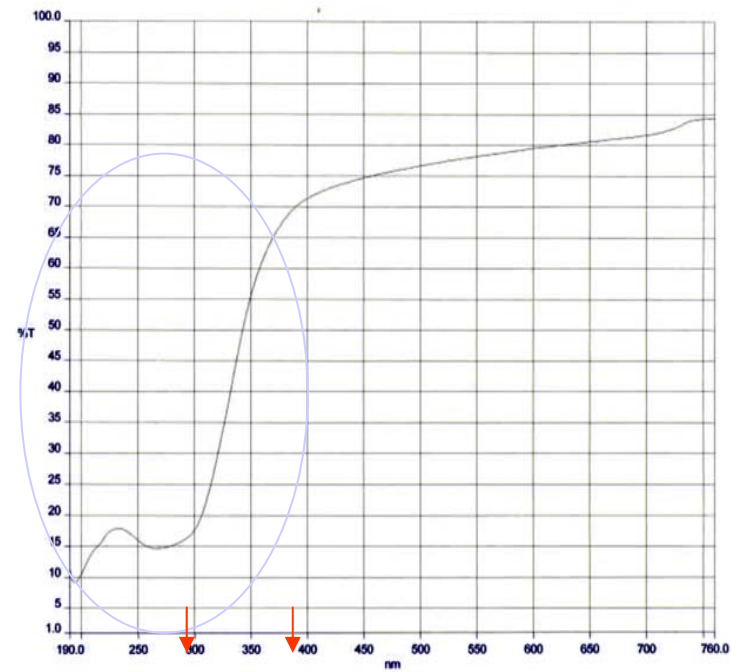


Vitamin C cream - No additive

## 無防曬劑的乳霜中添加奈米粒子之UV光譜圖

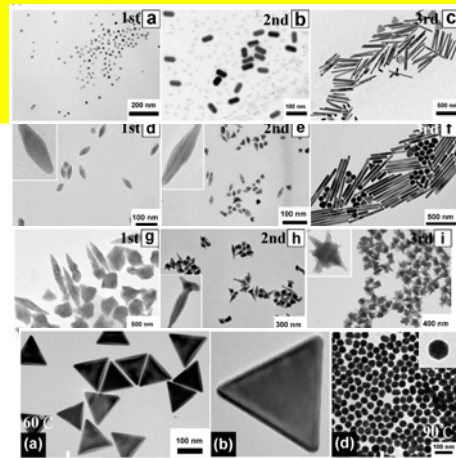


Vitamin C cream-No additive



Add nano particles to cream

# 奈米金屬化學製作技術



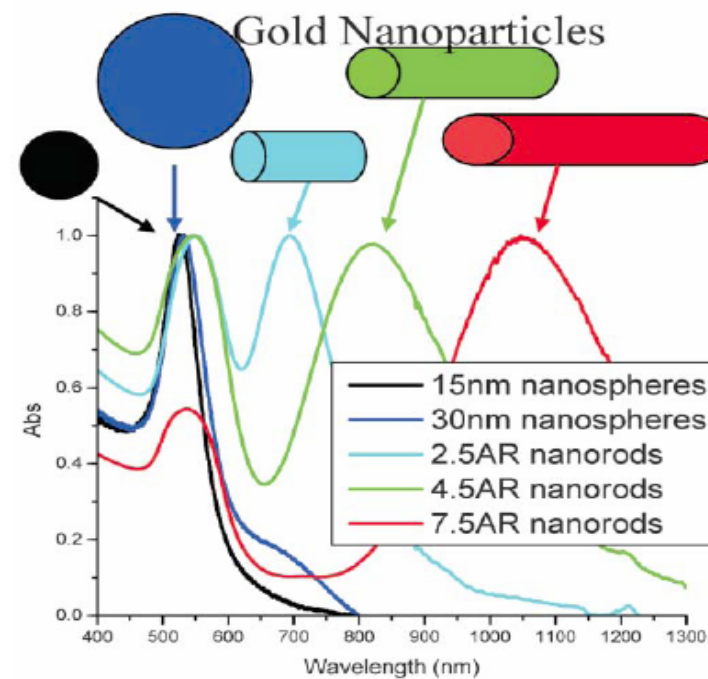
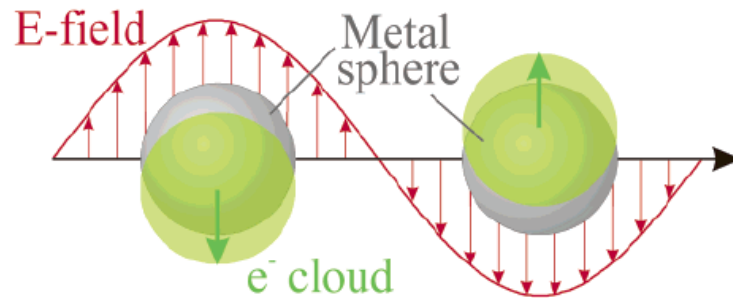


## 奈米材料之維度

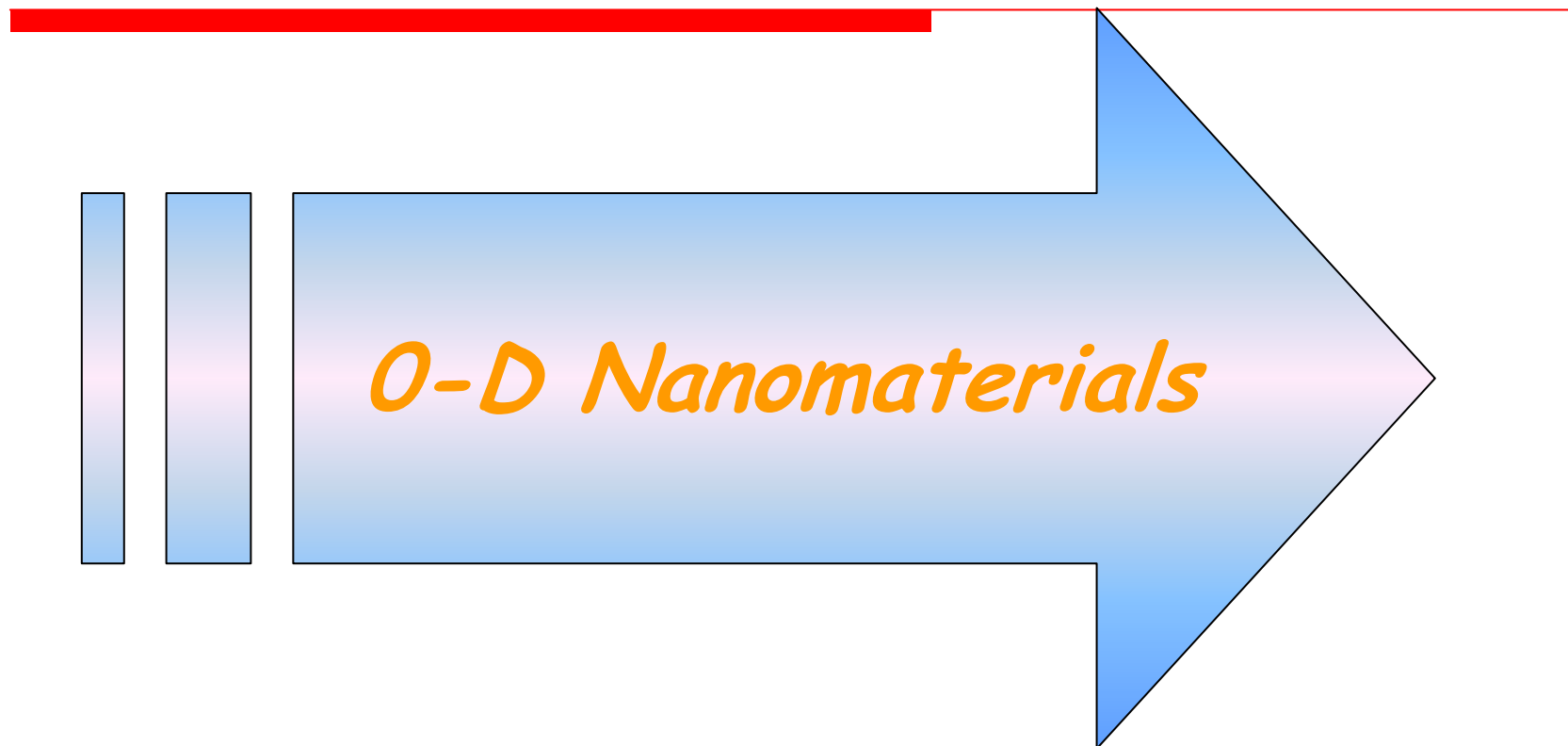
	定義	範例
零維材料	空間三維尺度均為 奈米尺寸	奈米顆粒、原子簇
一維材料	空間中有二維尺度處於奈米尺寸	奈米線、奈米管
二維材料	空間中有一維尺度處於奈米尺寸	超薄膜

# Surface Plasmon Resonance (SPR)

## Shape

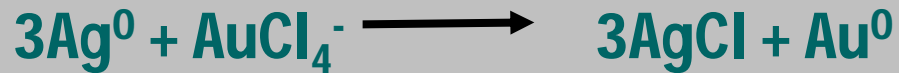
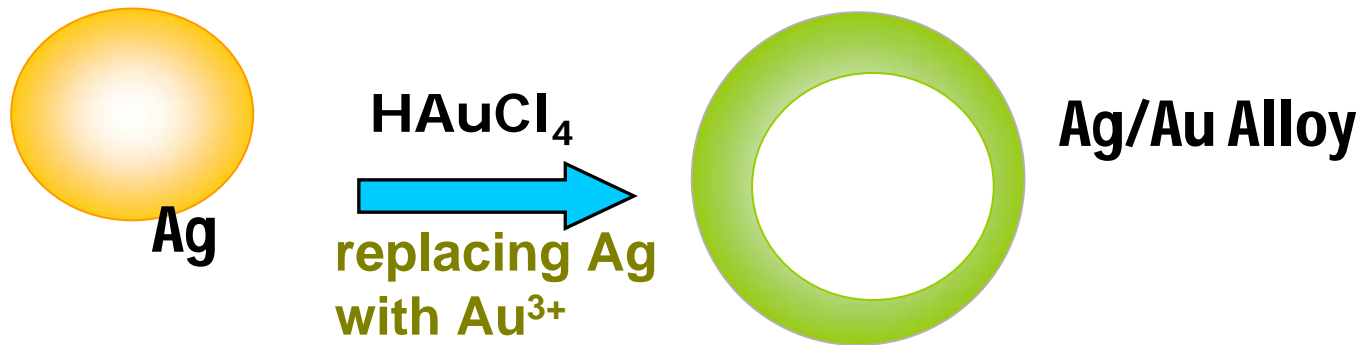






# Present Investigation

## Composition of Shell



## Catalytic Performance



## Ability of reducing agent



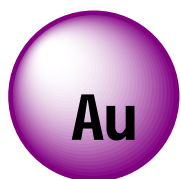
Anisotropic growth



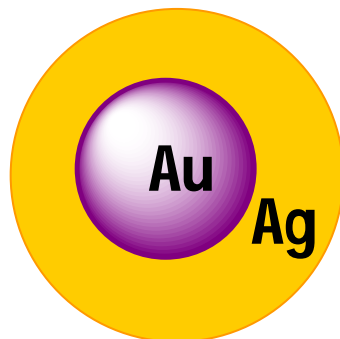
# Experimental



$\text{Na}_3$  Citrate / boiling condition  
(reducing agent)



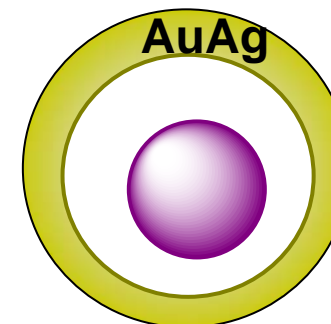
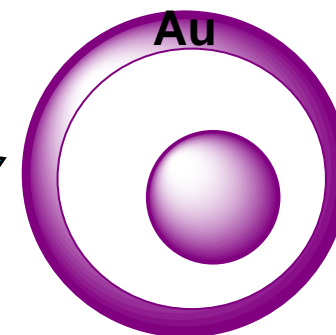
$\text{Na}_3$  Citrate  
Coating of Ag



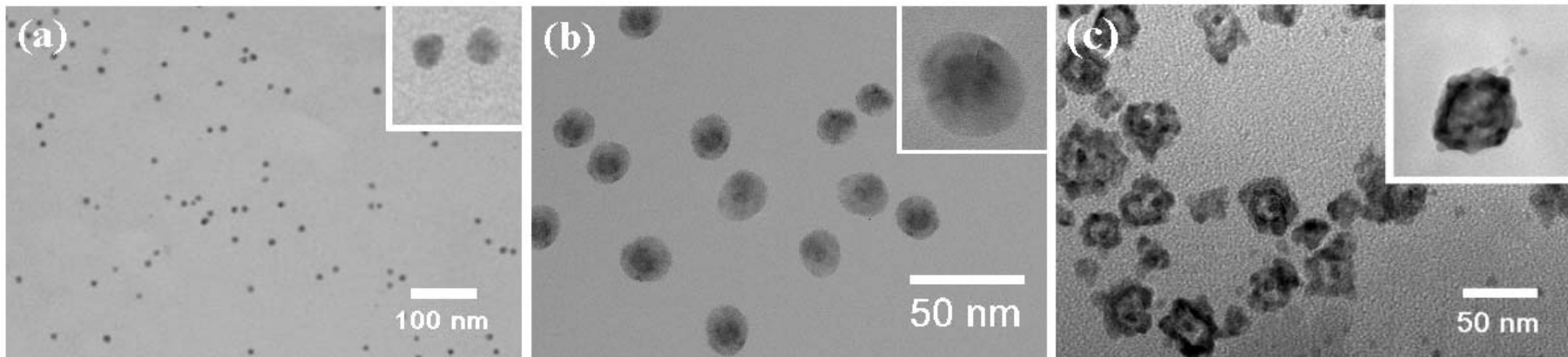
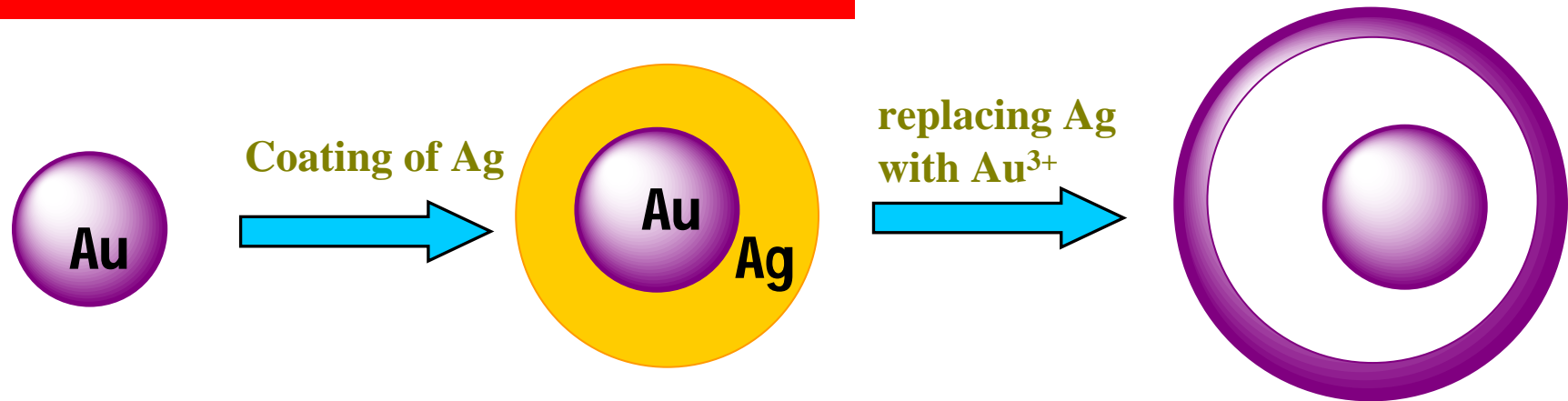
$\text{HAuCl}_4$   
replacing Ag  
with  $\text{Au}^{3+}$

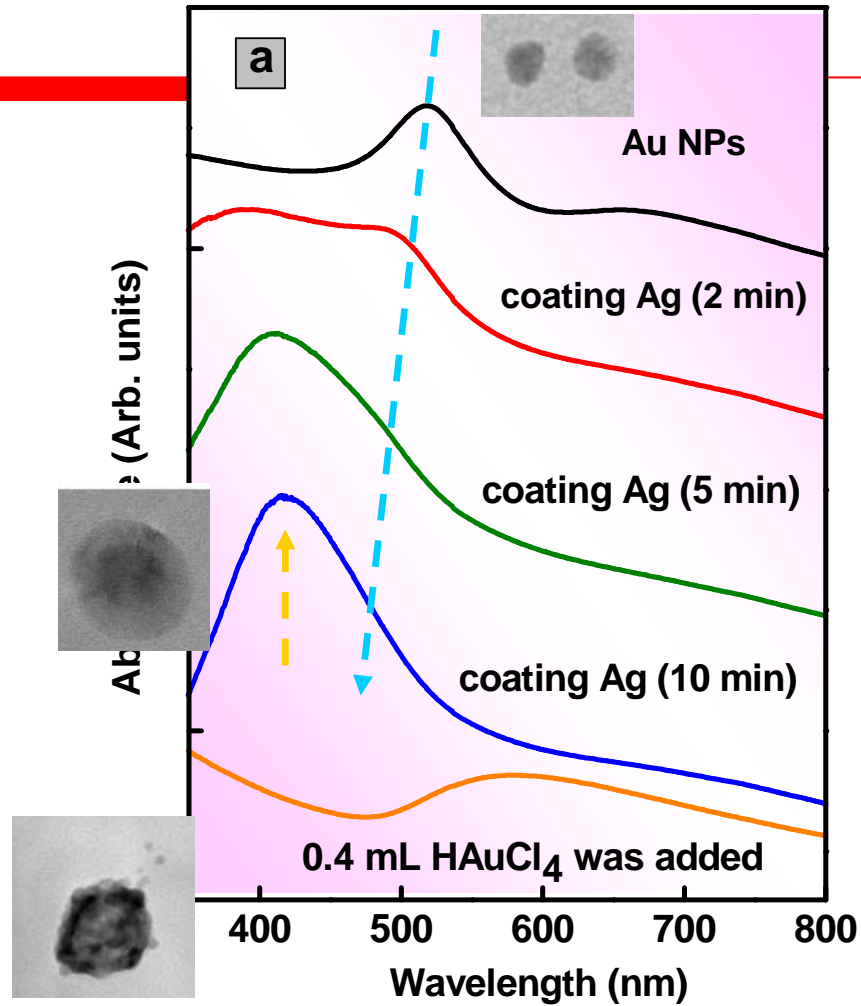
$25^\circ\text{C}$

$95^\circ\text{C}$

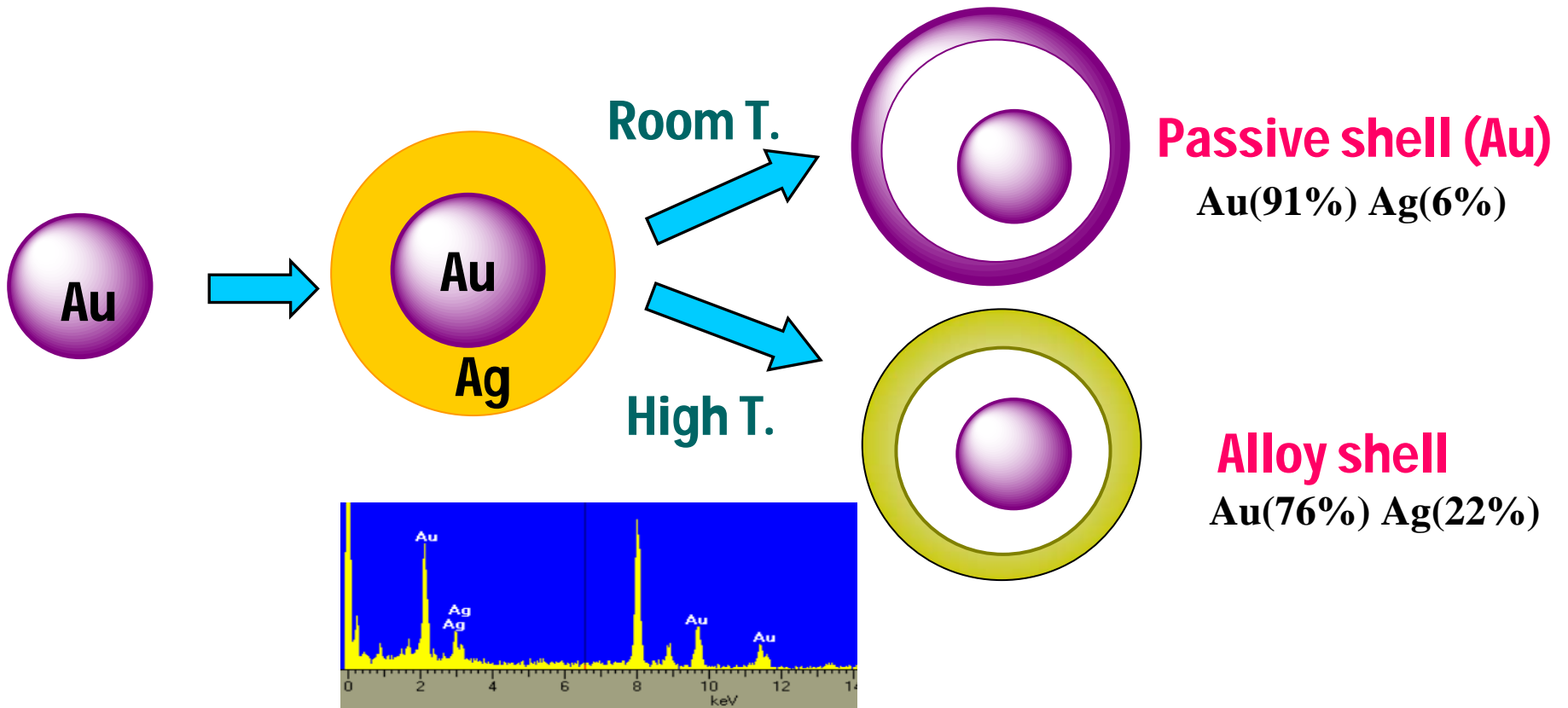
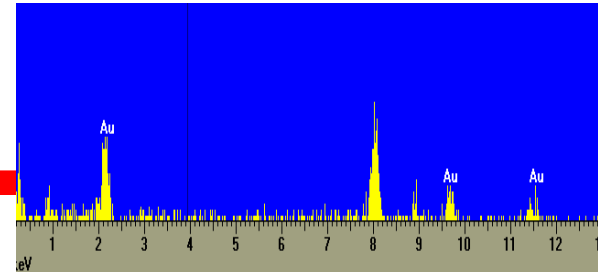


## Morphology

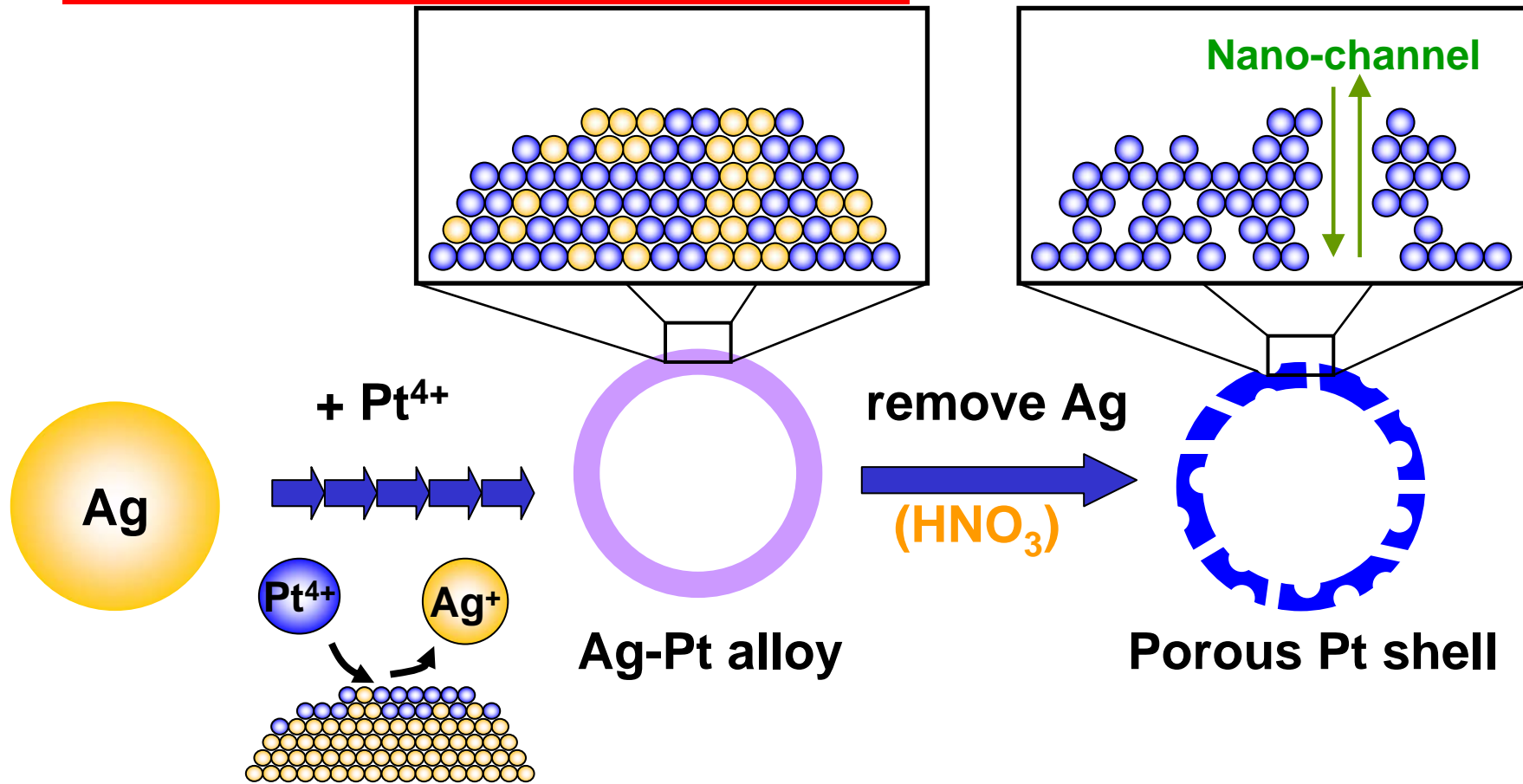




# Temperature Effect

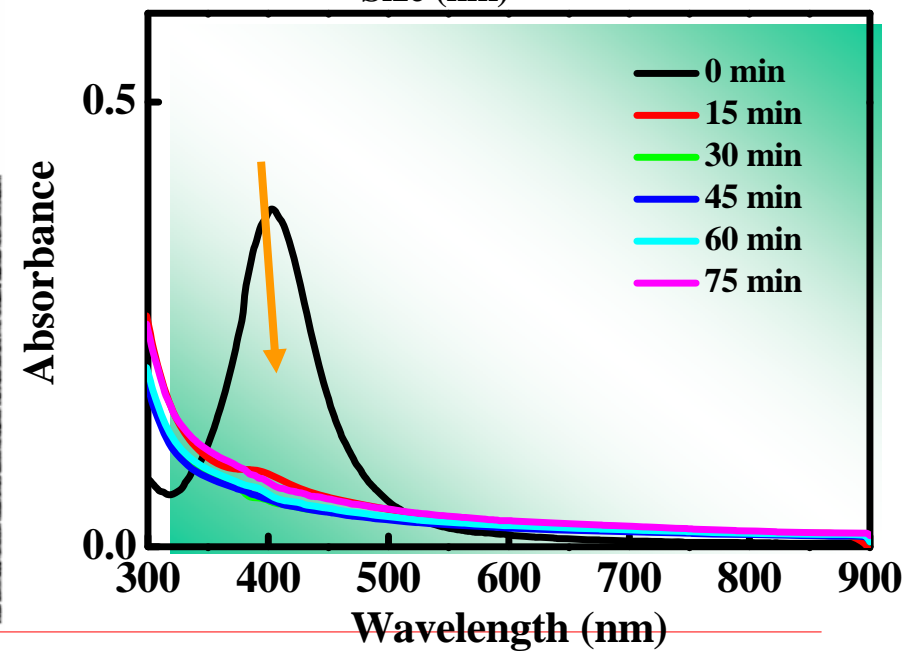
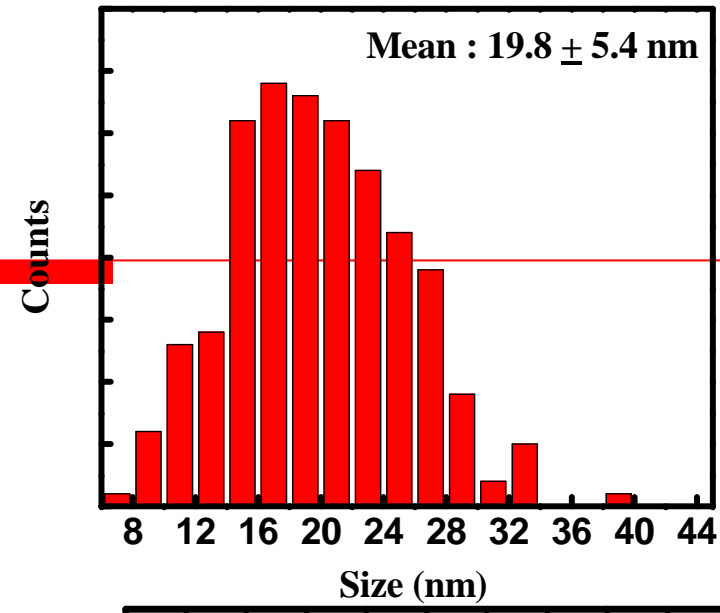
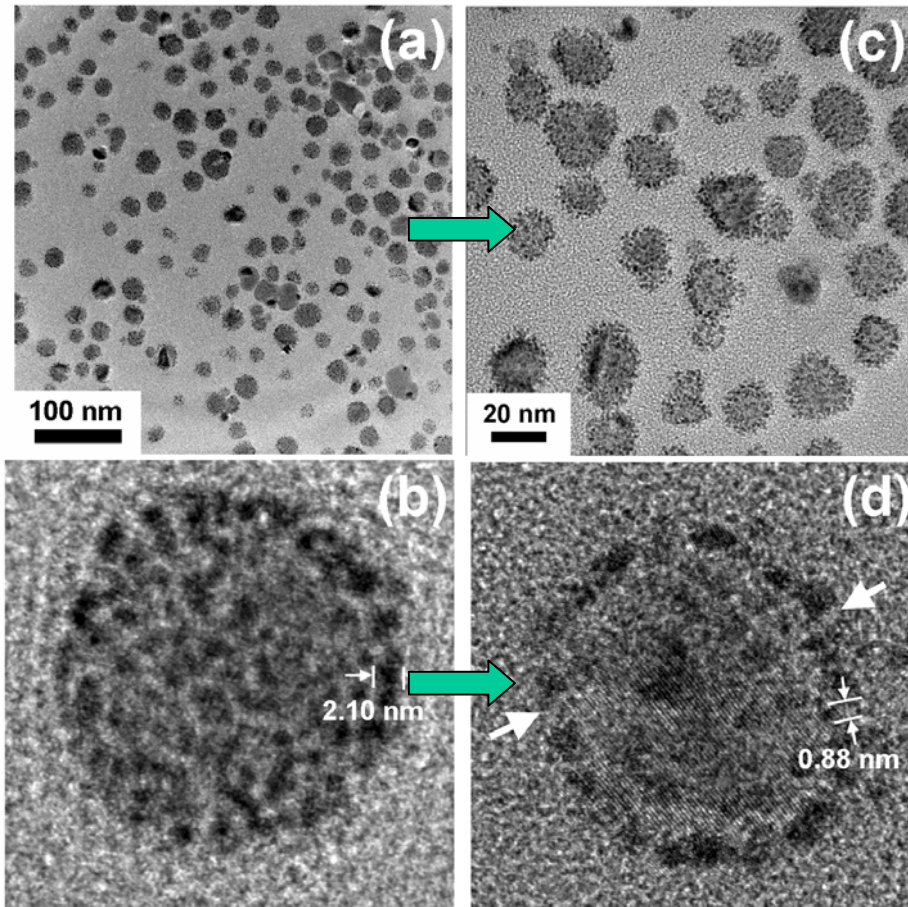


## Synthetic Strategy



# Morphology

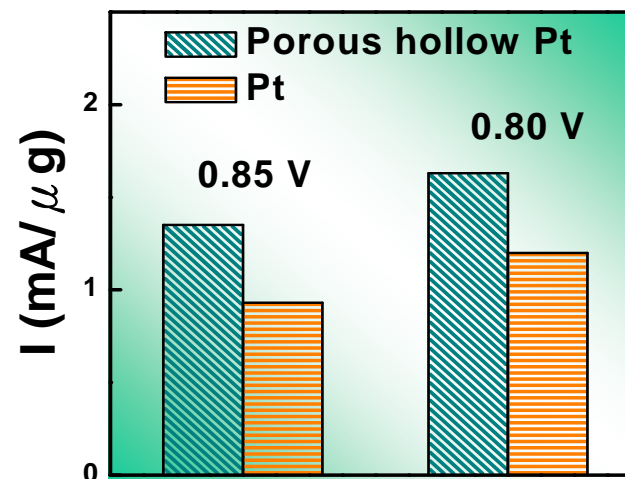
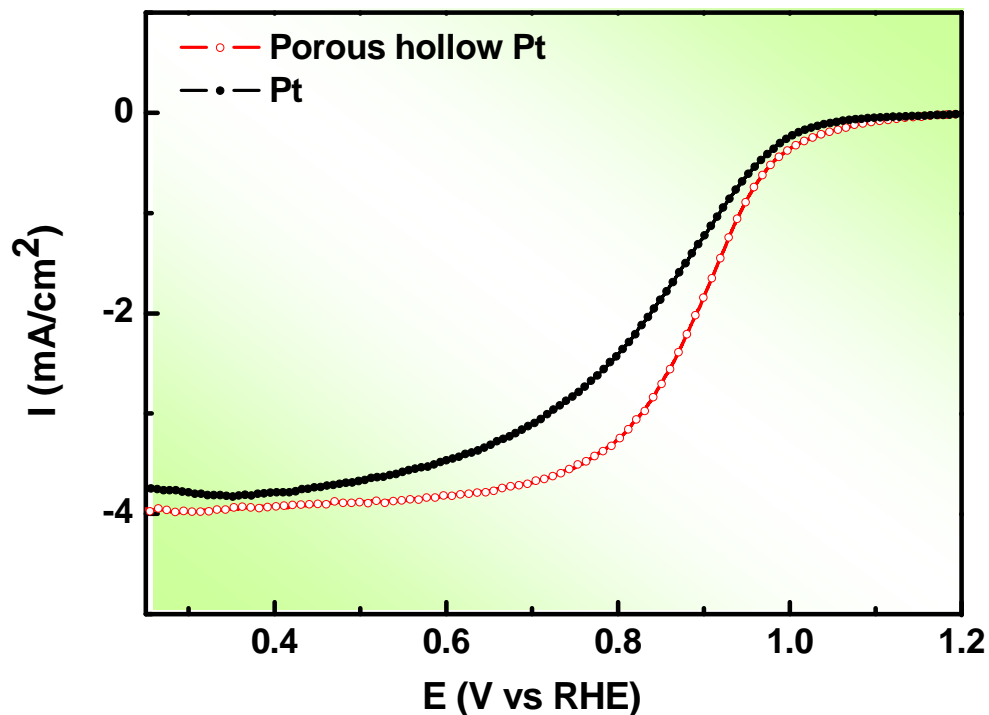
## Chemical etching





## Catalytic Performance

### Oxygen Reduction Reaction (ORR)



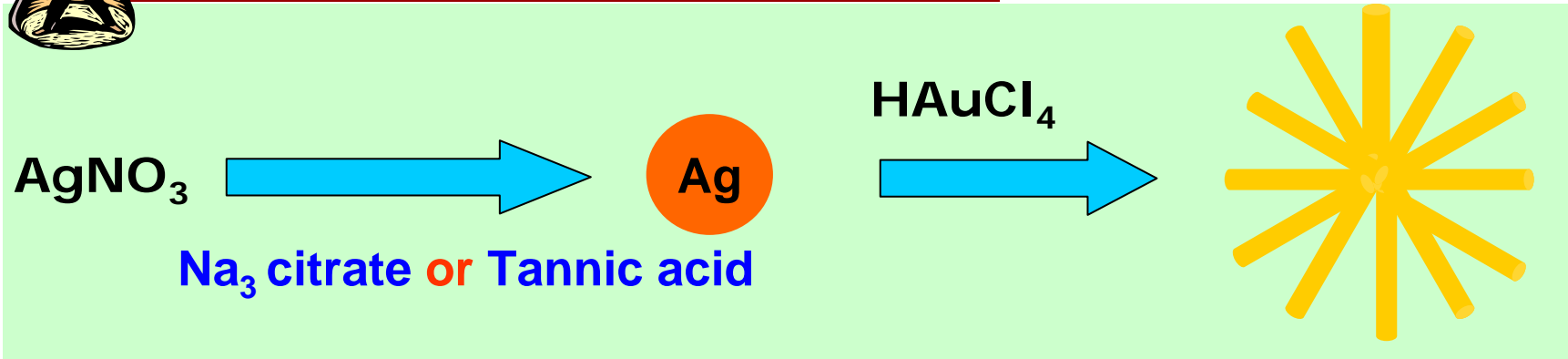


**Reducing Agent Effect**  
**Anisotropic growth**

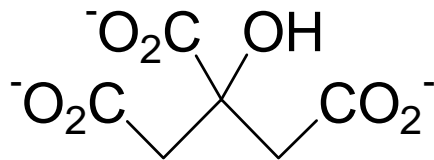


# Experimental

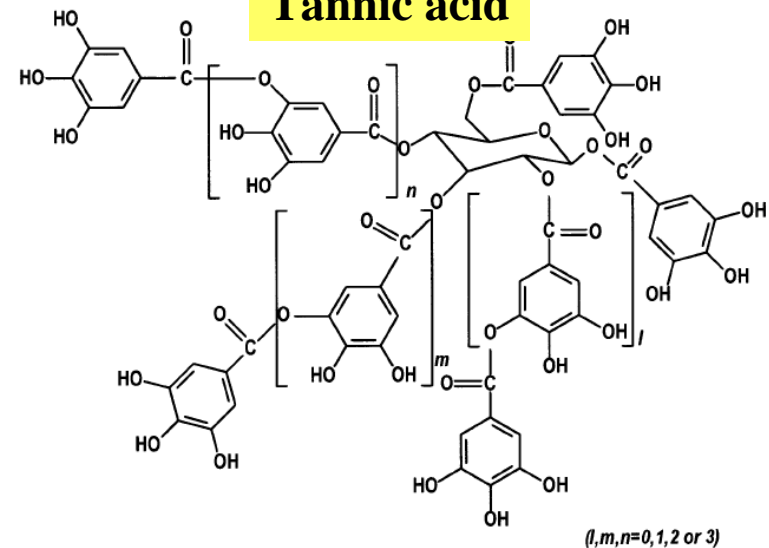
# Tannic acid



Na<sub>3</sub> citrate

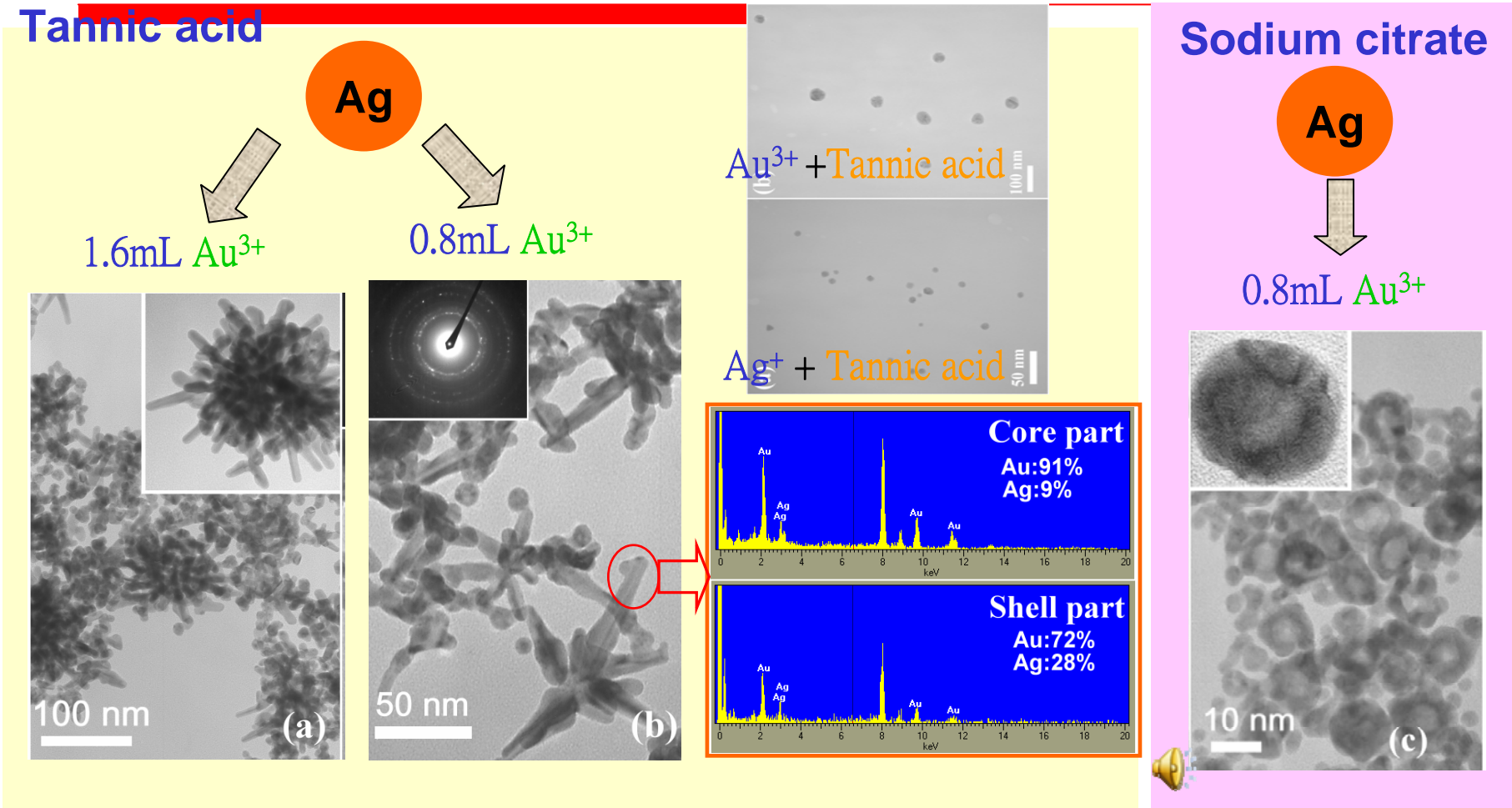


Tannic acid



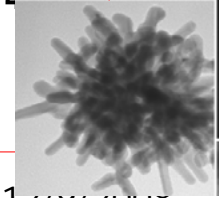
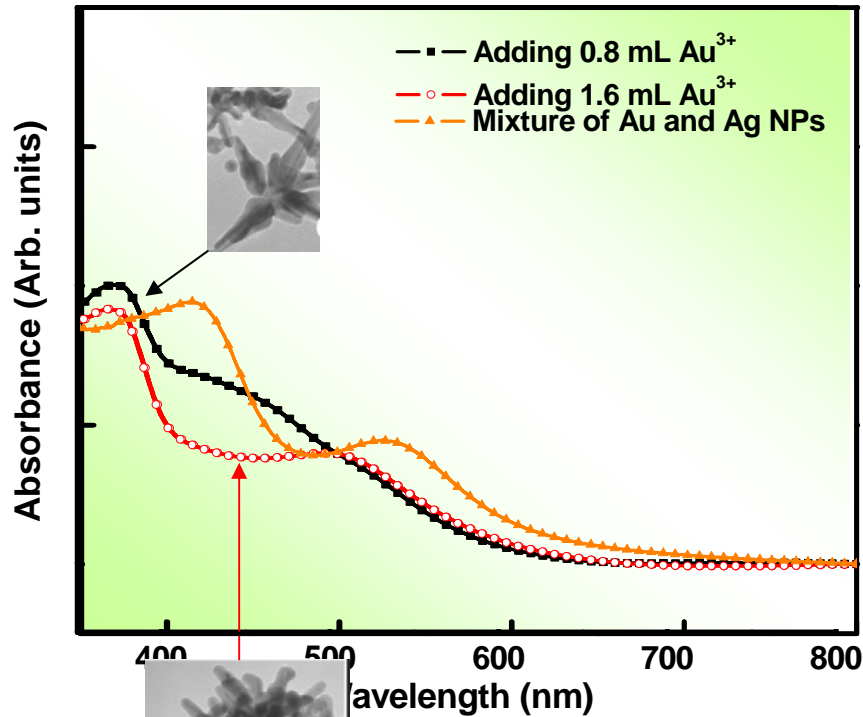


# Morphology

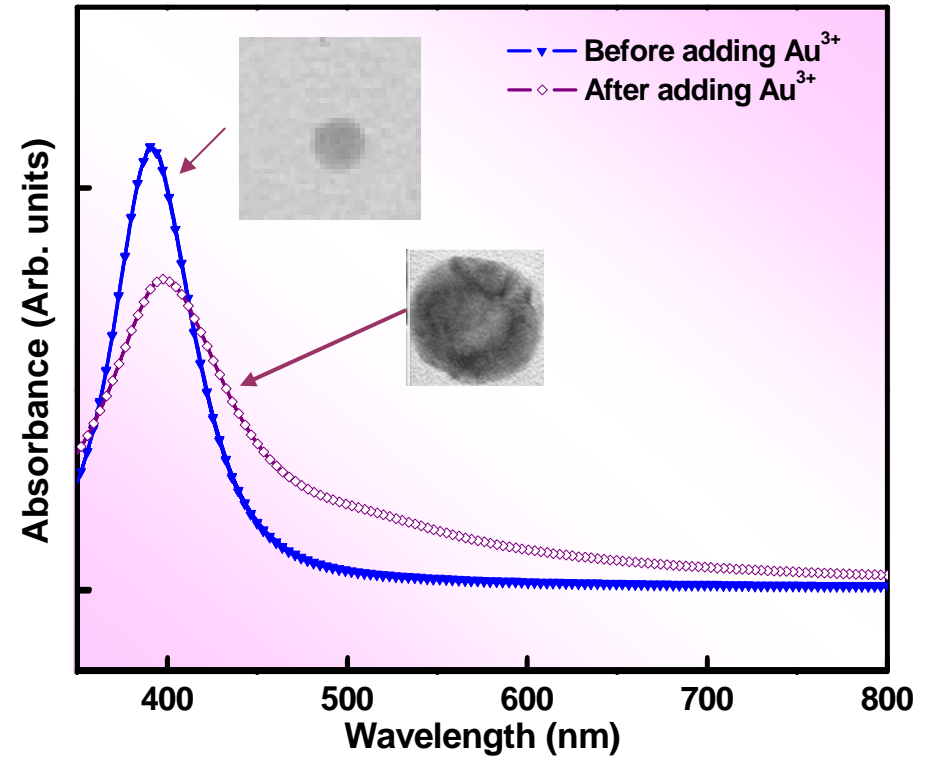




*Tannic acid*



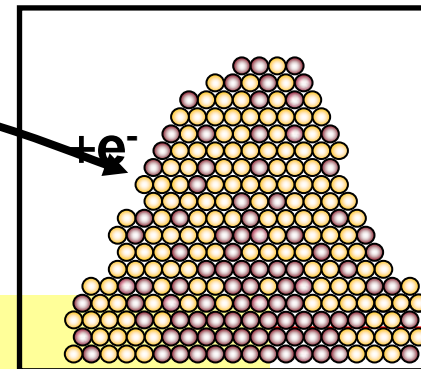
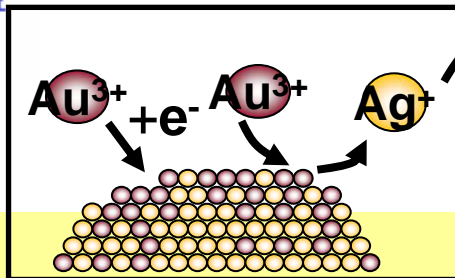
*Sodium citrate*



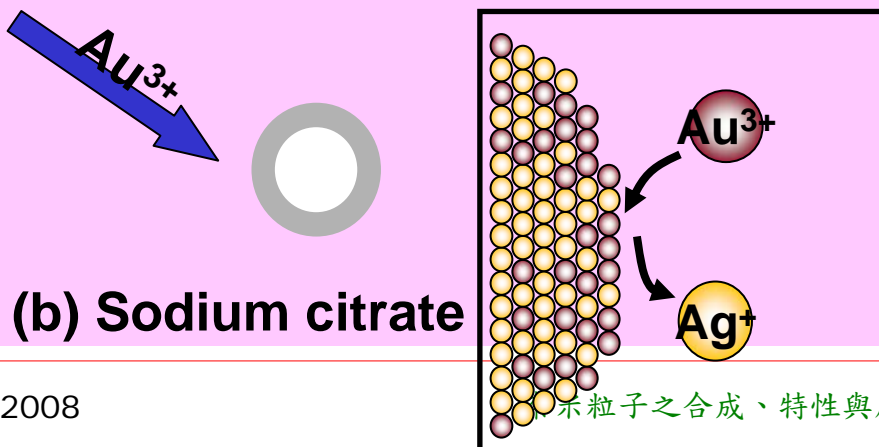
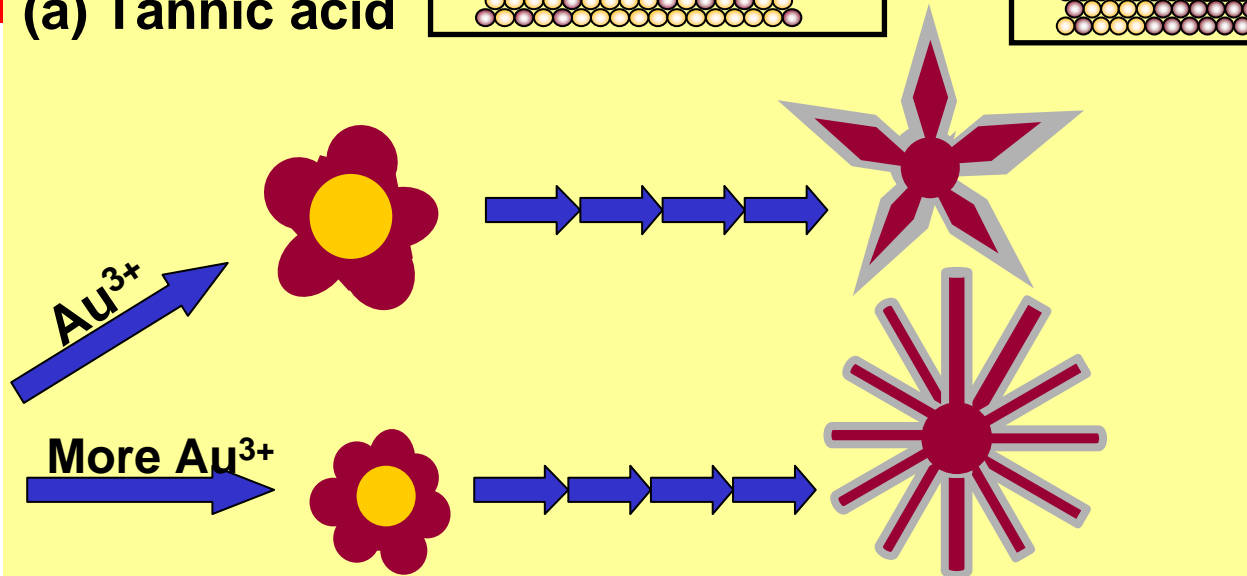


## Growth Mechanism

(a) Tannic acid

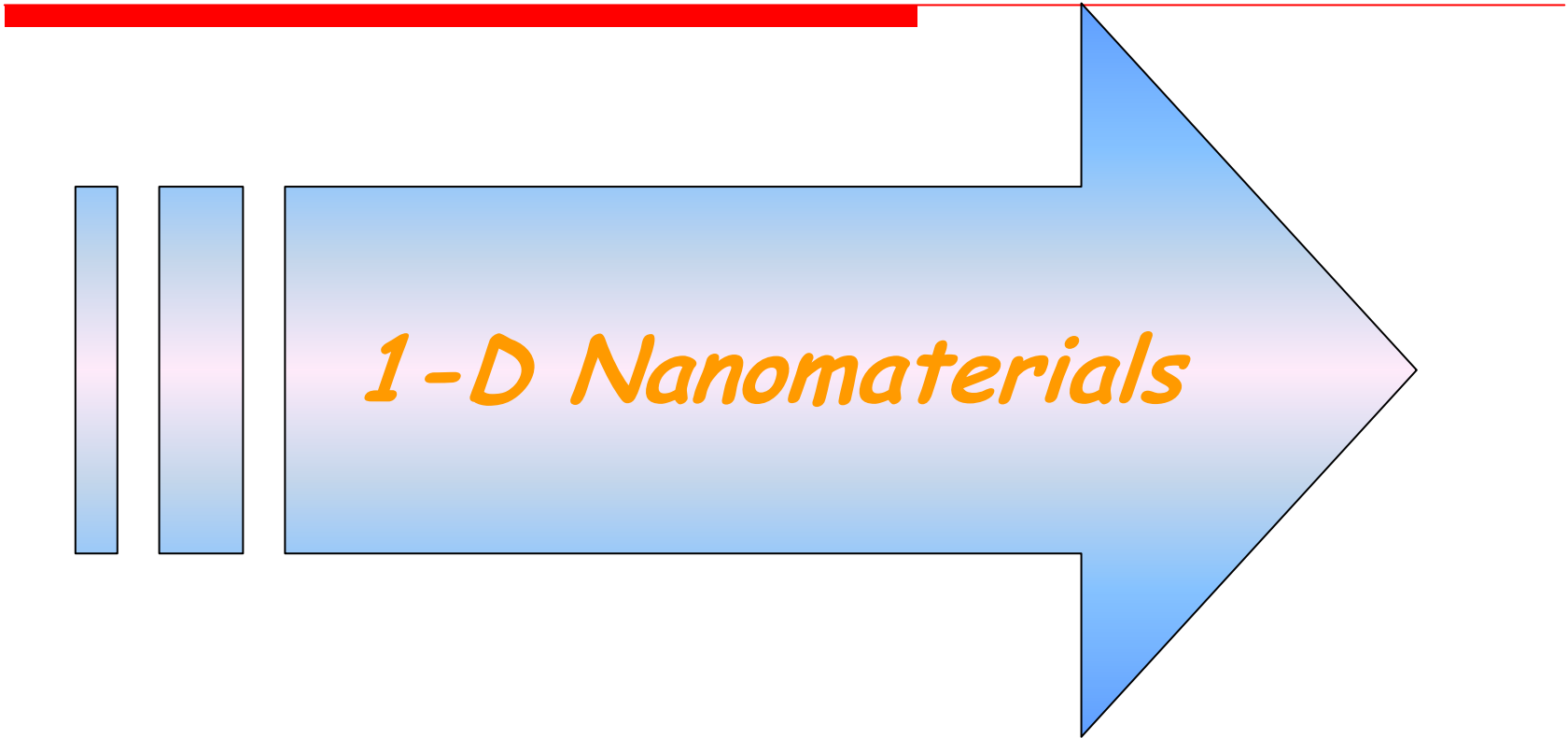


Ag



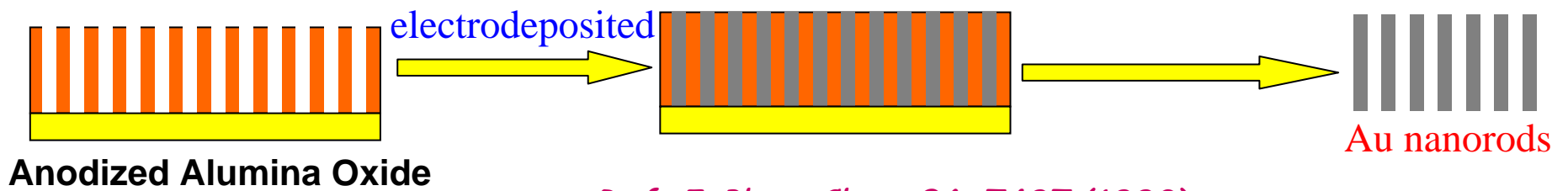
(b) Sodium citrate

Ag  
Au  
Ag-Au alloy



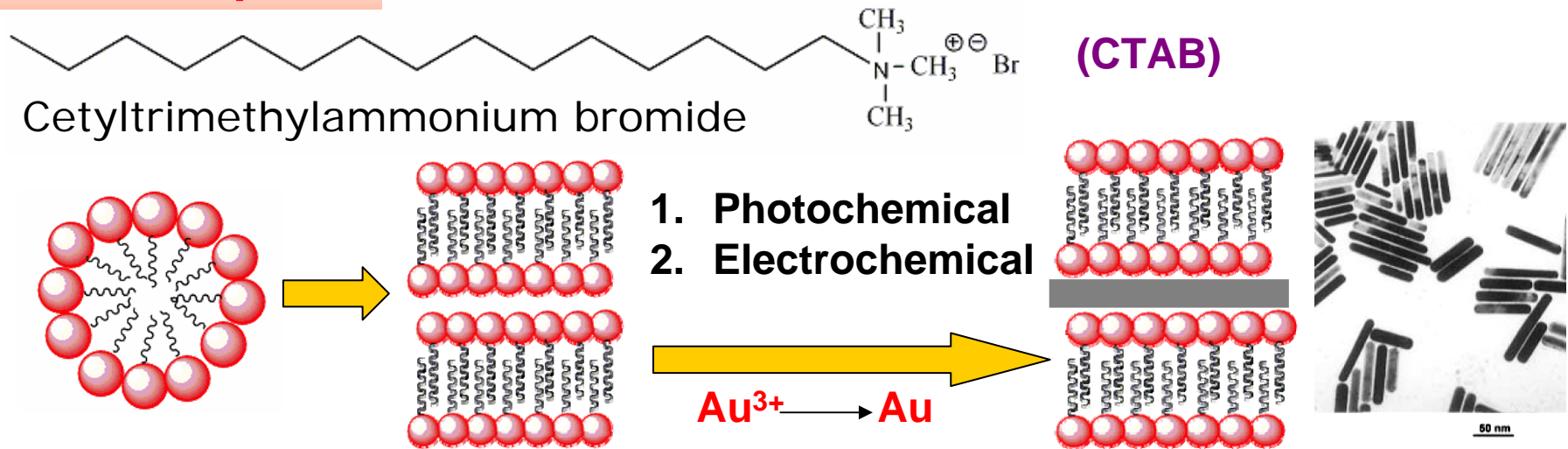
# Control of Shape 1-D Nanostructures

## Hard template



*Ref: J. Phys. Chem. 96, 7497 (1992).*

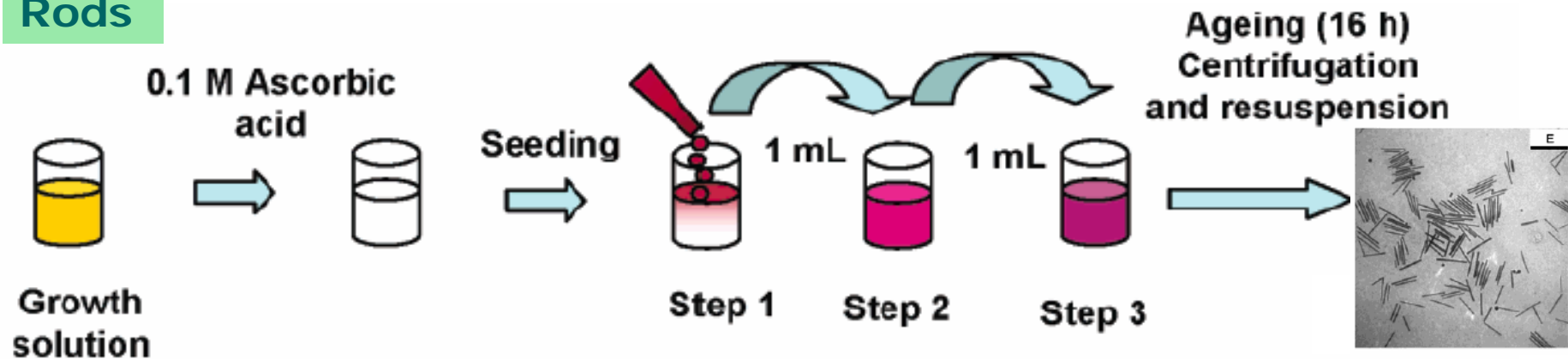
## Soft template





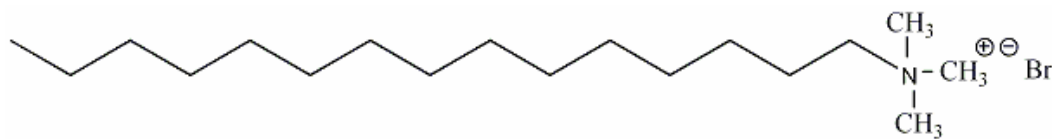
## Seed-Mediated Growth Method

### Rods

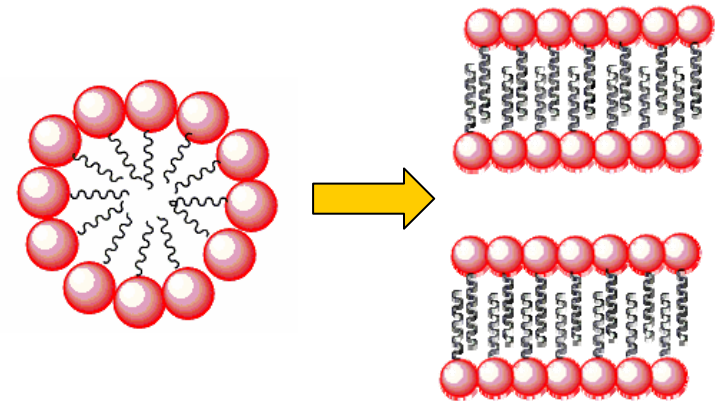


### Soft template

### CTAB



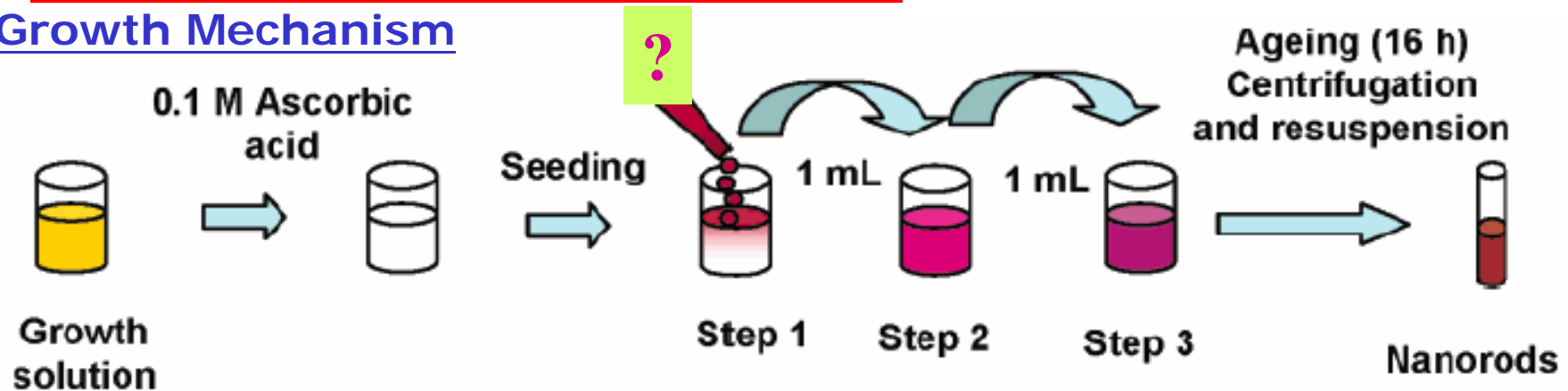
Cetyltrimethylammonium bromide



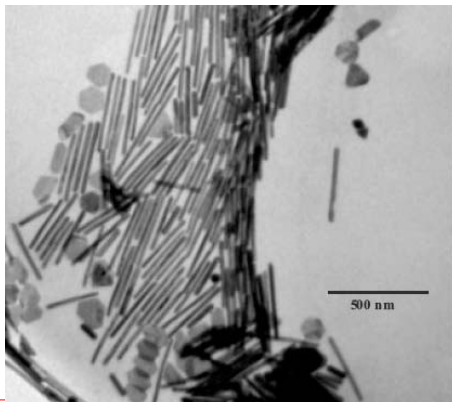


## Present Investigation aspect ratio = L/W

### Growth Mechanism



### Nanowires with micro-scale



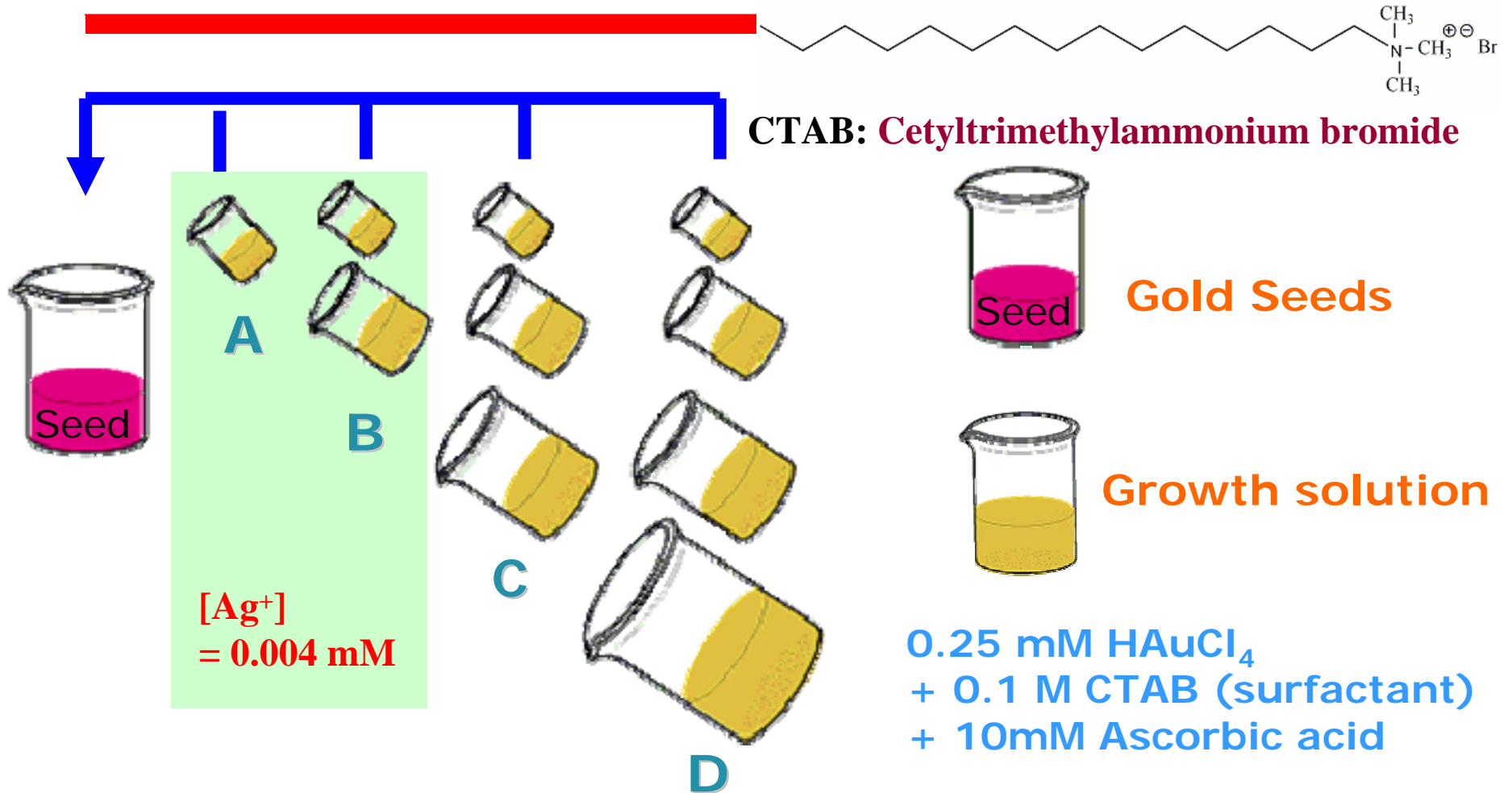
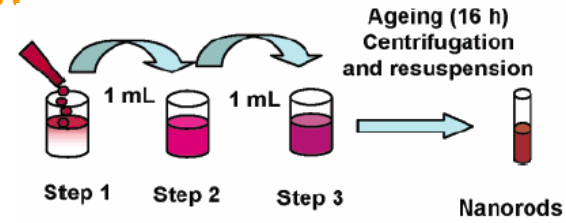
Aspect ratio = 25

Gold nanowires of micron scale don't be observed in wet-chemical method.

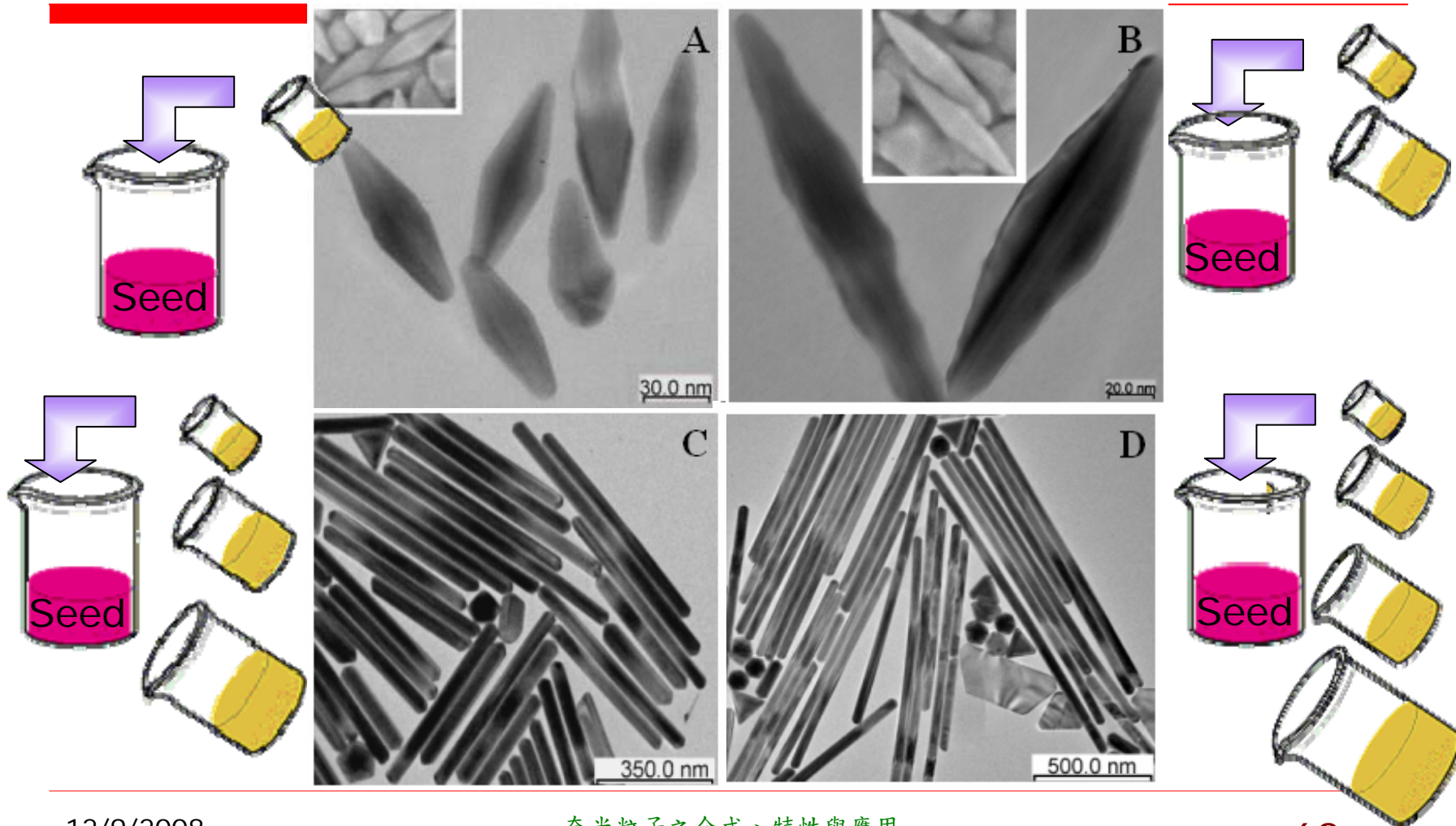
*Ref: Adv. Mater.* **15**, 414 (2003)



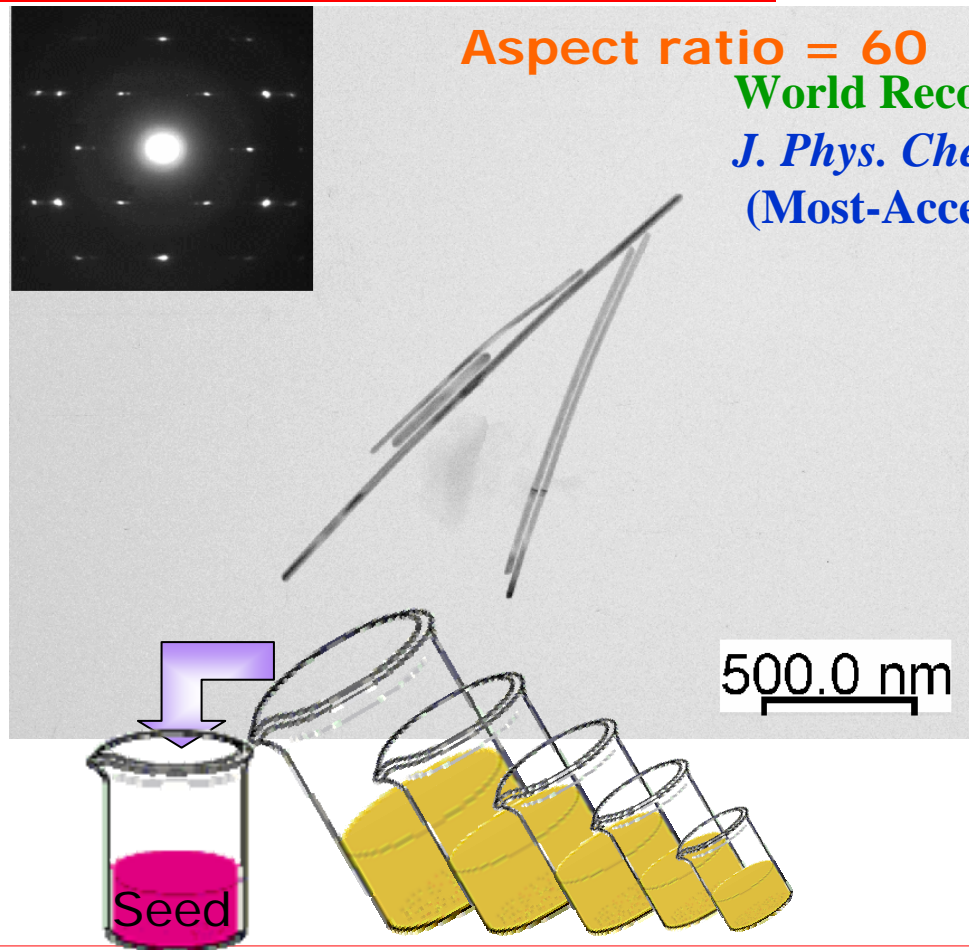
## Synthetic reactions



# Morphology



# Morphology



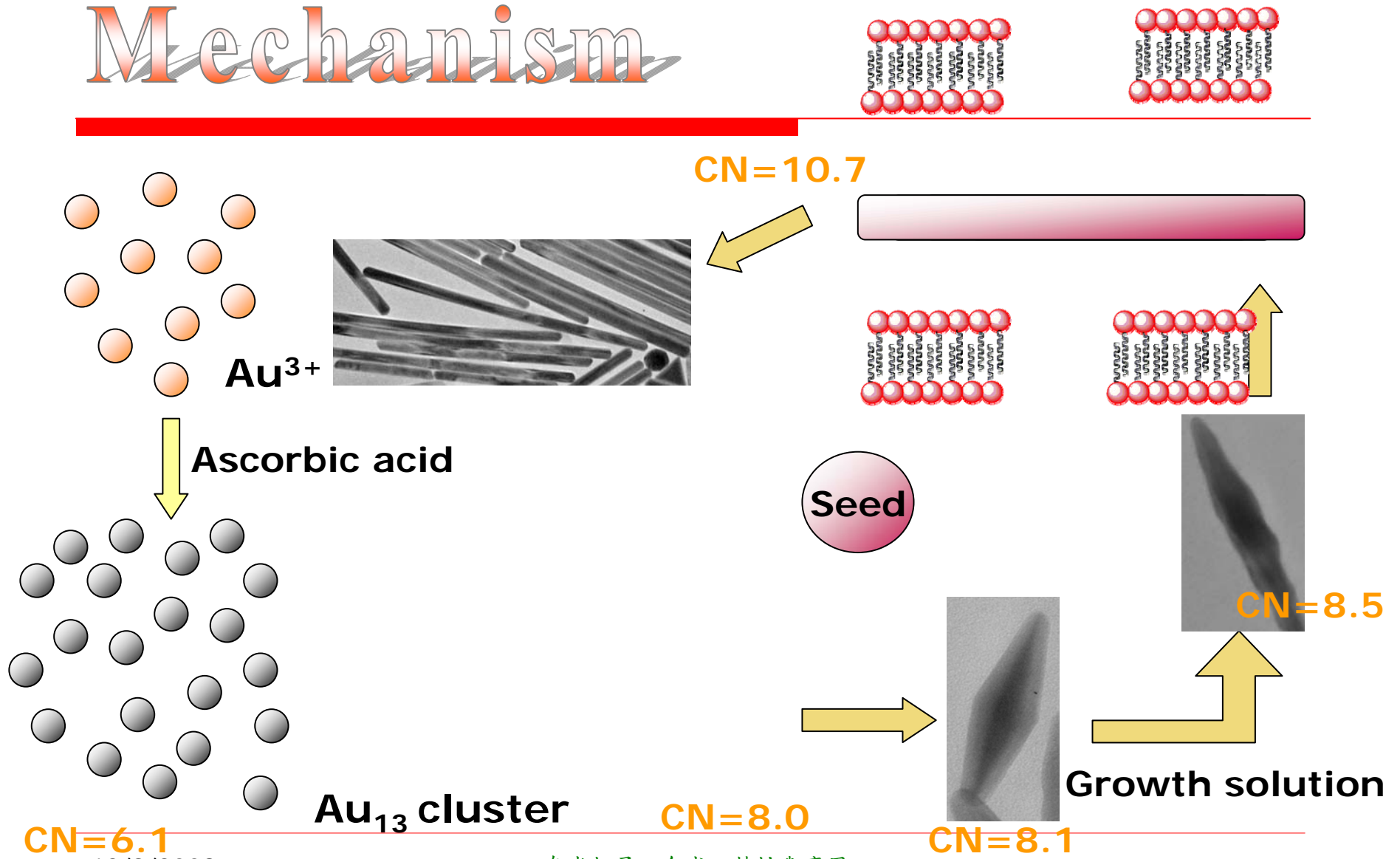
Aspect ratio = 60

World Record

*J. Phys. Chem. B* 2005, 109, 19553-19555.

(Most-Accessed Articles, 2005)

# Mechanism



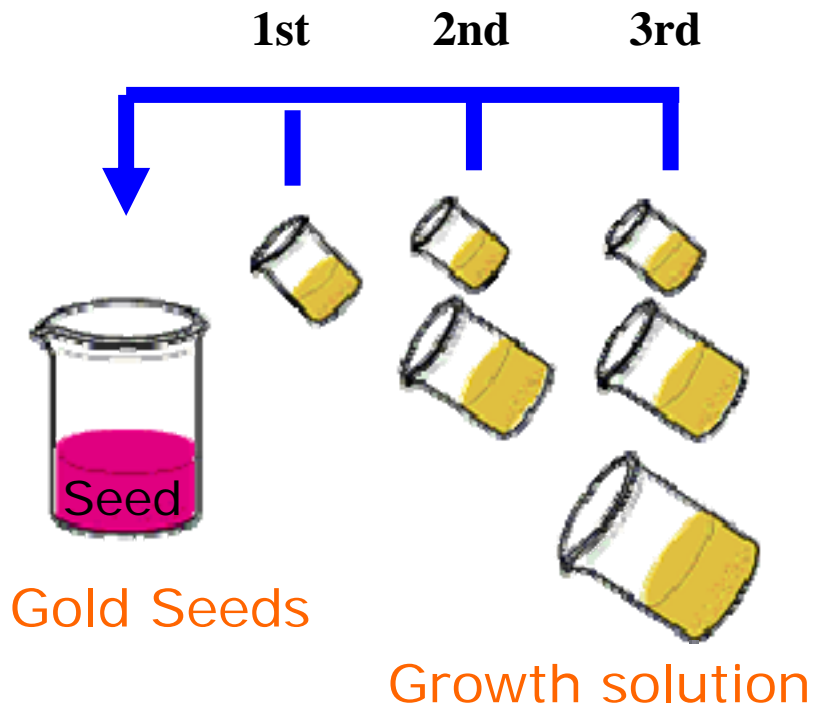
12/9/2008

奈米粒子之合成、特性與應用

62/78



## Synthetic reactions



0.25 mM  $\text{HAuCl}_4$   
+ 0.1 M CTAB (surfactant)  
+ 10mM Ascorbic acid

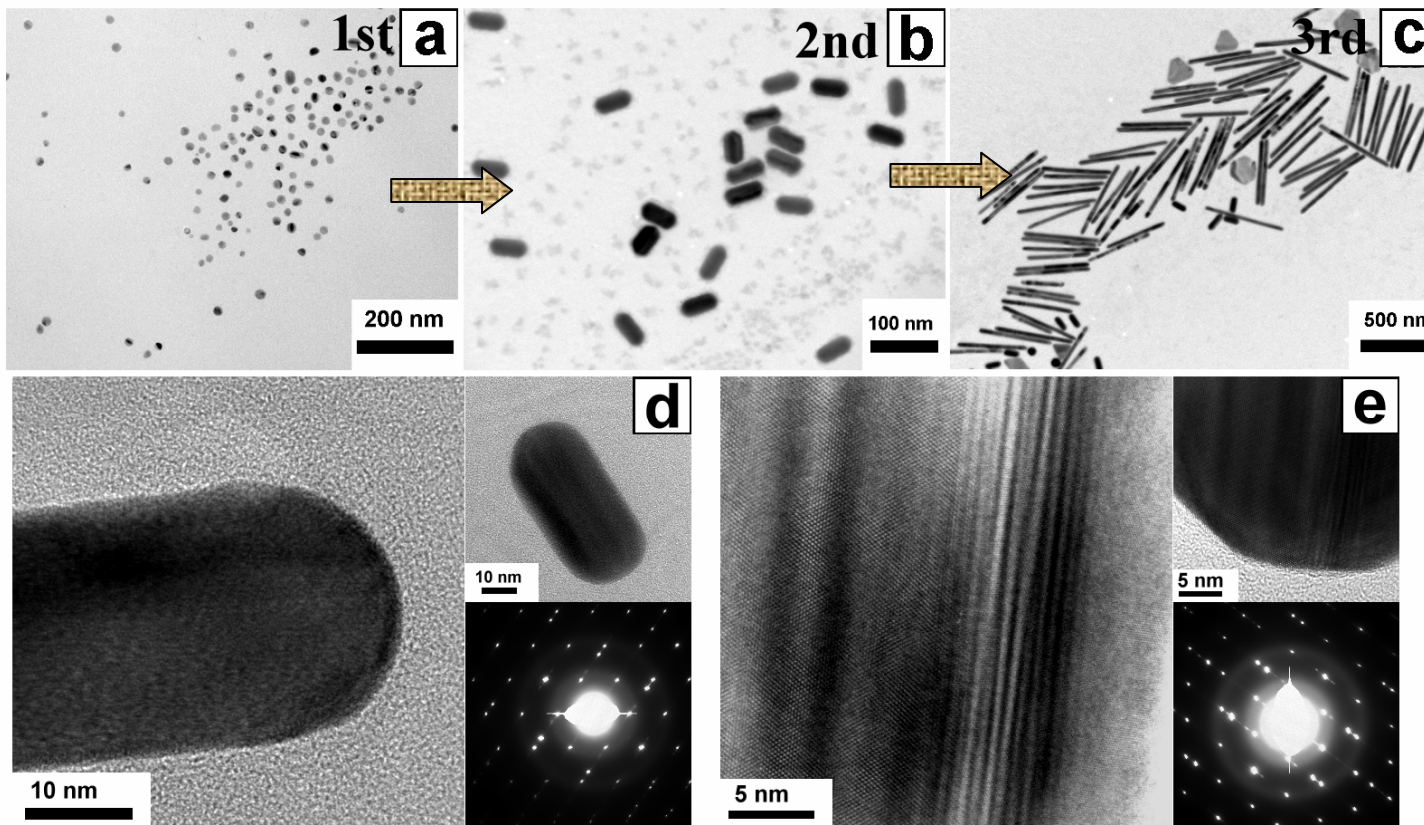
Room Temperature (28 °C)

■ Foreign ions (silver ions)

■ Thermal treatment

# Morphology

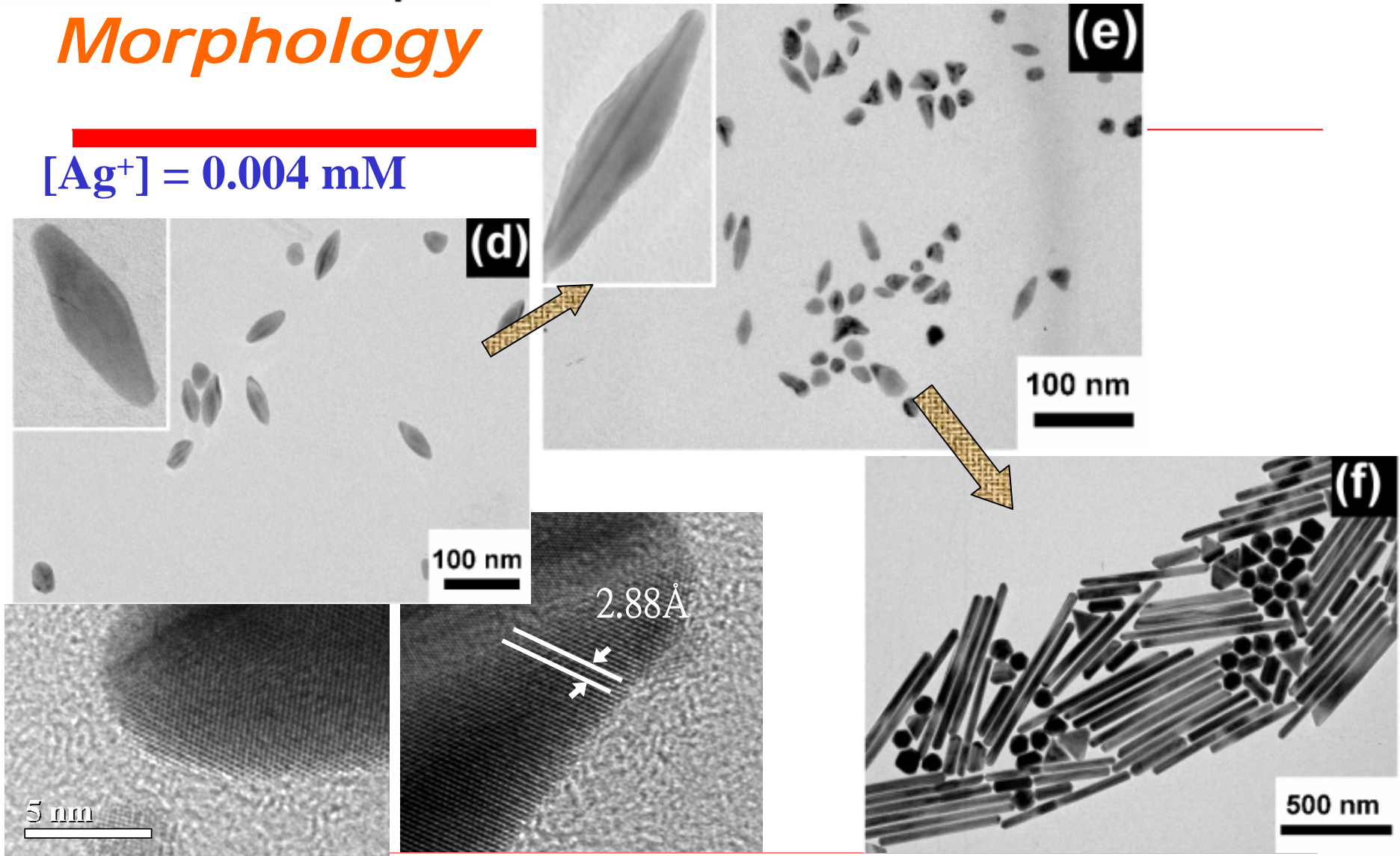
$[Ag^+] = 0 \text{ mM}$





# Morphology

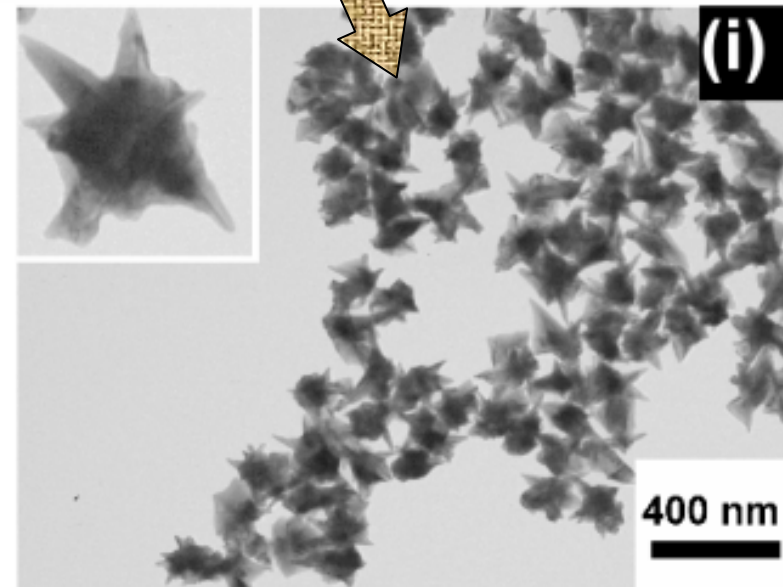
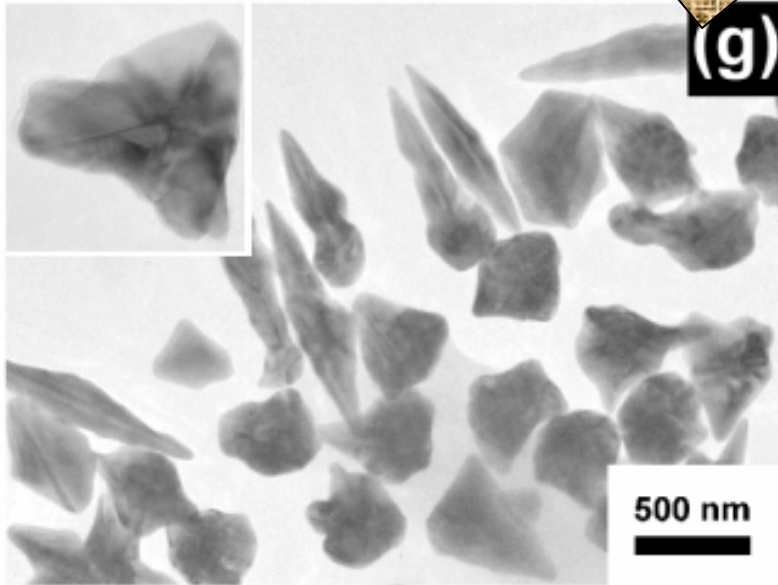
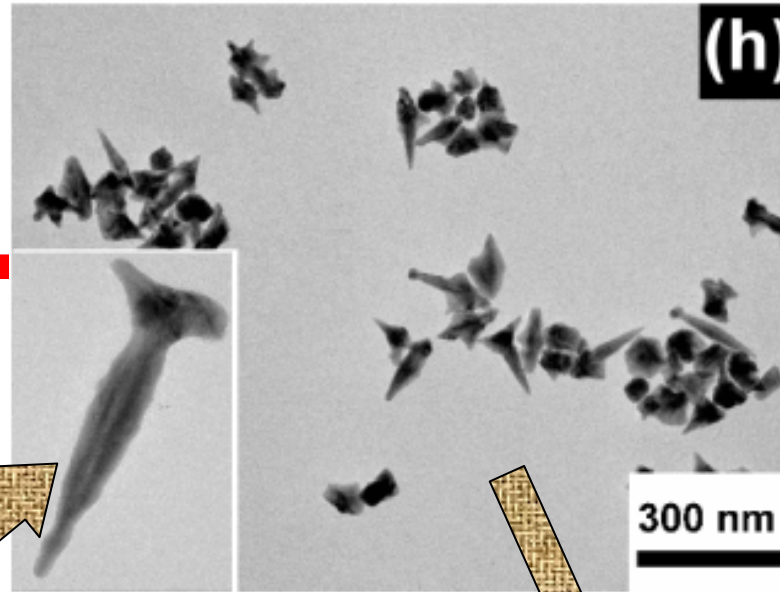
[Ag<sup>+</sup>] = 0.004 mM



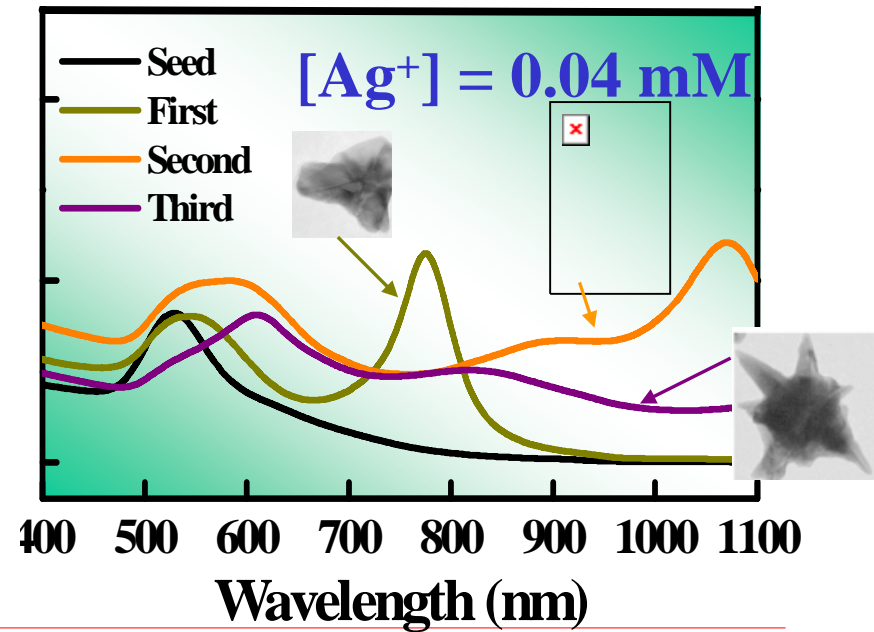
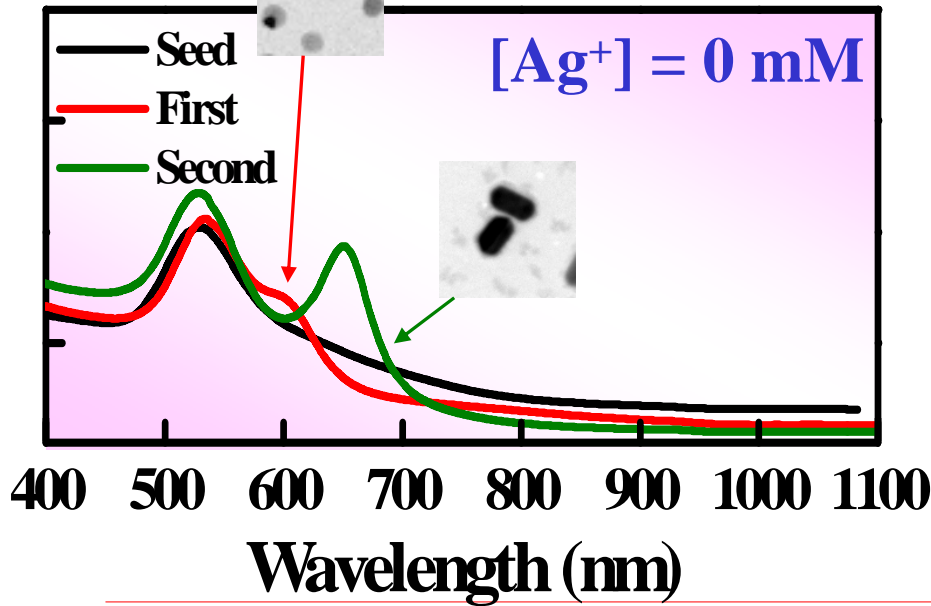
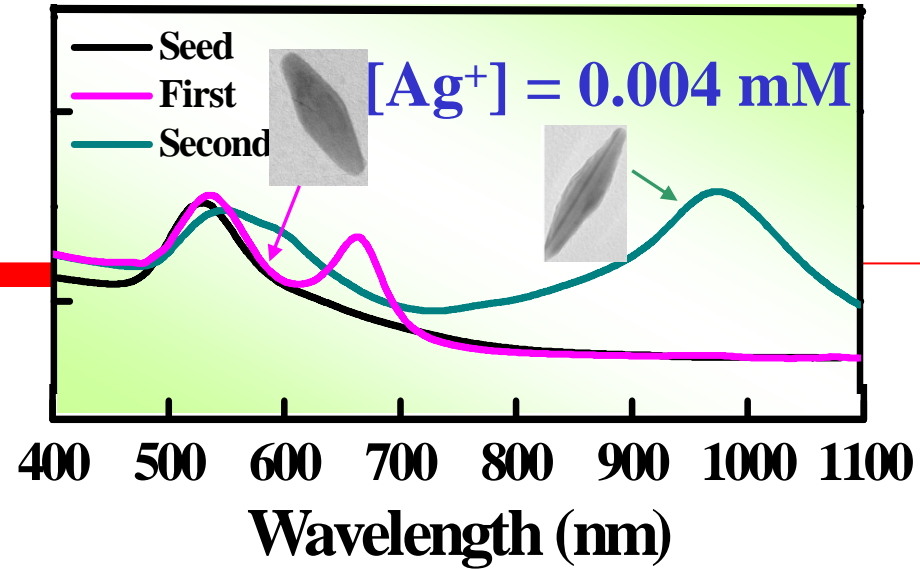
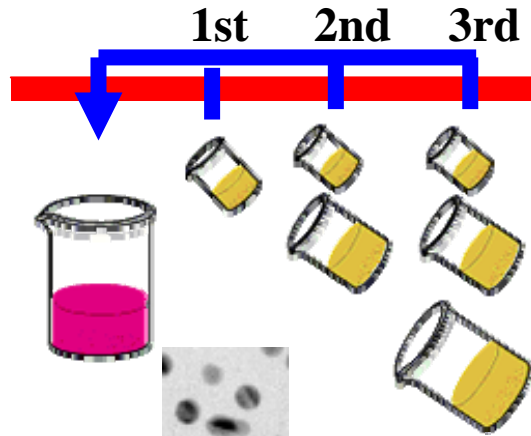


# Morphology

$[Ag^+] = 0.04 \text{ mM}$

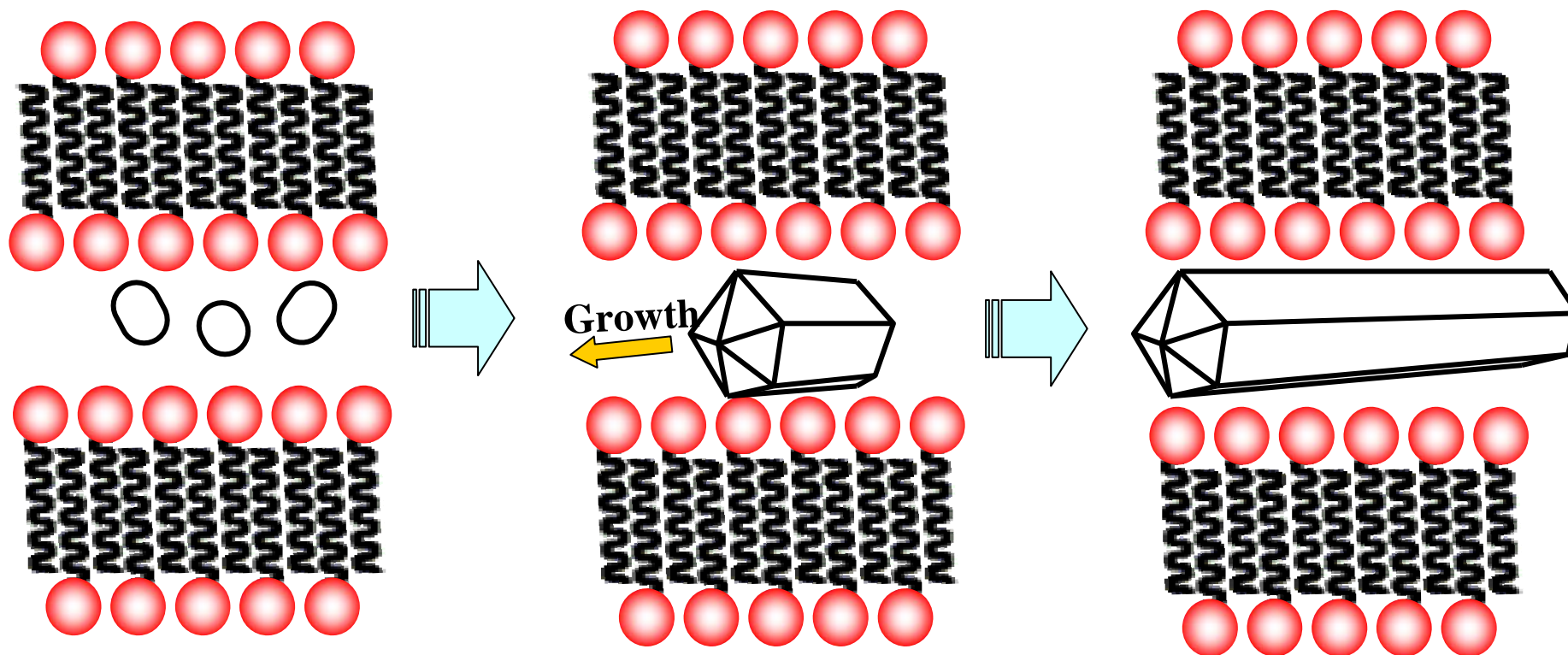


Optical properties



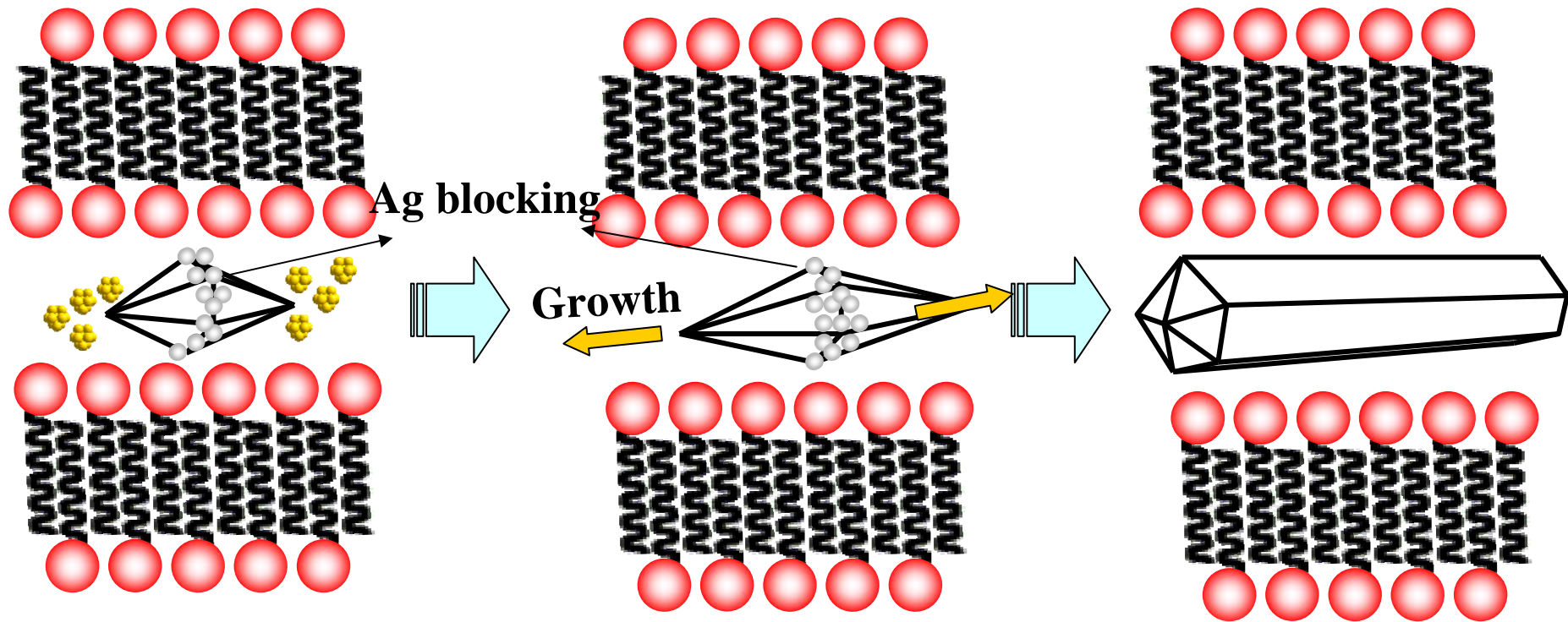
## Growth Mechanism

$[Ag^+] = 0 \text{ mM}$



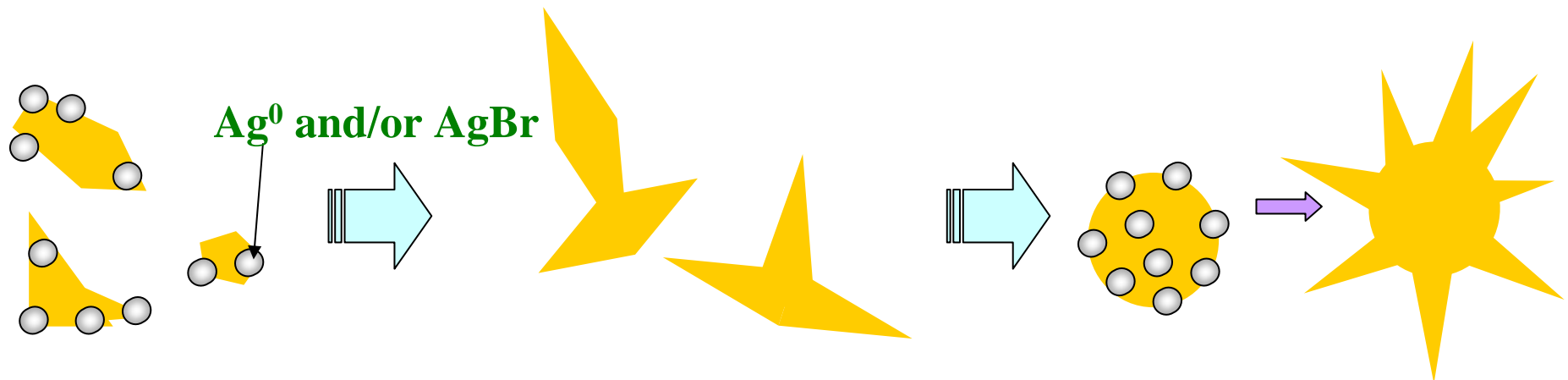
# Growth Mechanism

$[Ag^+] = 0.004 \text{ mM}$

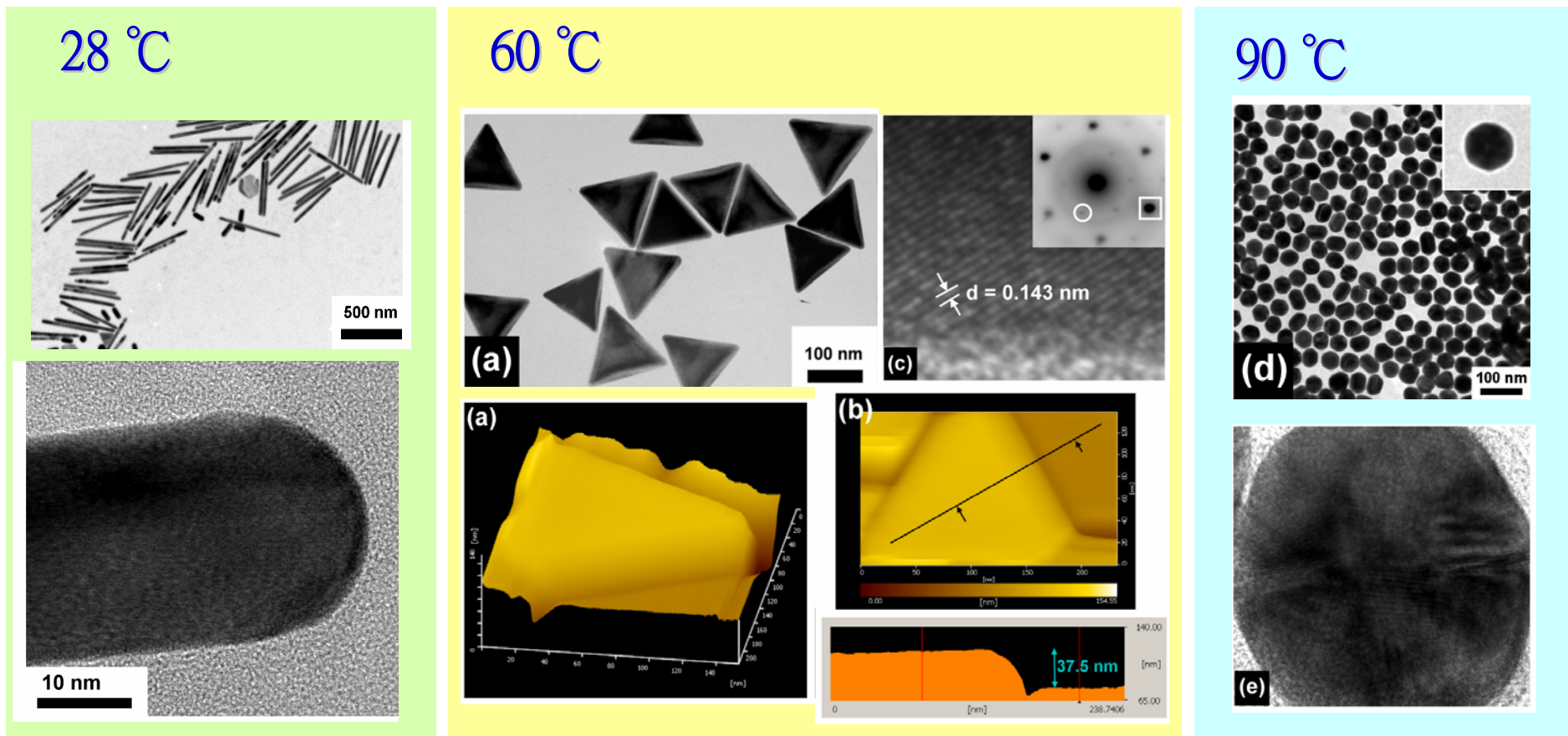


## Growth Mechanism

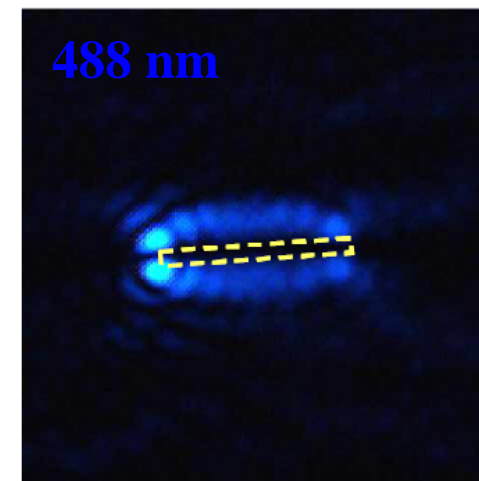
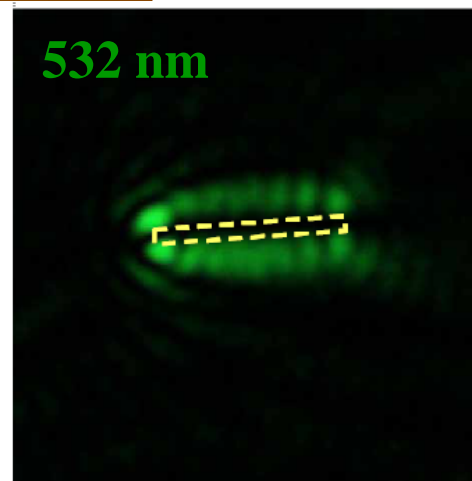
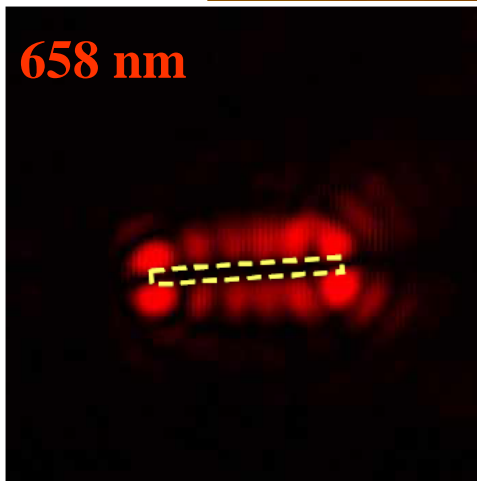
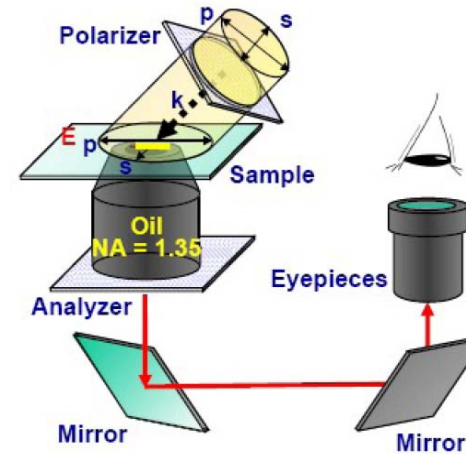
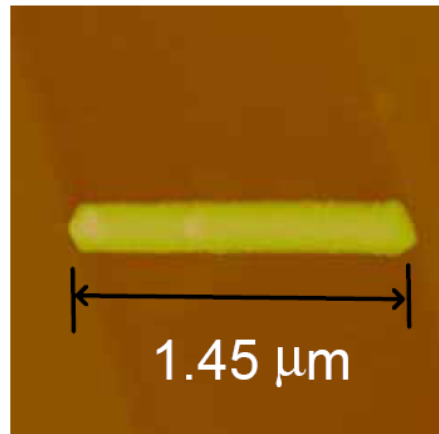
$[Ag^+] = 0.04 \text{ mM}$



## Morphology - Thermal treatment



## Plasmonic Optical Properties of a Single Gold Nanorods

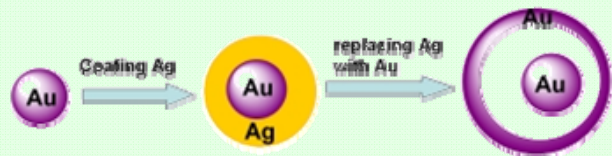




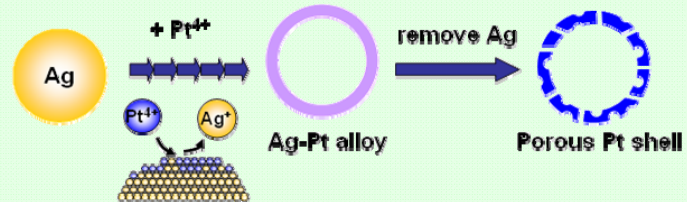
# Summary

## 0-D

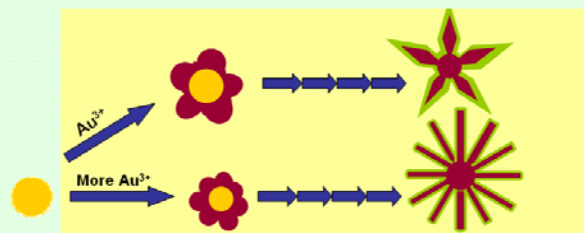
### Control of Shell Composition (Temperature)



### Catalytic Performance

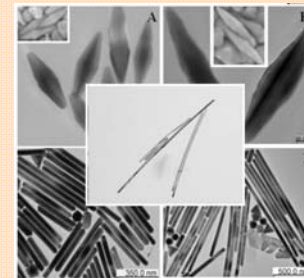


### Anisotropic Growth (Ability of reducing)

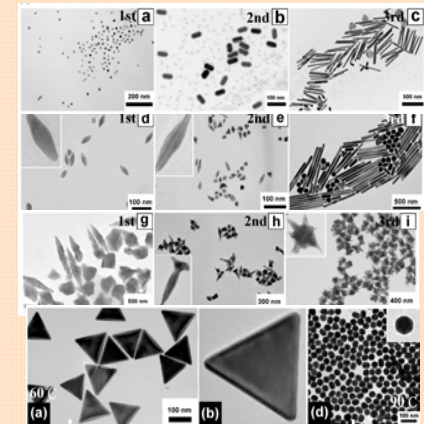


## 1-D

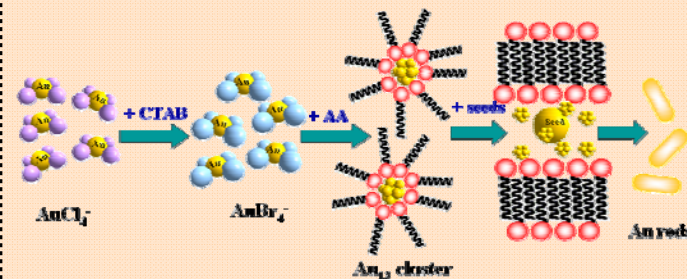
### Control of Length



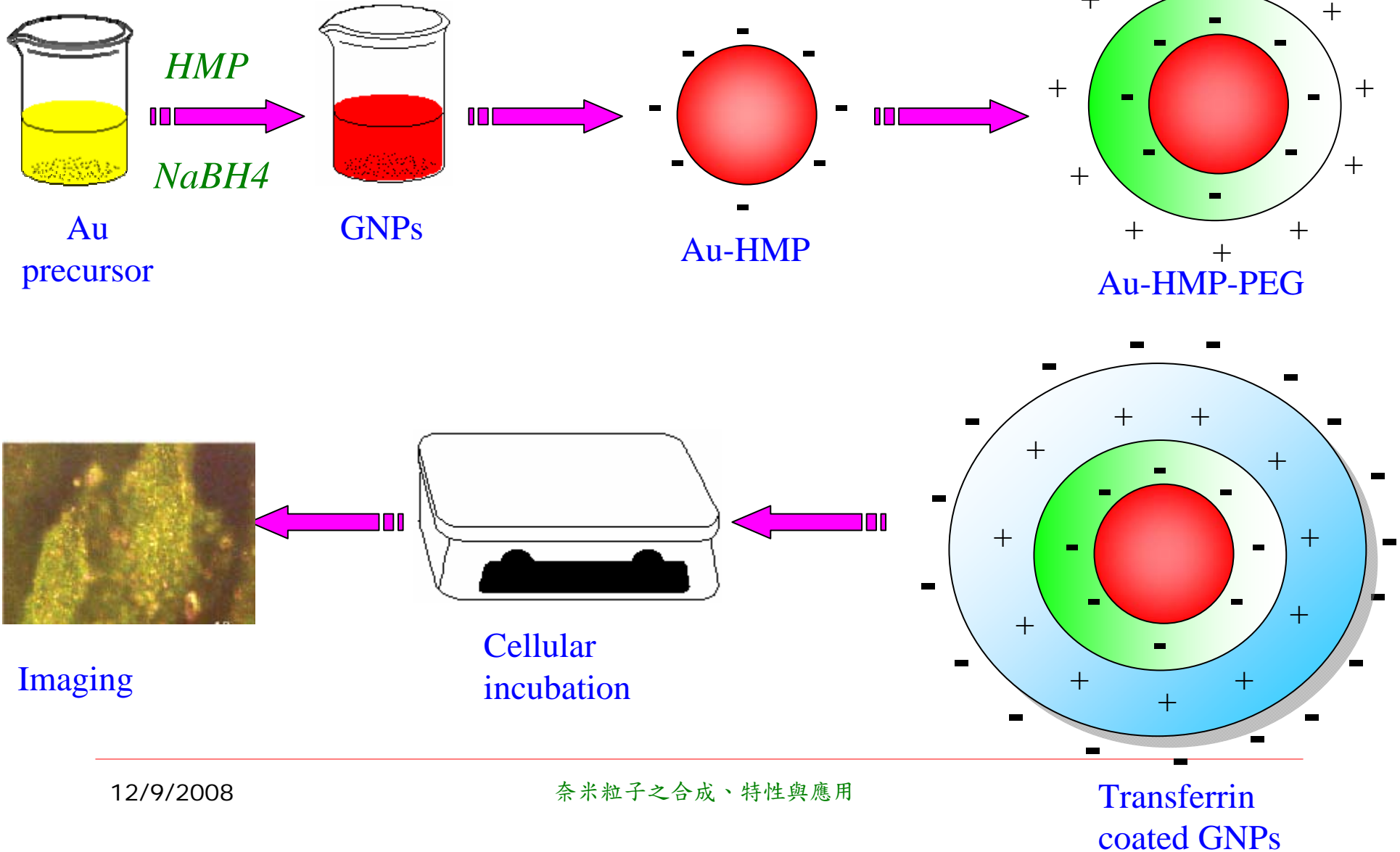
### Control of Shape



### Mechanism

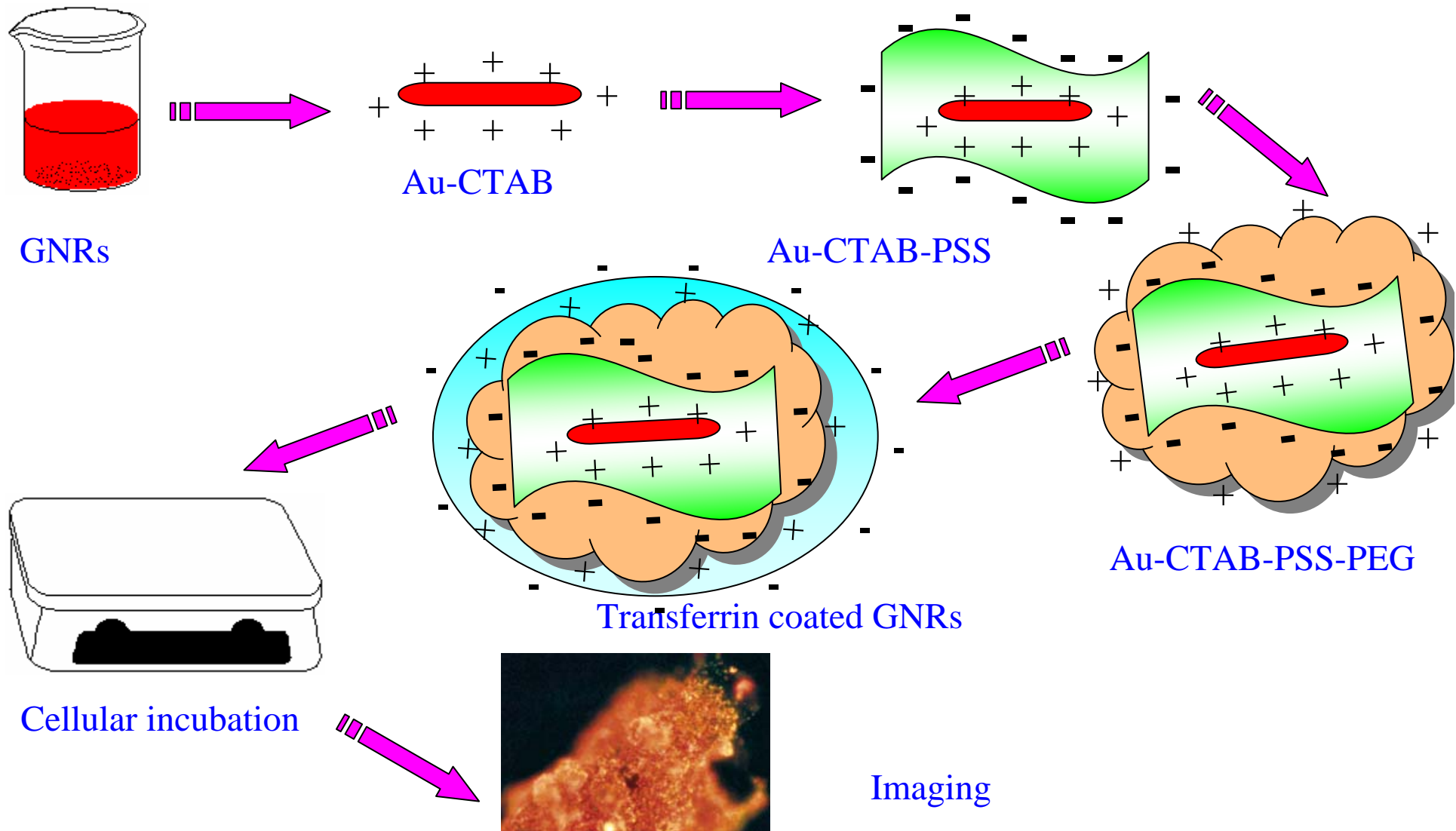


# Bioconjugation and Imaging

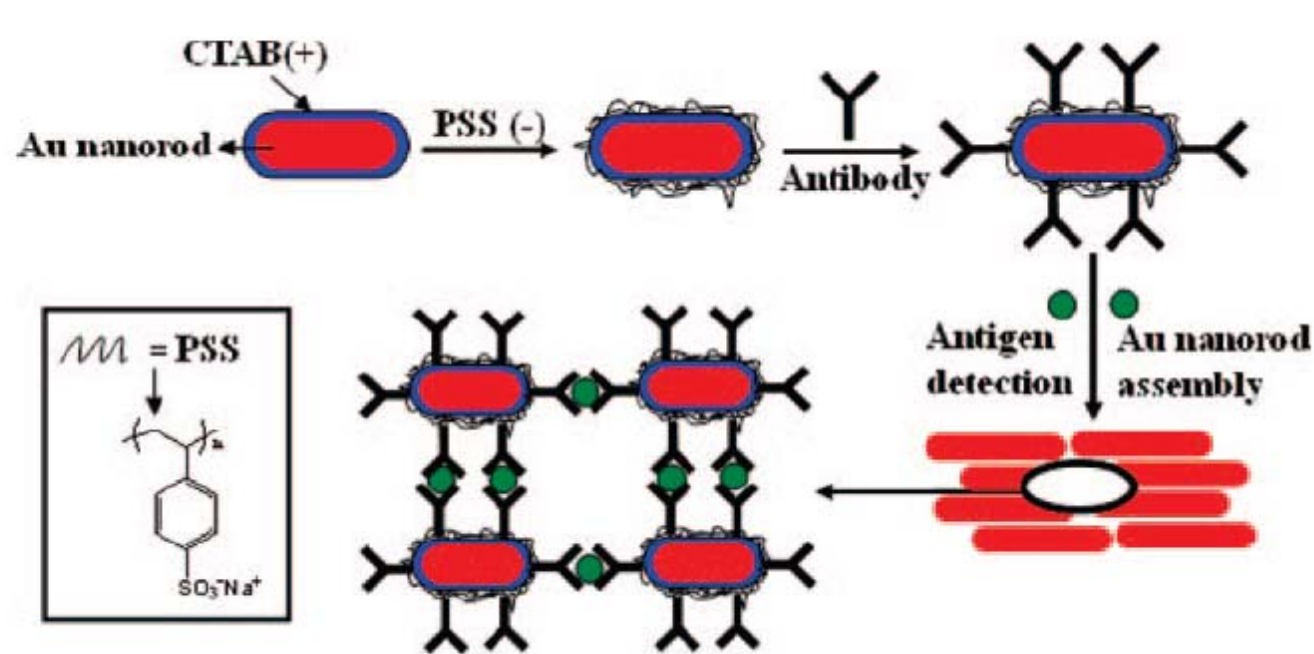




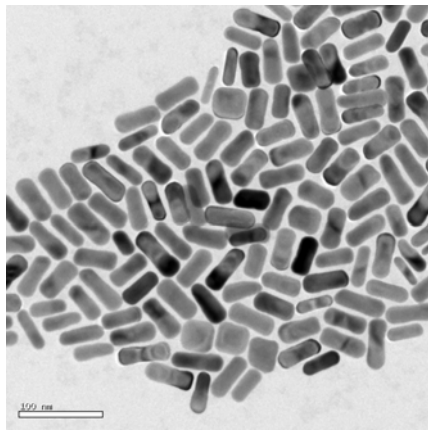
# Bioconjugation and Imaging



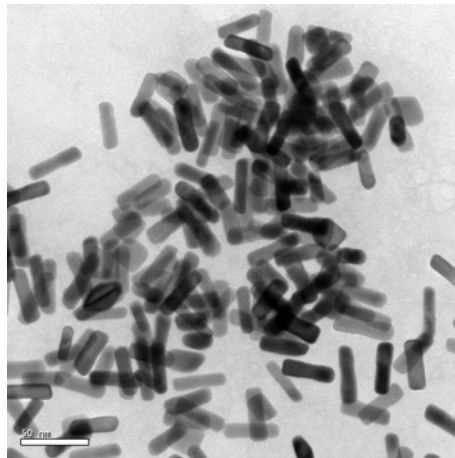
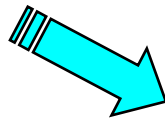
# Gold Nanorods as Biosensors



*Aggregation of GNRs by specific antibody–antigen binding process resulting in the marked wavelength shift and the reduction of intensity along with a significant widening of the plasmon*

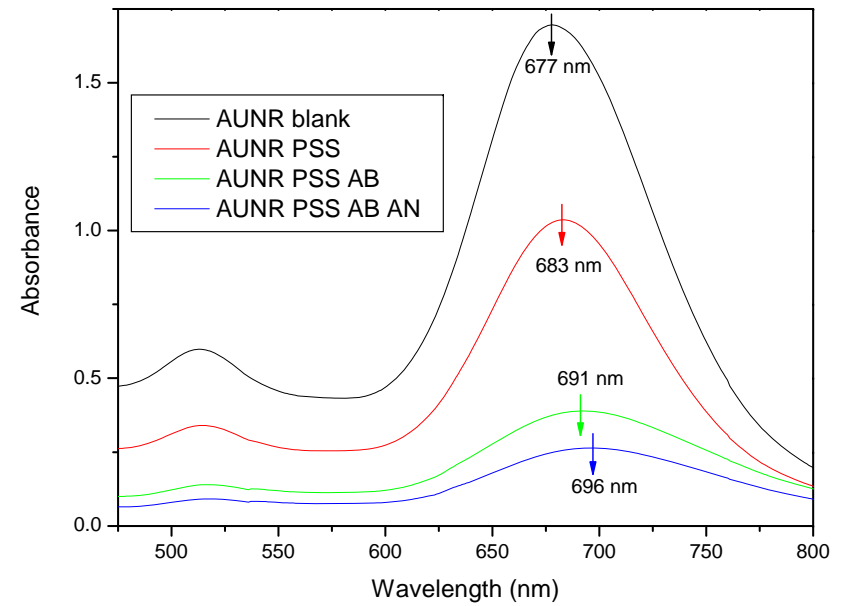


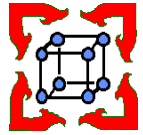
Before



After

## UV- Vis spectra





**Thanks for your attention!**