Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

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Lecture Plan

April 11, Introduction and Physical chemistry
April 18, Nanoparticles and colloids in our daily experiences
April 25, Nanoparticles and colloids in our daily experiences
May 9, Dispersion and aggregation of particles
May 16, Dispersion and aggregation of particles
May 23, DLVO theory
May 30, DLVO theory
June 6, Theory of monodispersed particles synthesis
June 13, Liquid-phase synthesis of functional nanoparticles
June 20, Liquid-phase synthesis of functional nanoparticles
June 27, Environmental catalysts
July 4, Adsorption phenomena and catalytic reaction
July 11, Catalyst preparation methods
July 18, Catalyst preparation methods
July 25, Summary

Gel-sol method

OUR INSTITUTE

PROF. SUGIMOTO, ETC.

2023/6/20

微粒子合成化学

General guidelines for monodisperse particle synthesis

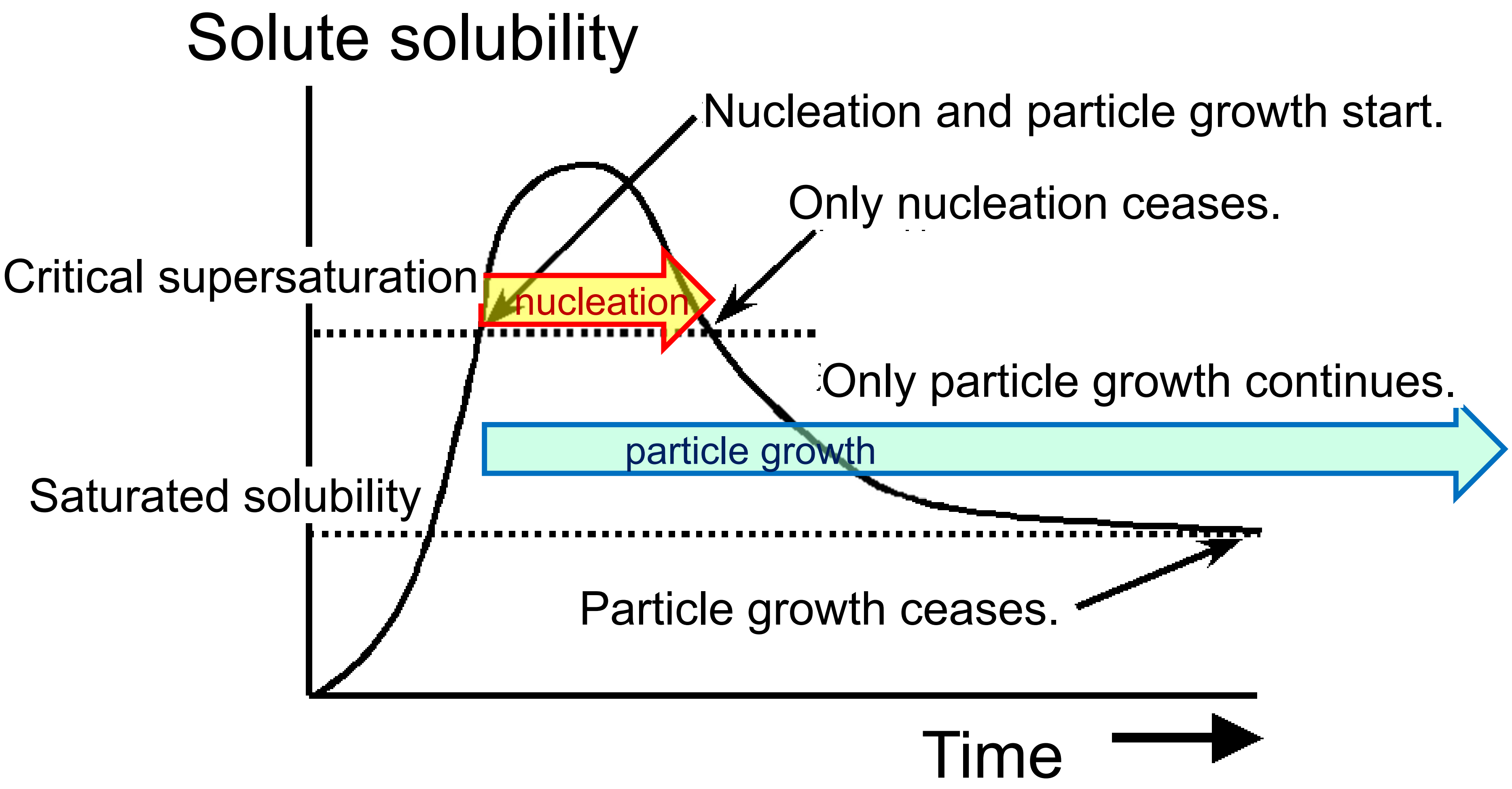
1. Separation of nucleation and particle growth

2. Prevention of inter-particle coagulation

3. Storing particle precursors

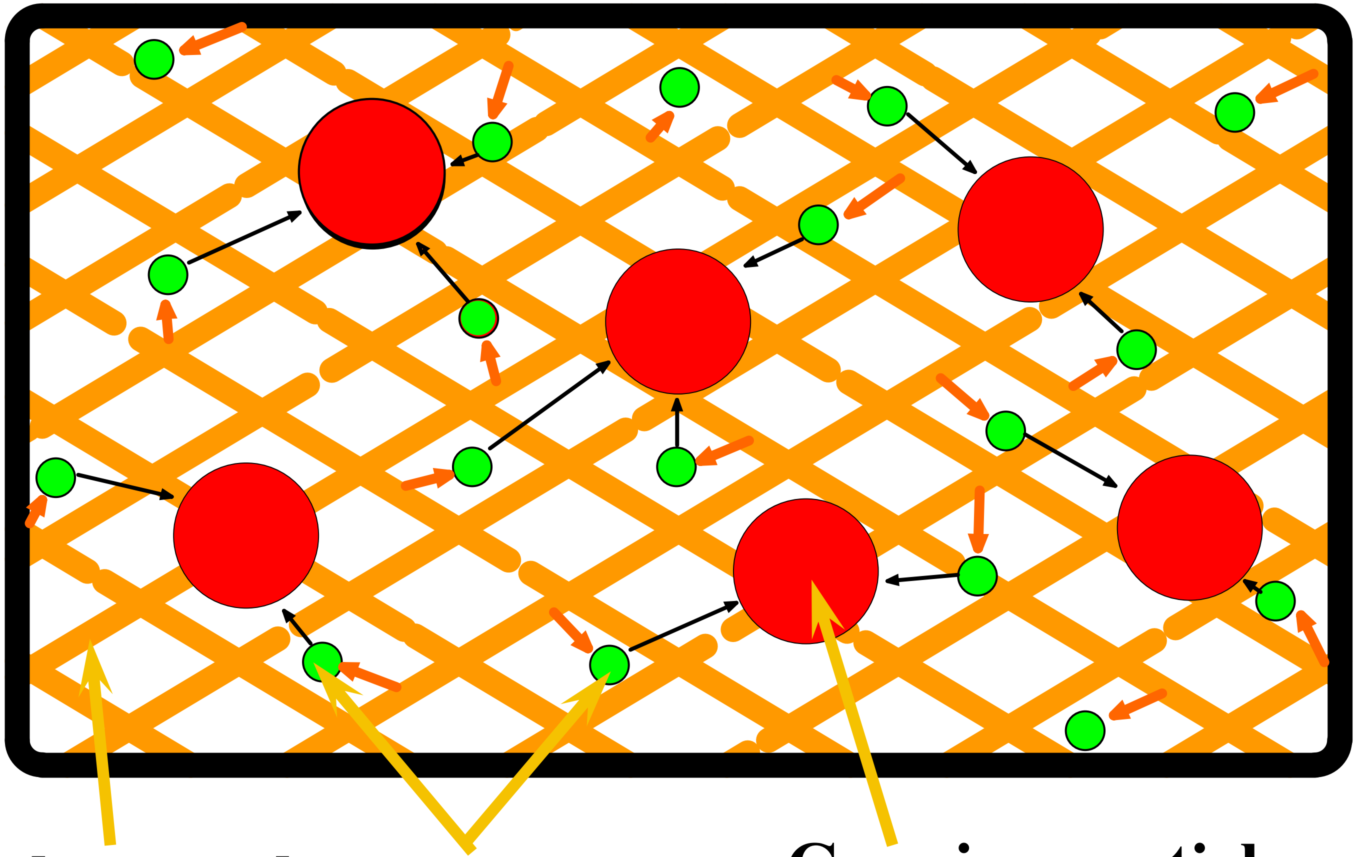
(T. Sugimoto, Adv. Colloid Interface Sci. 28, 65 (1987).)

LaMer model - kinetics



"Separation of Nucleation and Grain Growth"

Nucleation and particle growth can apparently be separated by increasing the time difference between them.



Aggregation prevention mechanism

Hematite (α-Fe_2O_3) particles are immobilized in the gel network.

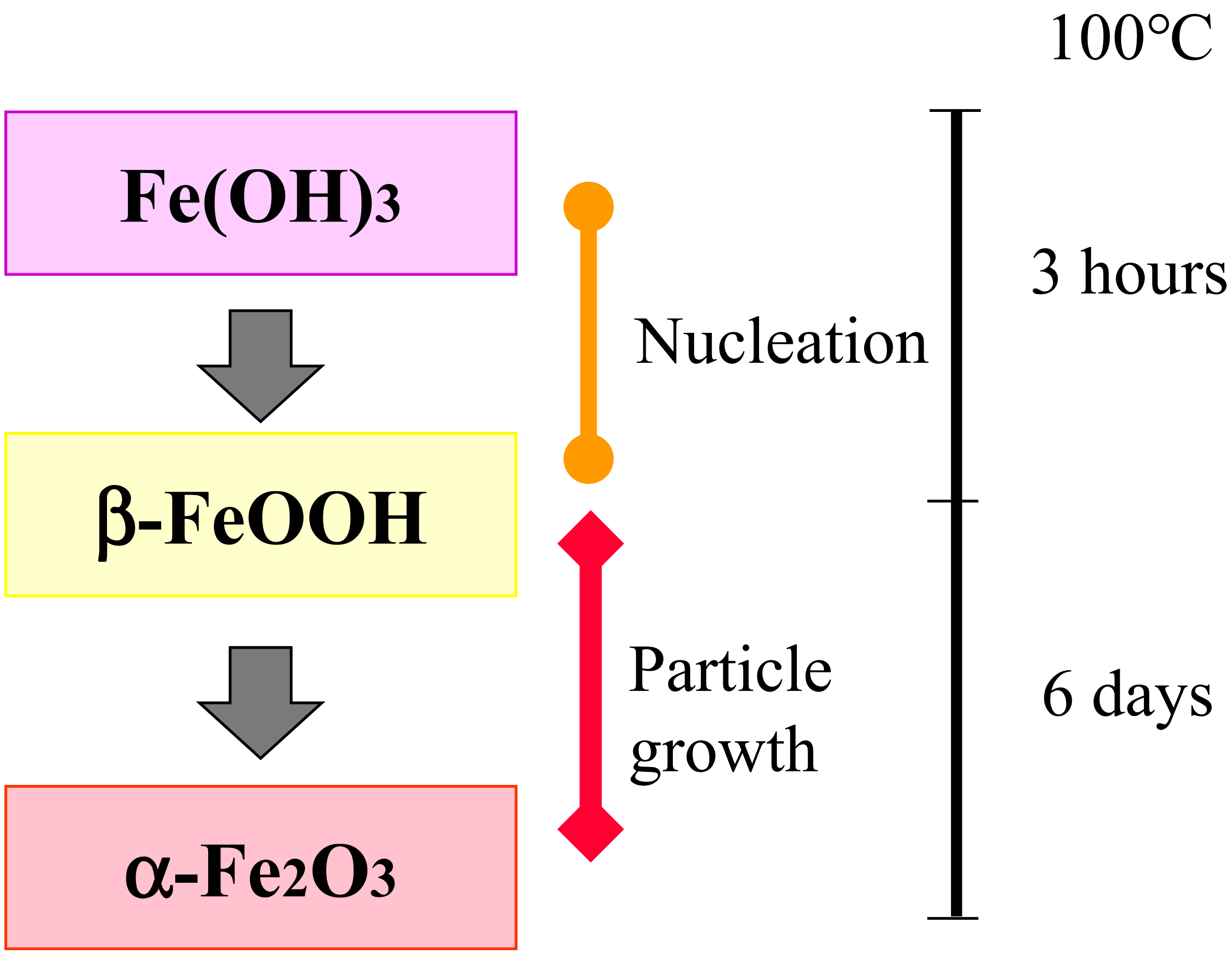
Gel network of β-FeOOH (intermediate product)

For example, in the synthesis of hematite (α-Fe_2O_3) particles, a dense amorphous iron hydroxide gel is used as a precursor solid, and the phase transition occurs in two steps: amorphous iron hydroxide → hydrated iron oxide (akaganite) → hematite. do. In this case, the intermediate product, iron oxide hydrate, serves as a reservoir for the hematite precursor and has an effect of suppressing aggregation. In addition, the control of the shape of hematite is achieved by the coexistence of adsorptive ions such as sulfate groups and phosphate groups.

one solution ：

Gel-sol method

Preparation of monodisperse hematite particles



Actual experiment

2 *M* $FeCl_3$ 100 ml

6.0 *M* NaOH 90 ml

0.9 *M* $Fe(OH)_3$ + 0.1 *M* Fe^{3+} **pH ~ 2.1**

100℃, 8 days

β-FeOOH

α-Fe_2O_3 pH ~ 0.6

Large-scale synthesis of monodispersed hematite particles

1) Set the solution conditions (temperature, pH, etc.) for generating hematite particles

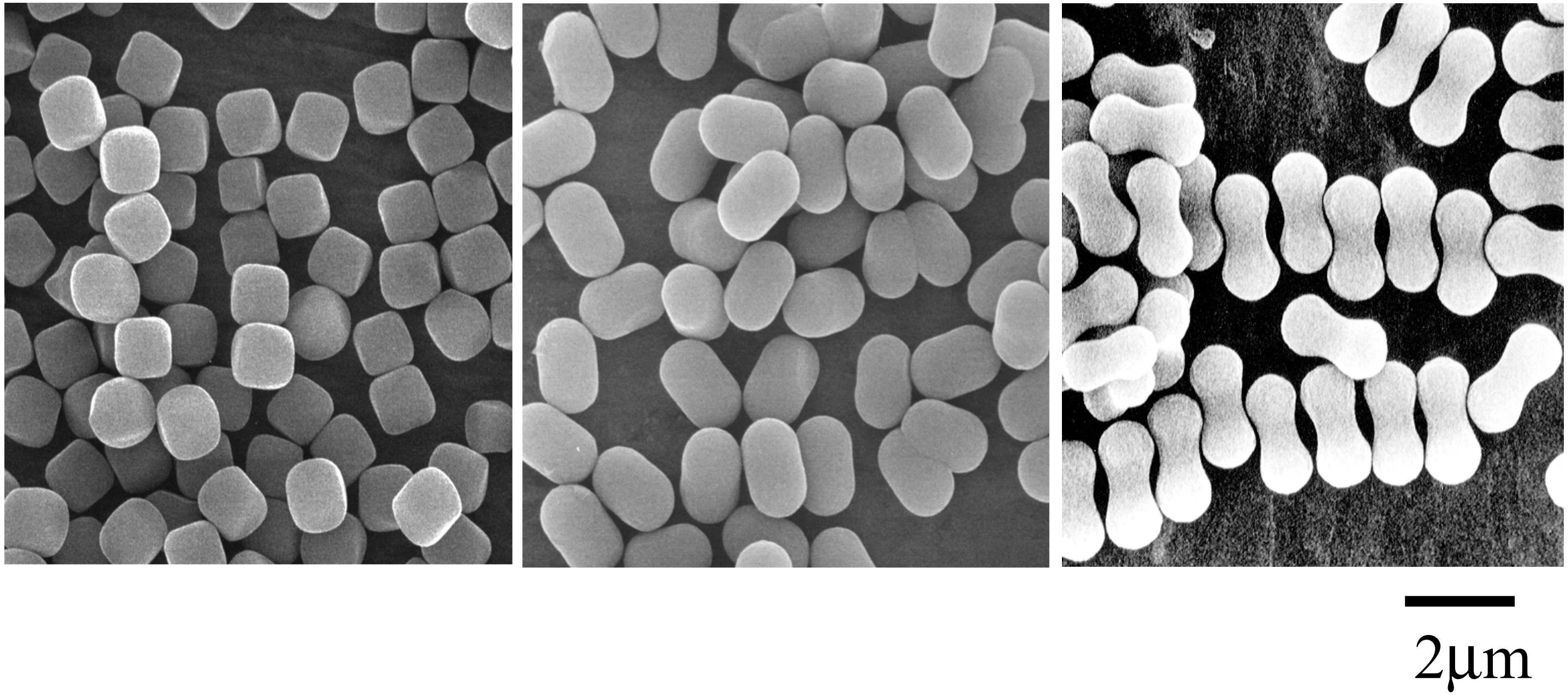
2) β-FeOOH is formed as an intermediate compound and finally only hematite is produced without any by-products

3) nucleation ends only in the first maximum 8 hours, after which the particles grows for a week

4) Particles are trapped in a gel network of ferric hydroxide and β-FeOOH, preventing them from easily moving like Brownian motion, thereby completely suppressing aggregation between particles.

By Gel-sol method

Synthesis of monodisperse hematite particles

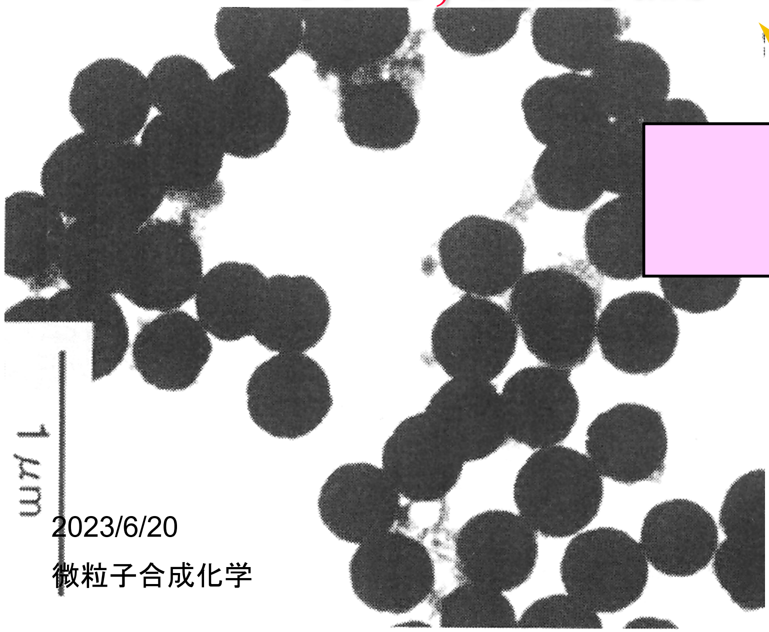


Synthesis of Uniform Metallic Nickel Particles from Concentrated Nickel Hydroxide Suspension

$Ni(OH)_2$ suspension
With PEG

↓ 50℃, 12 hours ← NaH_2PO_2 addition

Ni



- **0.1 M $Ni(OH)_2$ + 4 M NaH_2PO_2**
- **0.5 wt% PEG（400,000）**

Synthesis of spindle-shaped uniform titania particles by gel-sol method

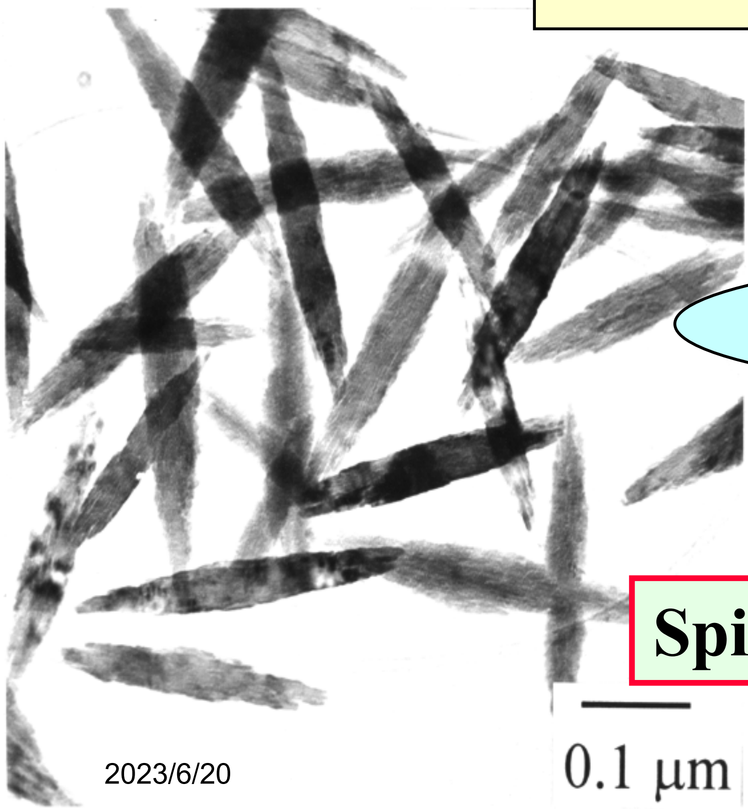
Titanium isopropoxide: 0.5 M
Triethanolamine: 1.0 M
（inhibitor to rapid hydrolysis）

↓ ⇐ 2M NH3 aq.

Highly viscous gel-like substance

↓

Spindle type uniform titania particles

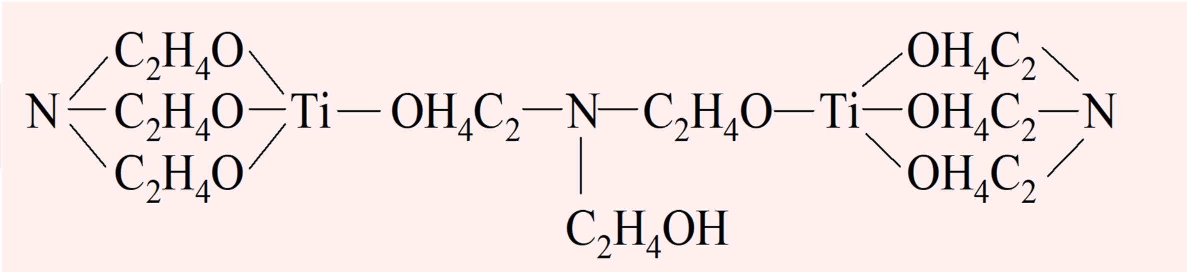


Titanium(IV) isopropoxide (TIPO) $[Ti(OC_3H_7)_4]$

↓ ← Triethanolamine (TEOA) $[N(C_2H_4OH)_3]$

TIPO:TEOA = 1:2
($[TIPO]_0$ = 0.25 mol dm^{-3})

Stable complex



↓ ← H_2O (+$HClO_4$ or + NaOH)

← Shape controller

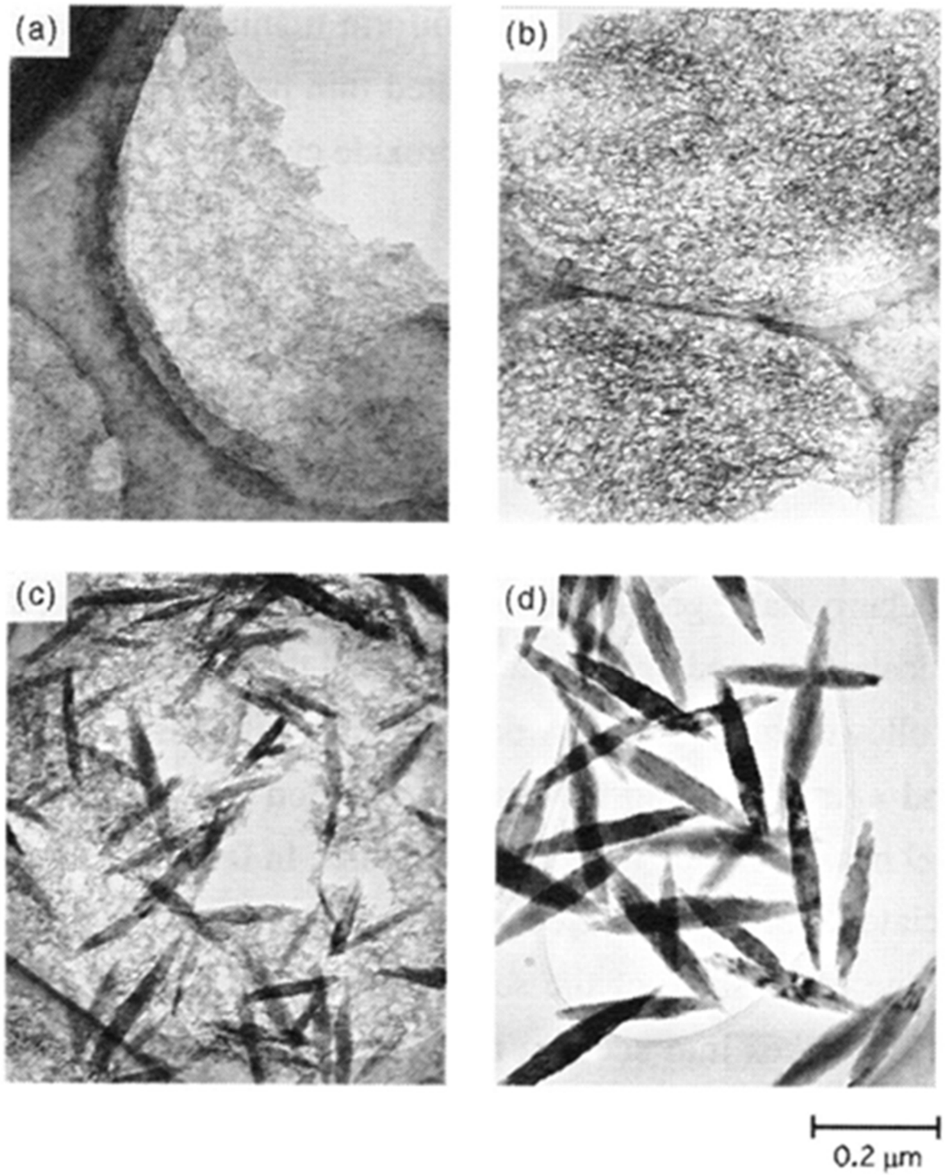
1st aging (100°C, 1 day)

$Ti(OH)_4$ gel

↓ 2nd aging (140°C, 3 days)

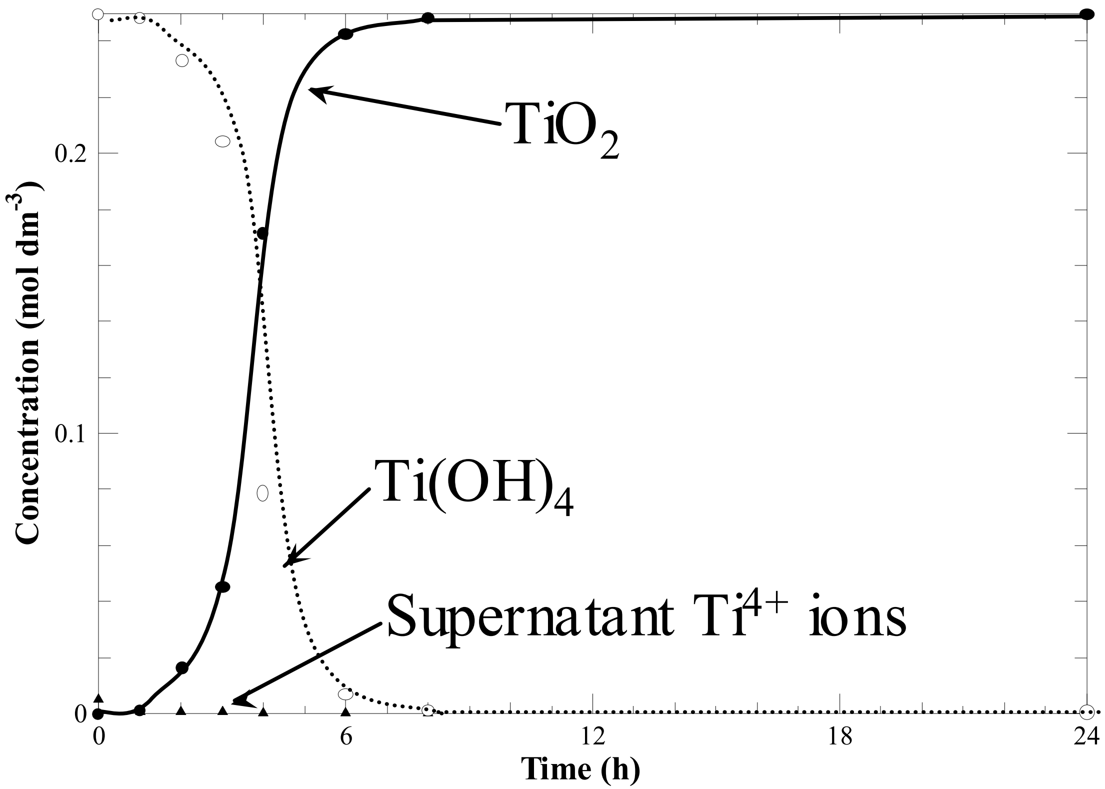
TiO_2 (anatase)

Synthesis scheme of monodisperse titanium oxide (titania) particles by Gel-Sol method



Time evolution in titania particle synthesis
(a) 0, (b) 1 day, (c) 2 days, and (d) 3 days

② Concentration changes of TiO_2, $Ti(OH)_4$, and supernatant Ti^{4+} ions during the 2nd aging (pH = 10)



Phase transformation: $Ti(OH)_4 \longrightarrow TiO_2$

Monodispersed metal sulfide particles

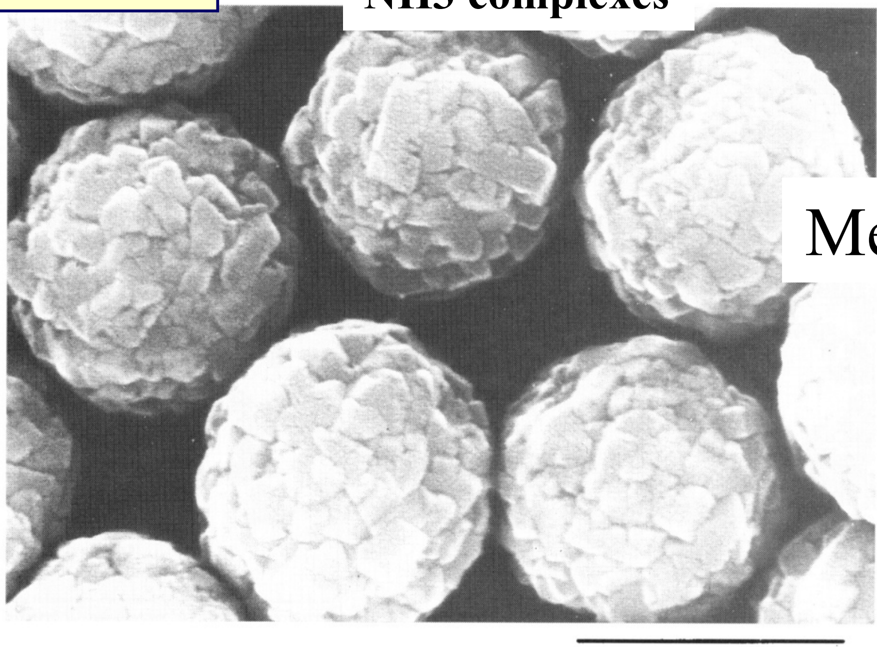
Reservoir of M^{2+}

Reservoir of S^{2-}

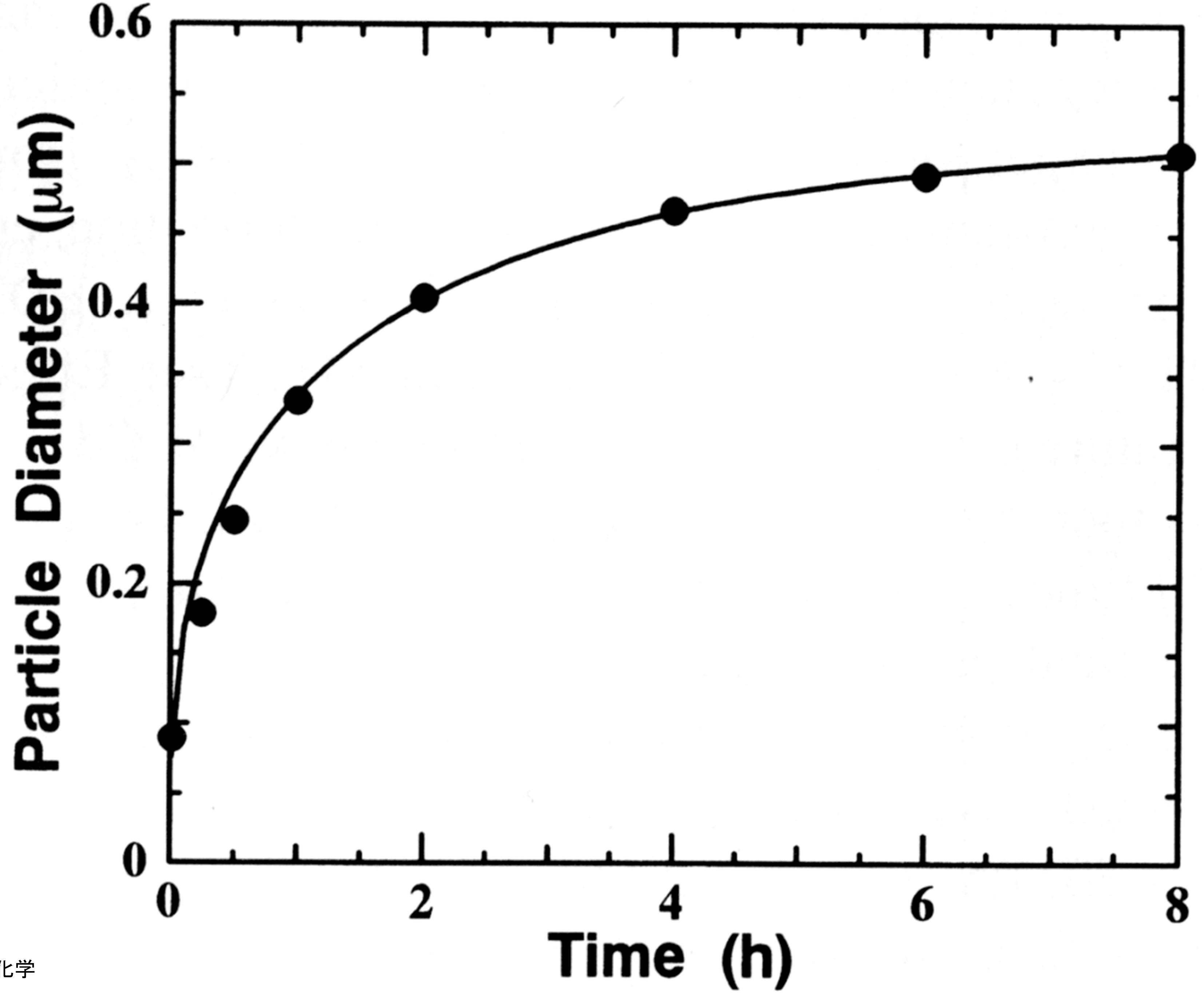
$Cd(OH)_2$ or Metal chelates	⇒	$M(NH_3)_n^{2+}$	⇌ $M^{2+} + S^{2-}$ ⇌	TAA
		NH3 complexes		Thioacetamide

↓ Gelatin

Metal sulfides



M=Cd, Zn, Pb etc.


0.6
0.4
0.2
0
Particle Diameter (μm)
0
2
4
6
8
Time (h)

$BaTiO_3$, $SrTiO_3$

Synthesis of perovskite oxides

Direct synthesis from the liquid phase is possible using the gel-sol method.

Commercial products are made by solid phase reaction.

Synthesis method of $BaTiO_3/SrTiO_3$ fine particles

gel-sol method

$Ti[OCH(CH_3)_2]_4$
$N(CH_2CH_2OH)_3$
(solution-A)

$Ba/Sr(OH)_2 \cdot 8H_2O$

← de-carbonated water →

Stock solution
(solution-B)

(solution-C)

gel formation
stirring:10 min
aging: 1h
(solution-D)

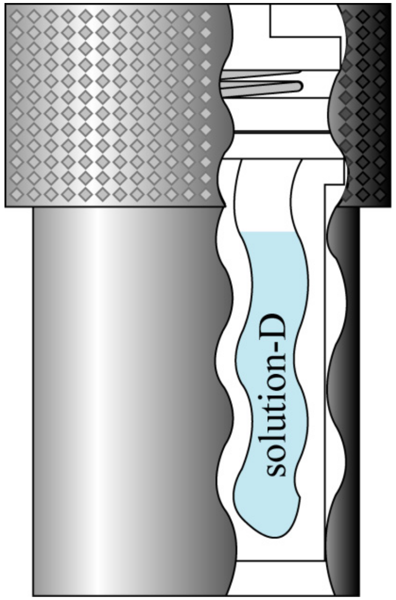
↓

Aging (250 ℃ for 3 hours)

↓

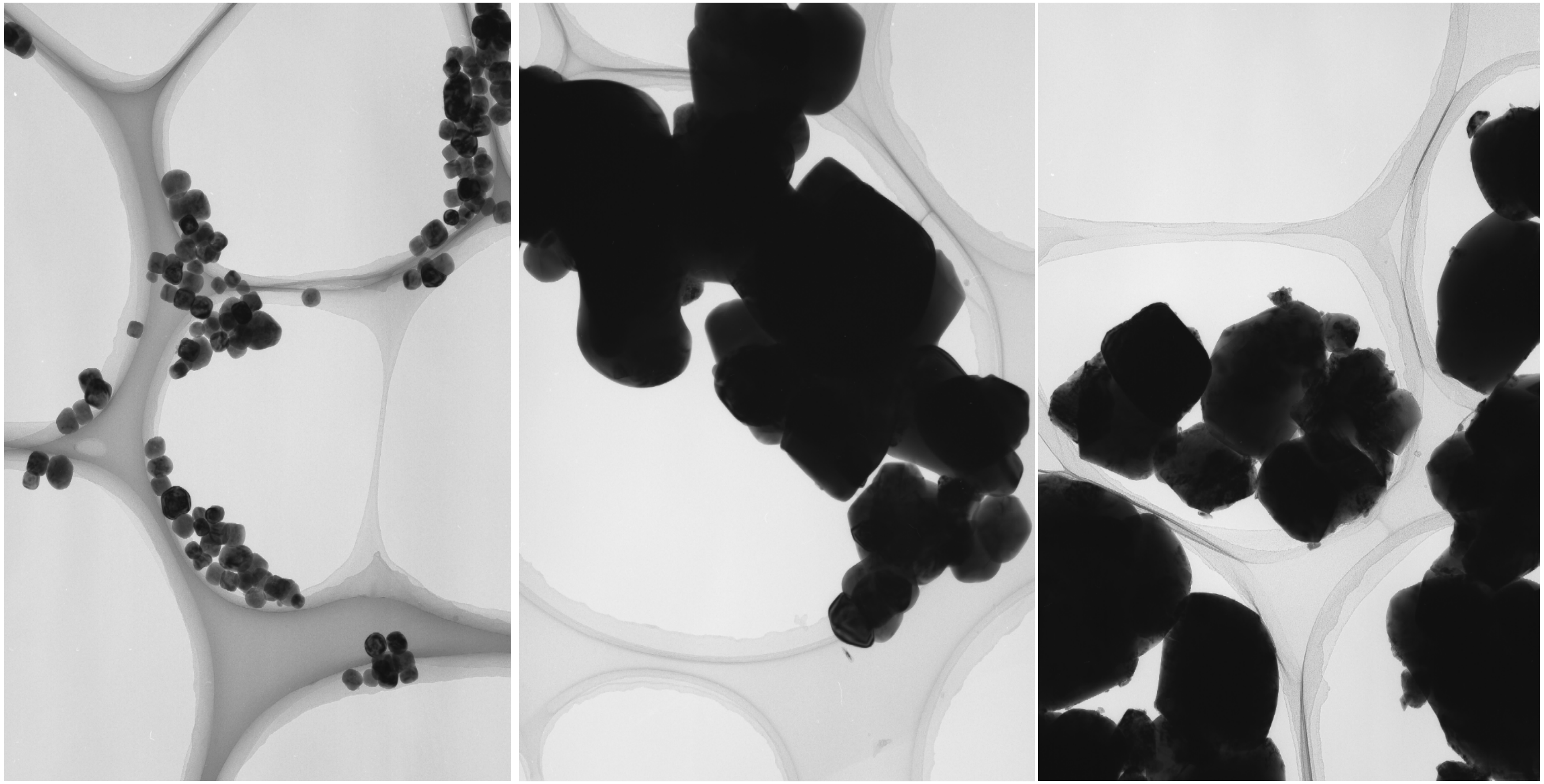
$BaTiO_3/SrTiO_3$ fine particles

Similar to TiO2 synthesis, a very viscous gel is formed.



Schematic drawing of reaction vessel (autoclave)

Cubic $BaTiO_3$



200 nm

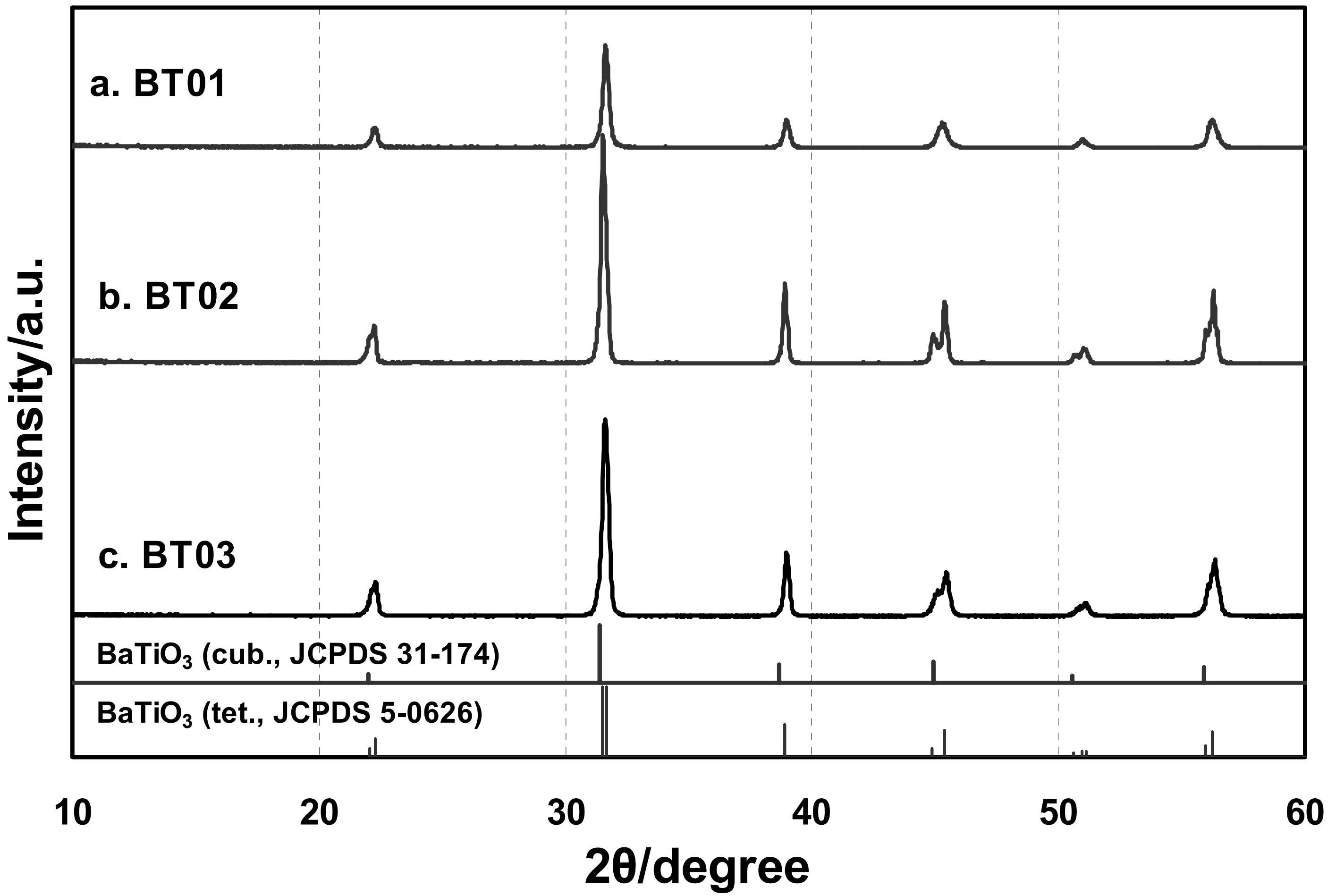
Our method
BT01

Commercial

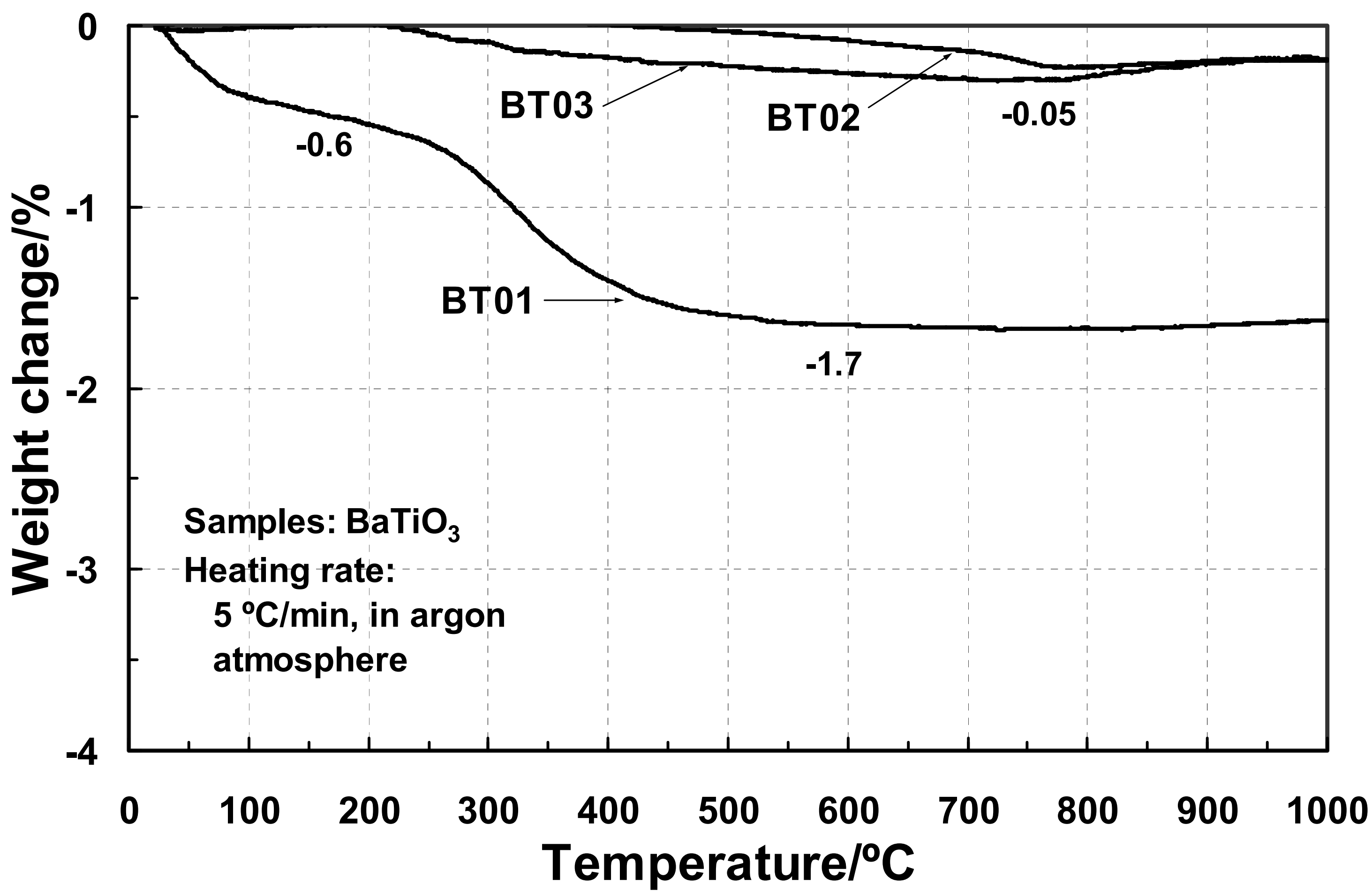
BT02
(High Purity Chemicals)

BT03
(Wako Pure Chemicals)

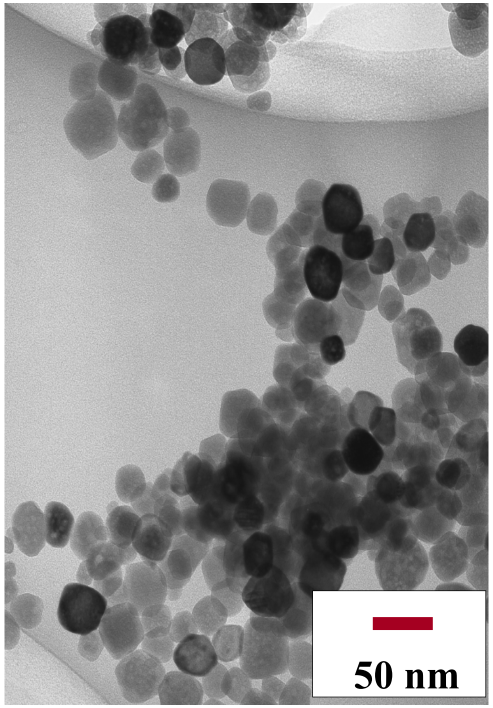
XRD


a. BT01
b. BT02
c. BT03
BaTiO3 (cub., JCPDS 31-174)
BaTiO3 (tet., JCPDS 5-0626)
Intensity/a.u.
10
20
30
40
50
60
2θ/degree

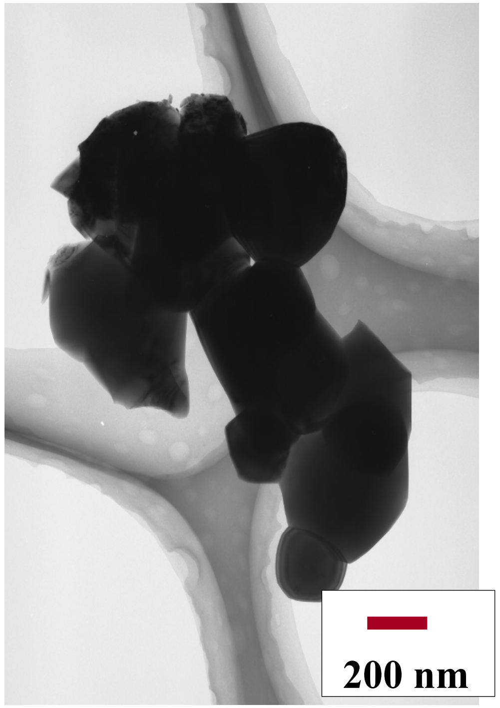
TG curves in Ar



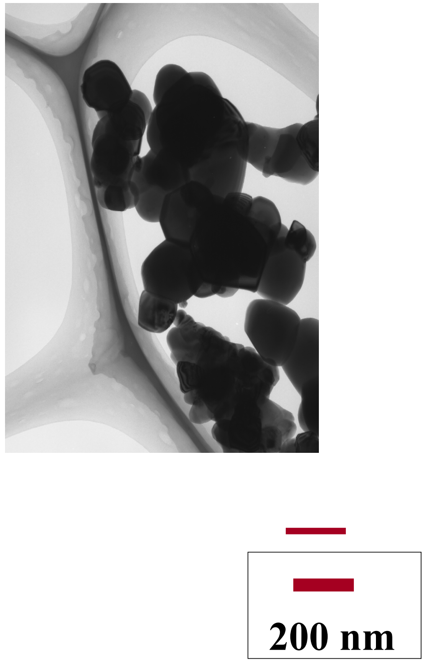
Cubic $SrTiO_3$



SR-01



SR-02

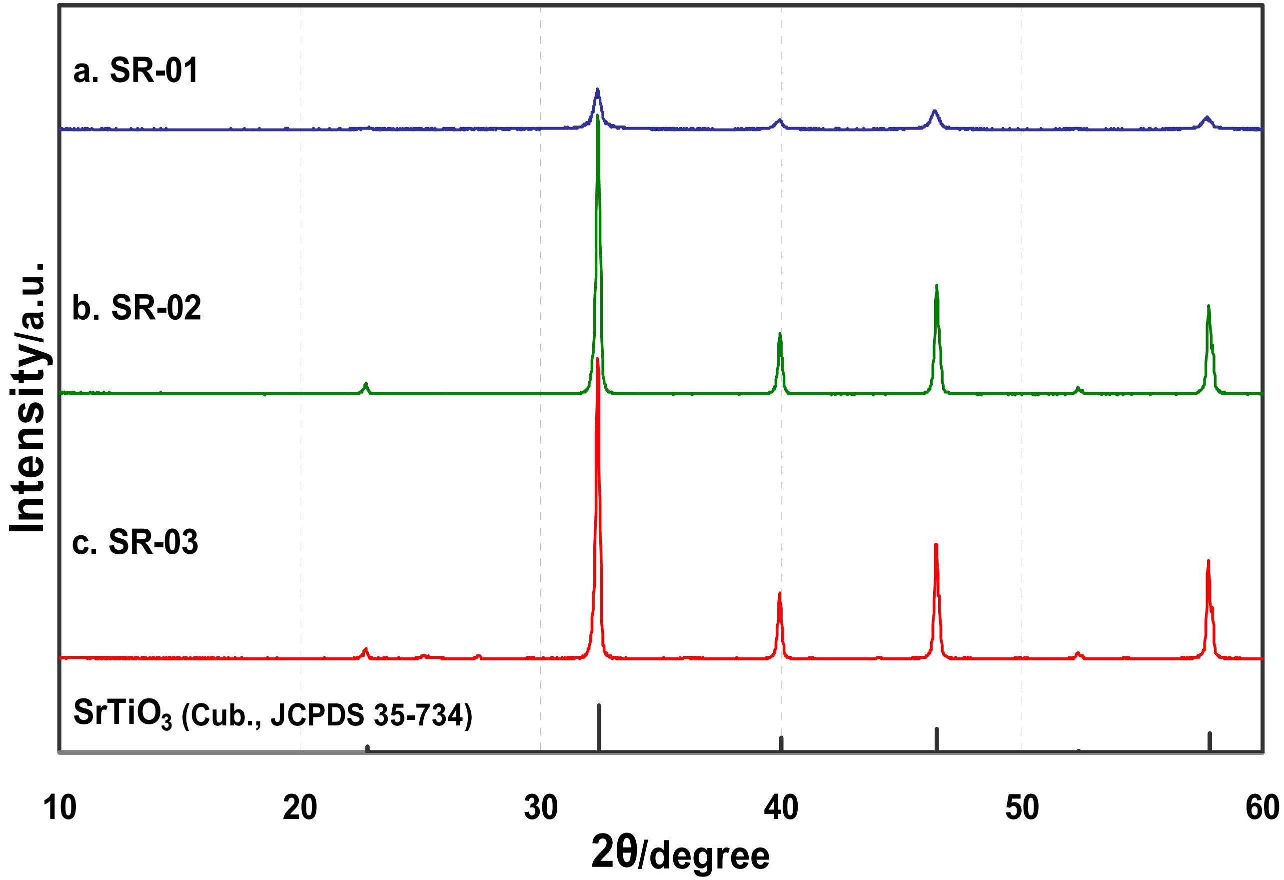


SR-03

Commercial

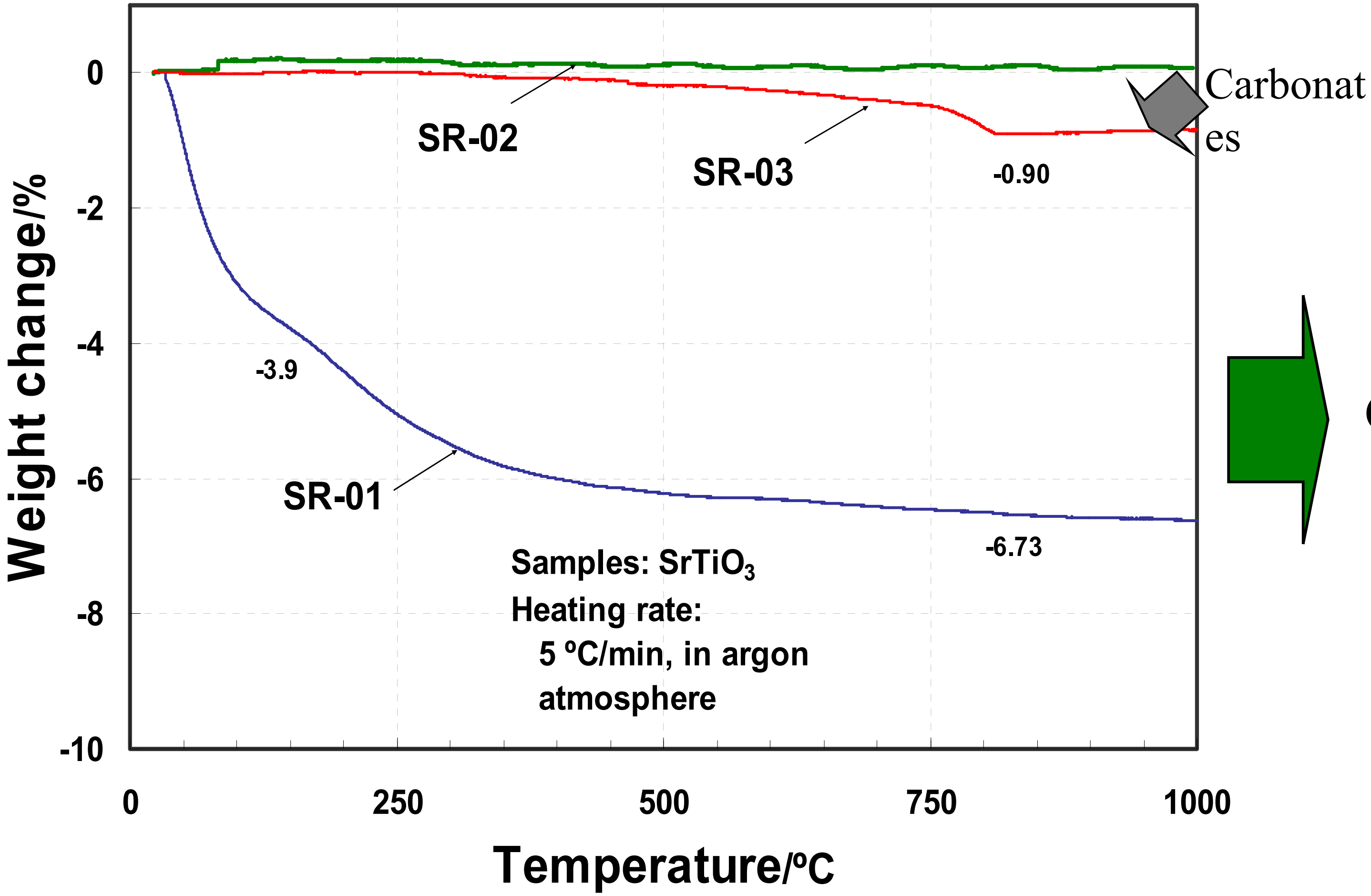
The particle size of SR-01 is smaller than 40 nm.

XRD



A cubic $SrTiO_3$ phase was founded in initial materials .

TG curves in Ar



SR-01 only contents 3.9 % of adsorbed water and 2.83 % of OH groups.

Morphology control of uniform particles

Selective adsorption on specific crystal planes

particle morphology

Shape in equilibrium or growth

- Equilibrium control or kinetic control

Mostly growth shape

Equilibrium shapes are found in some minerals.

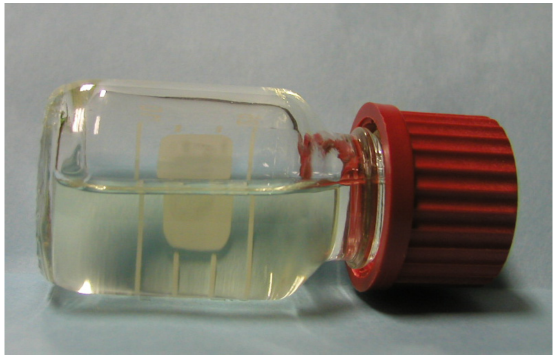
The growth shape is created by the difference in growth speed in the normal direction of each surface.

Therefore, the particle morphology can be controlled by varying the growth rate.

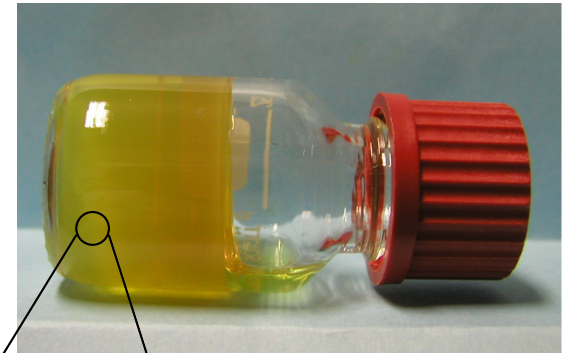
Synthesis of Monodispersed Anisotropic TiO_2 Particles

Gel-Sol Method: Particle Preparation Technique by using Metal Hydroxide Gels

Synthesis of Monodispersed Anisotropic TiO_2 Particles

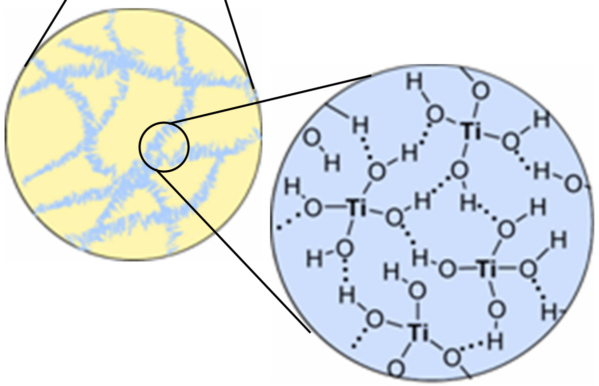


100 °C
24 h

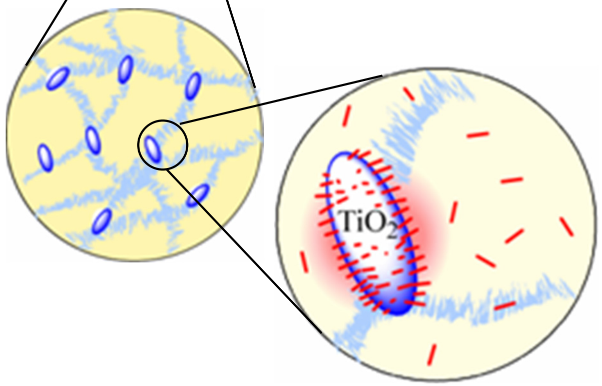


140 °C

- $Ti(OPr^i)_4$
- Stabilizer ($N(CH_2CH_2OH)_3$)
- Shape Controller
  (Amine, Amino Acid)
- pH Controller



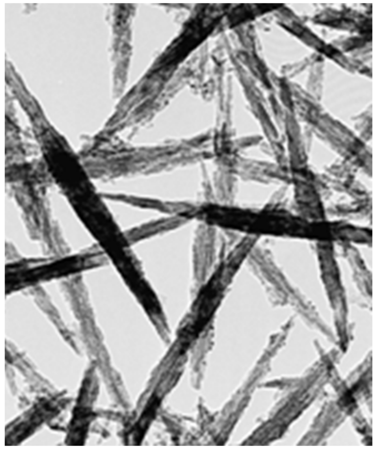
Gel Formation by H-Bonding Network of $Ti(OH)_4$



Sol Formation by Crystal Growth

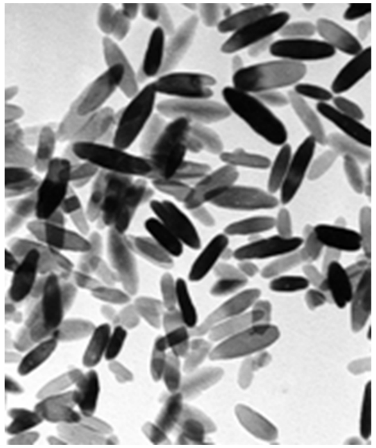
T. Sugimoto, *"Monodispersed Particles,"* Elsevier, Amsterdam, 2001.
K. Kanie and T. Sugimoto, *Chem. Commun.*, **2004**, 1584.

Anisotropic TiO_2 Particles Obtained by the "Gel-Sol" Method

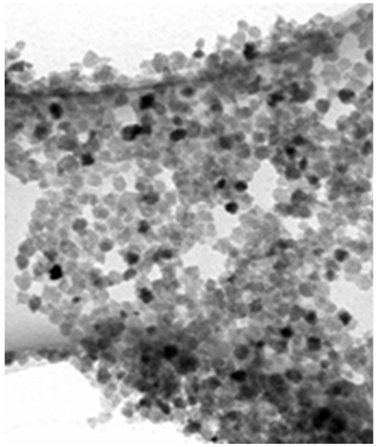


Ethylenediamine
Init pH: 10.5

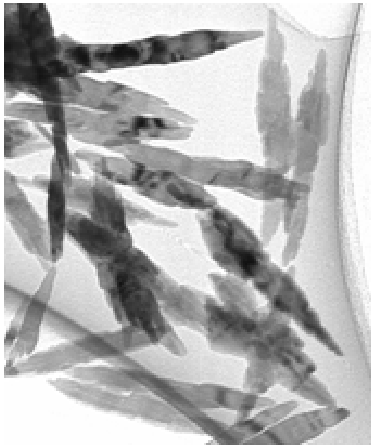
Ethylenediamine
Init pH: 10.5, Seeds



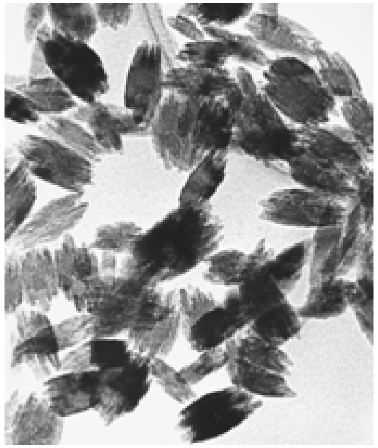
Succinic Acid
Init pH: 10.5



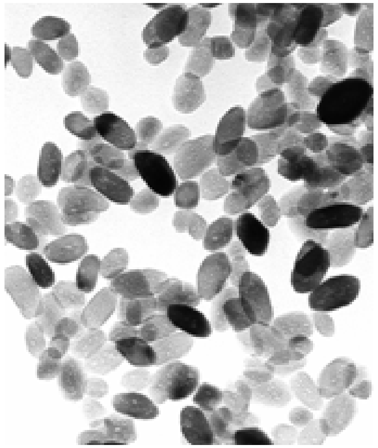
Gluconic Acid
Init pH: 9.5



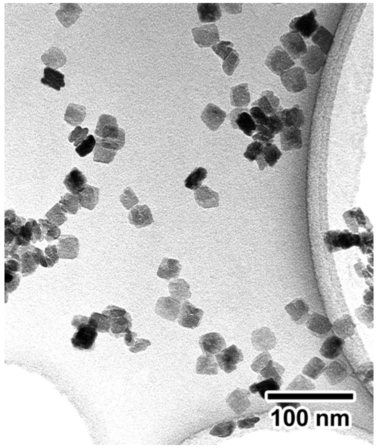
Glutamic Acid
Init pH: 10.5



Oleic Acid
Init pH: 11.5



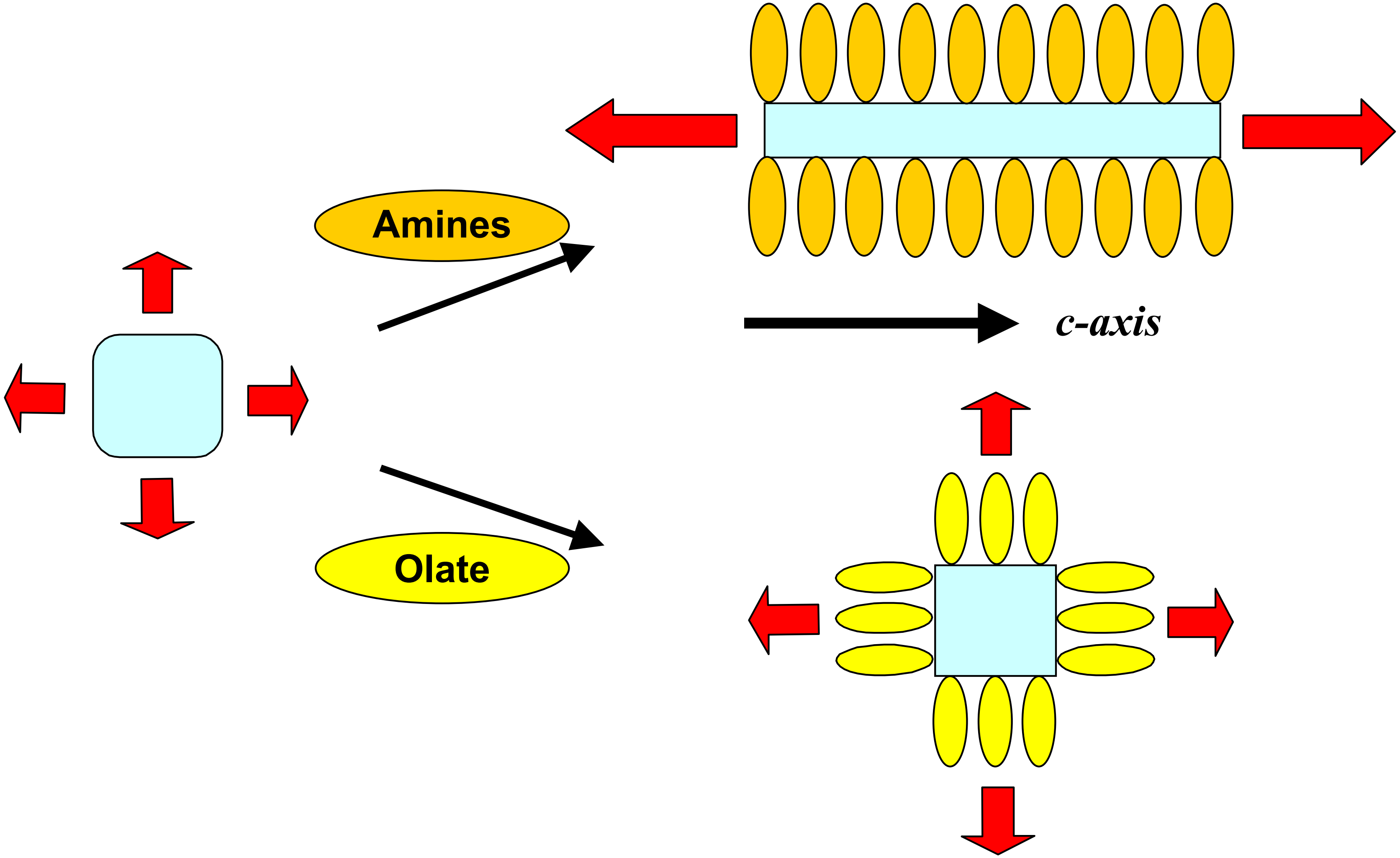
none
Init pH: 10.5



Oleic Acid
Init pH: 9.9

T. Sugimoto, X. Zhou, and A. Muramatsu, *J. Colloid Interface Sci.*, **259**, 53 (2003).
K. Kanie and T. Sugimoto, *Chem. Commun.*, **2004**, 1584.

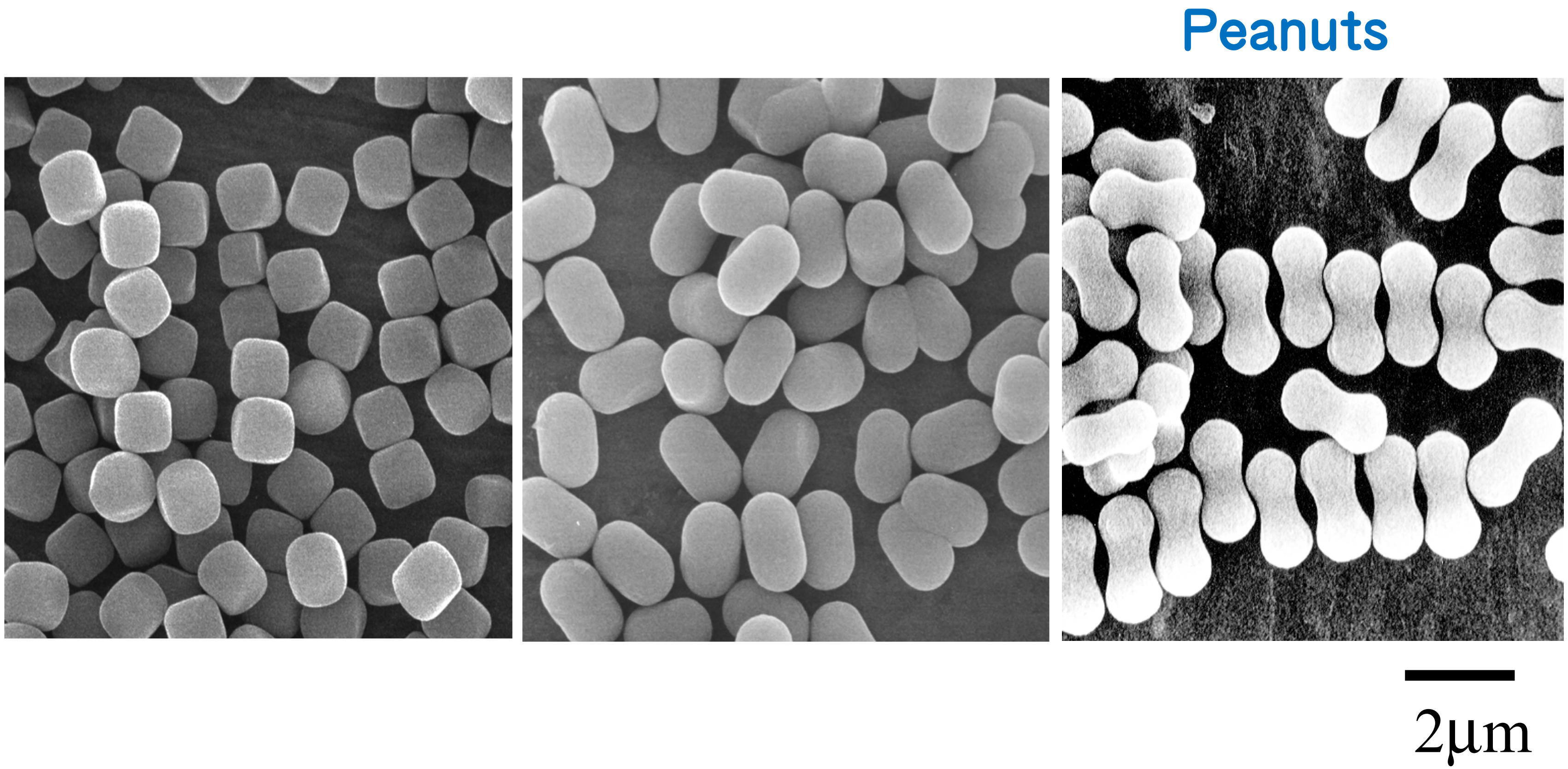
Shape Control by Amines and Oleate



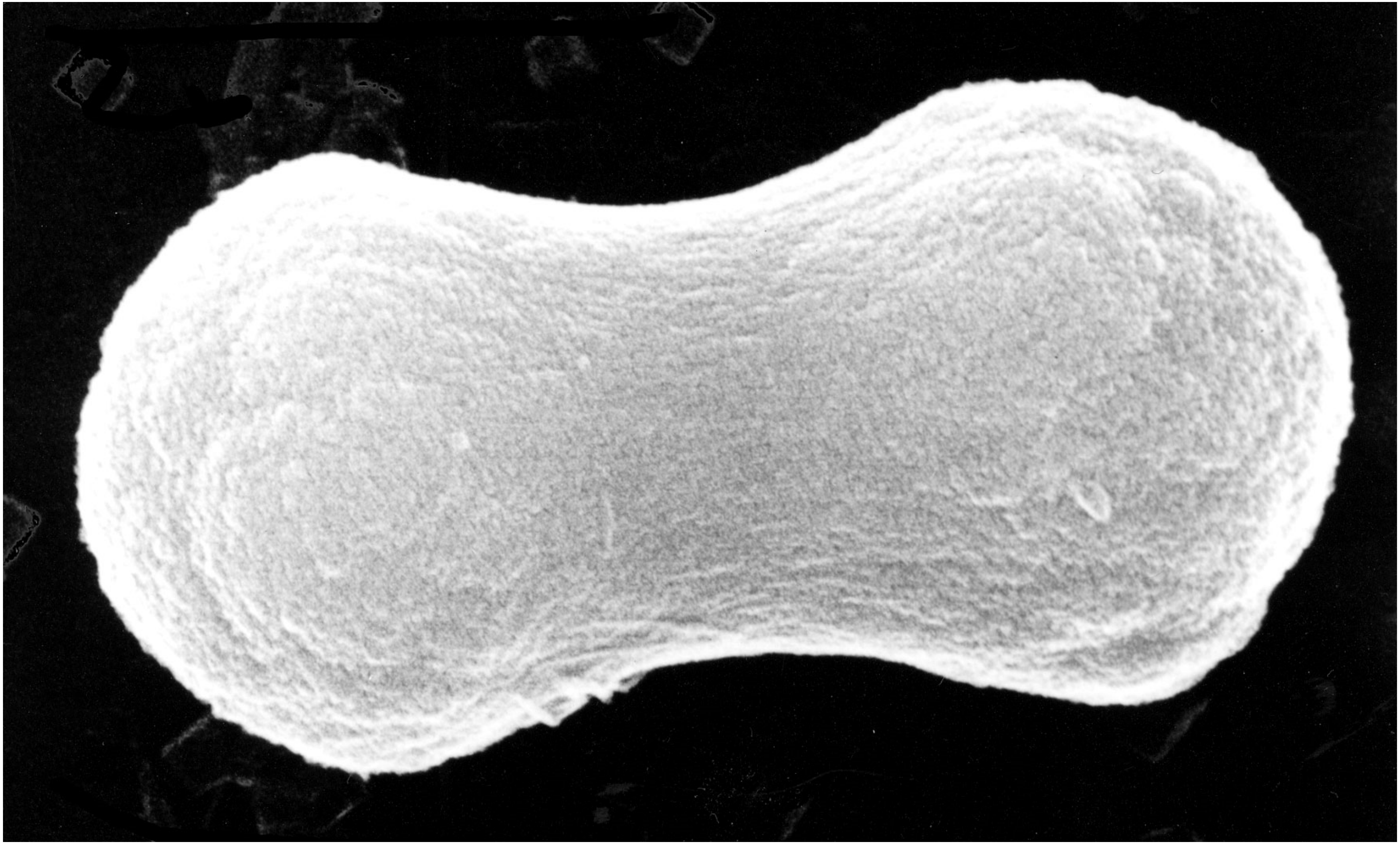
Organic Amines ⇨ Adsorb on TiO_2 Surfaces

⇨ Utilization for Organic-Inorganic Hybridization

Morphology control of monodispersed hematite fine particles



Peanuts



Shape control by SO_4^{2-}

How are peanut-shaped particles made?

2 *M* $FeCl_3$ 100 ml

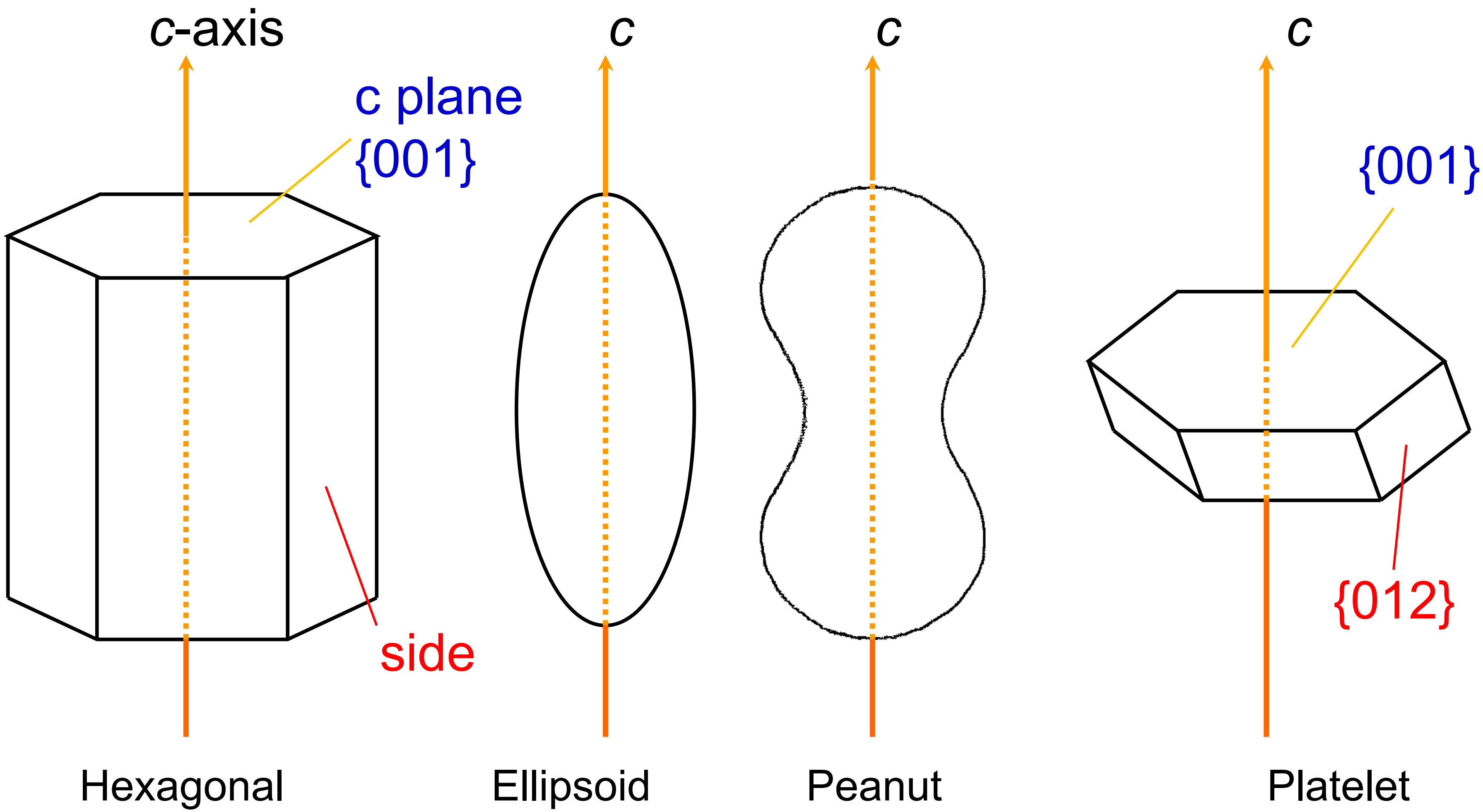
↓ ← 6.0 *M* NaOH 90 ml

↓ ← ***x M*** **Na_2SO_4 10 ml**

0.9 *M* $Fe(OH)_3$ + 0.1 *M* Fe^{3+} **pH ~ 2.1**

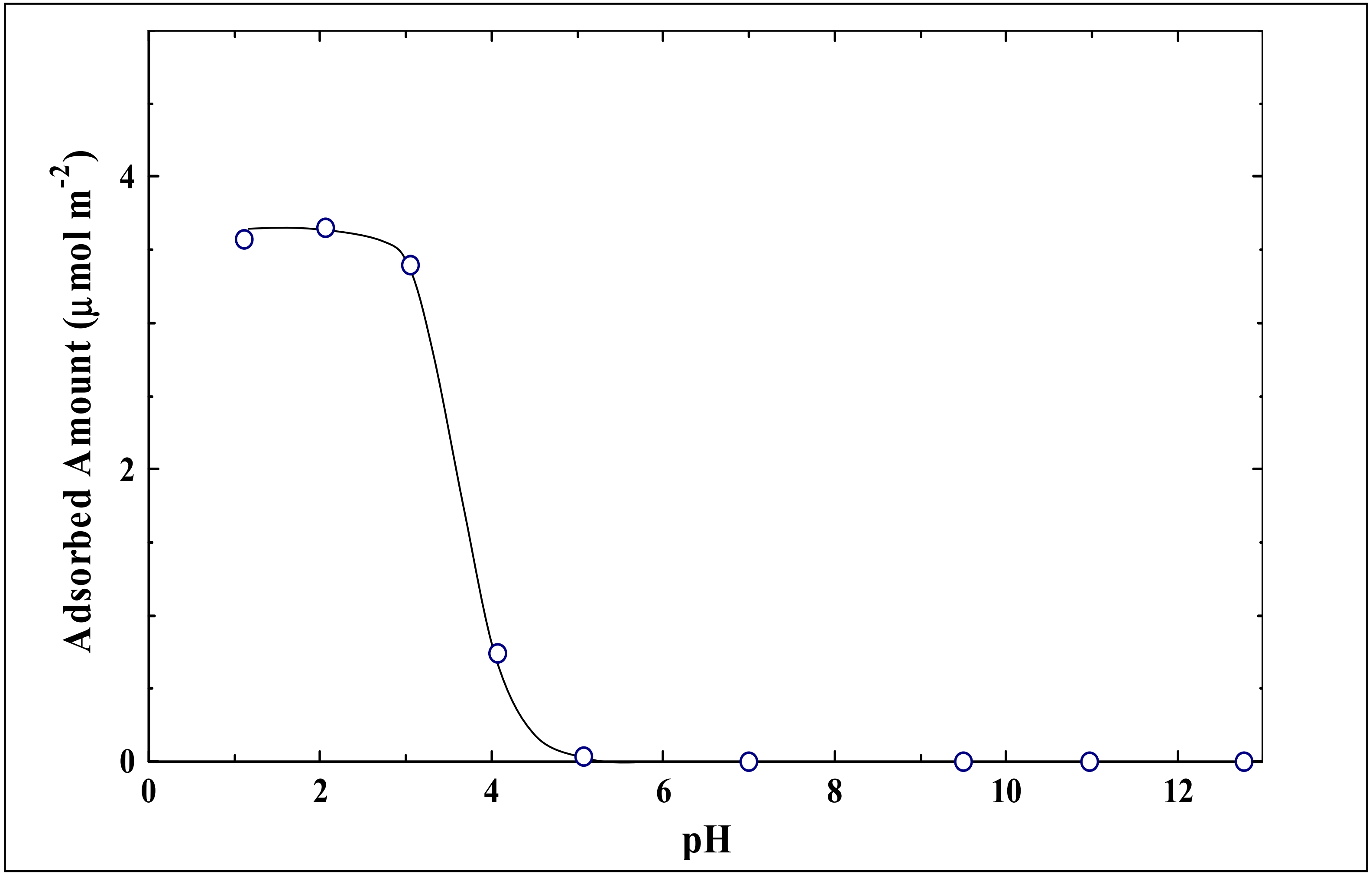
↓ **100℃, 8 days**

α-Fe_2O_3 **pH ~ 0.6**



★ The strong adsorption of SO_4^{2-} to side is estimated.

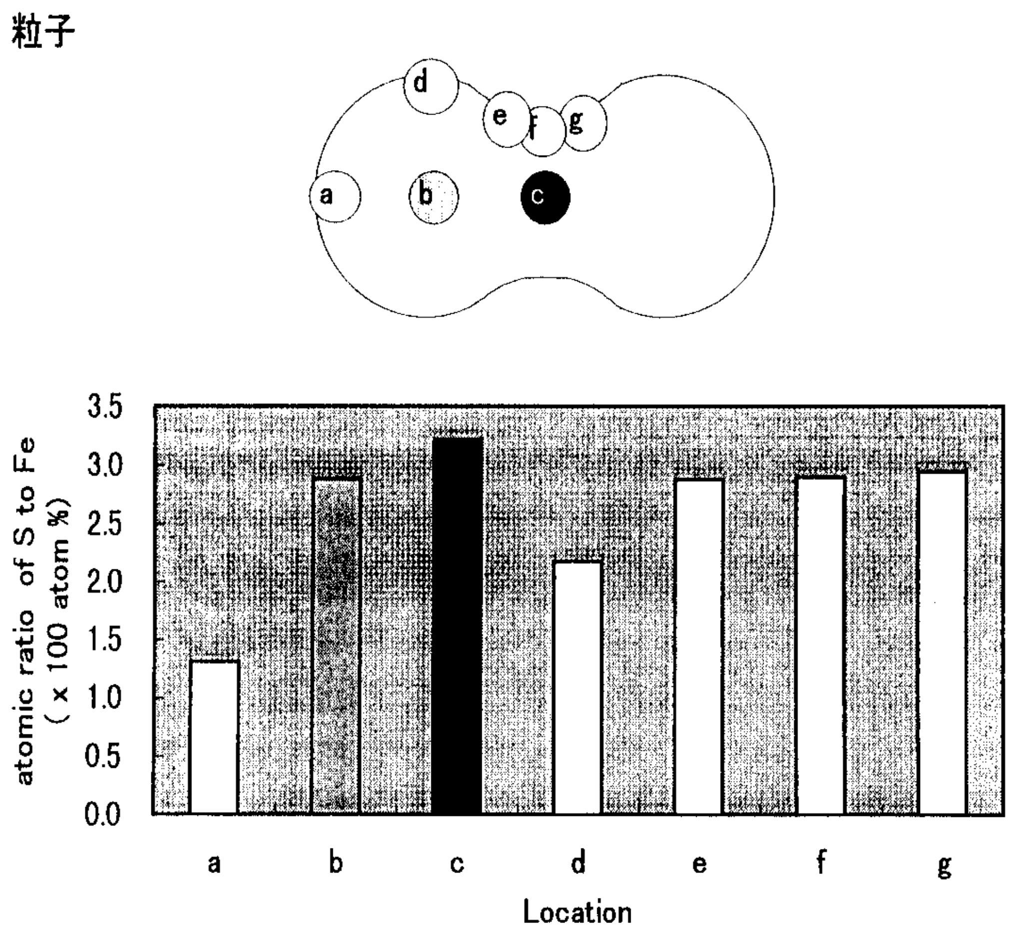
Adsorption uptake of sulfate depends on pH



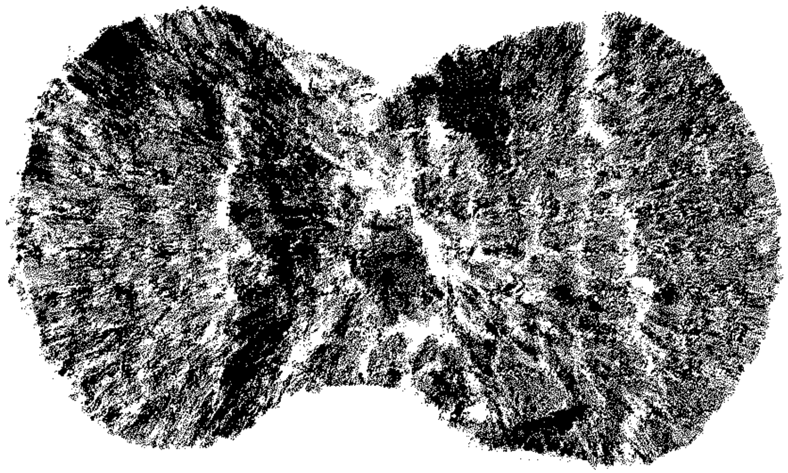
★ Above pH 4, almost no SO_4^{2-} is adsorbed. This may be due to competitive adsorption with OH^-.（Isoelectric point of hematite is ca 7.5.）

Distribution of SO_4^{2-} in a peanut particle

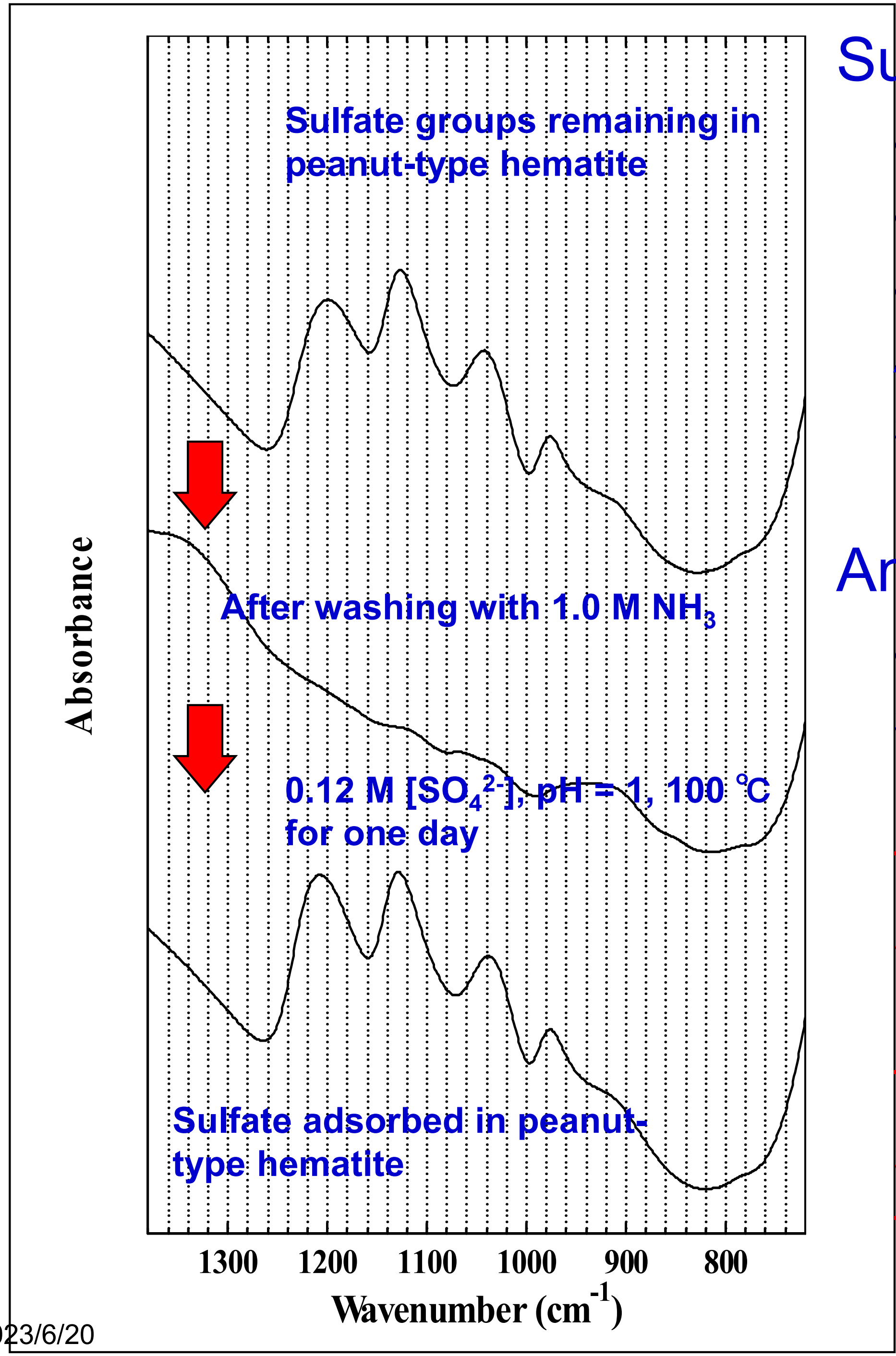
EDX analysis



Ultra-thin section TEM image



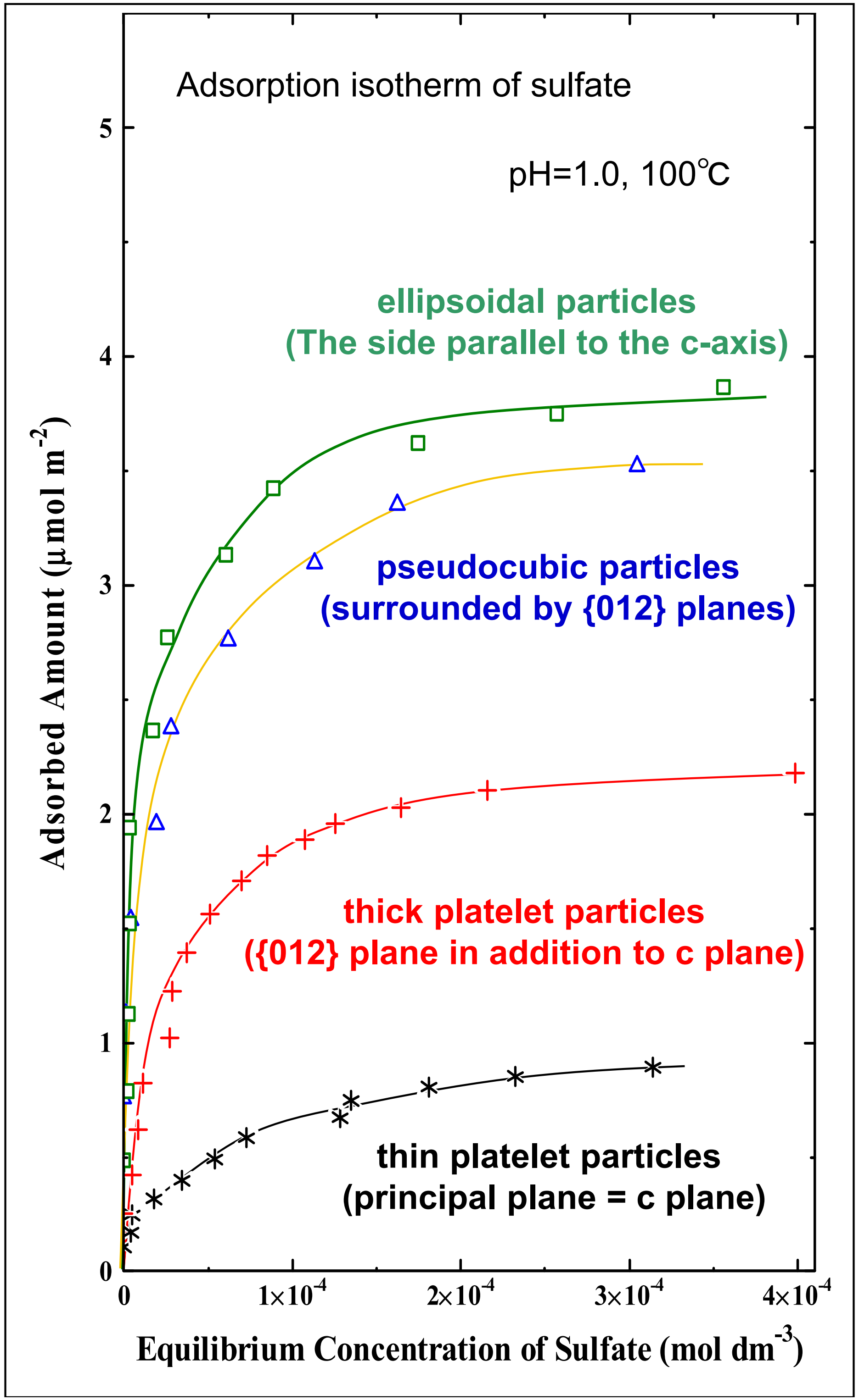
★ About 90% of the added amount of SO_4^{2-} is incorporated into the particles, and is distributed almost evenly on the surface and inside.



Sulfate ions remaining in the particles are desorbed by ammonia treatment, and then adsorbed again by adsorption treatment at 100° C. Also, the adsorbed species are the same as the sulfate species that remained in the particles.

Anisotropic growth is due to the adsorption of free sulfate ions on specific surfaces.

The morphology control is due to the adsorption of sulfate ions to specific surfaces. There is no possibility that complexes derived from sulfate were formed in the solution phase and participated in the anisotropic growth.



Adsorption isotherm of sulfate
pH=1.0, 100℃
ellipsoidal particles
(The side parallel to the c-axis)
pseudocubic particles
(surrounded by {012} planes)
thick platelet particles
({012} plane in addition to c plane)
thin platelet particles
(principal plane = c plane)
Adsorbed Amount (μmol m-2)
Equilibrium Concentration of Sulfate (mol dm-3)
0
1
2
3
4
5
0
1×10-4
2×10-4
3×10-4
4×10-4

Adsorption uptake of sulfate (pH 1, 100℃, 24h)

	Specific surface area m^2/g	Maximum uptake $\mu mol/m^2$	Occupied area Å^2
ellipsoidal particles	12.4	3.60	46.1
pseudocubic particles	2.67	3.16	52.6
thick platelet particles	2.10	2.28	72.9
thin platelet particles	0.70	0.86	193

peanut particles
↓
Surf. Area: 61.2 m^2/g
↓
Maximum uptake
5.59 $\mu mol/m^2$
(29.7 Å^2)

Maximum adsorption amount:
Ellipsoid > pseudocube > thick plate > thin plate

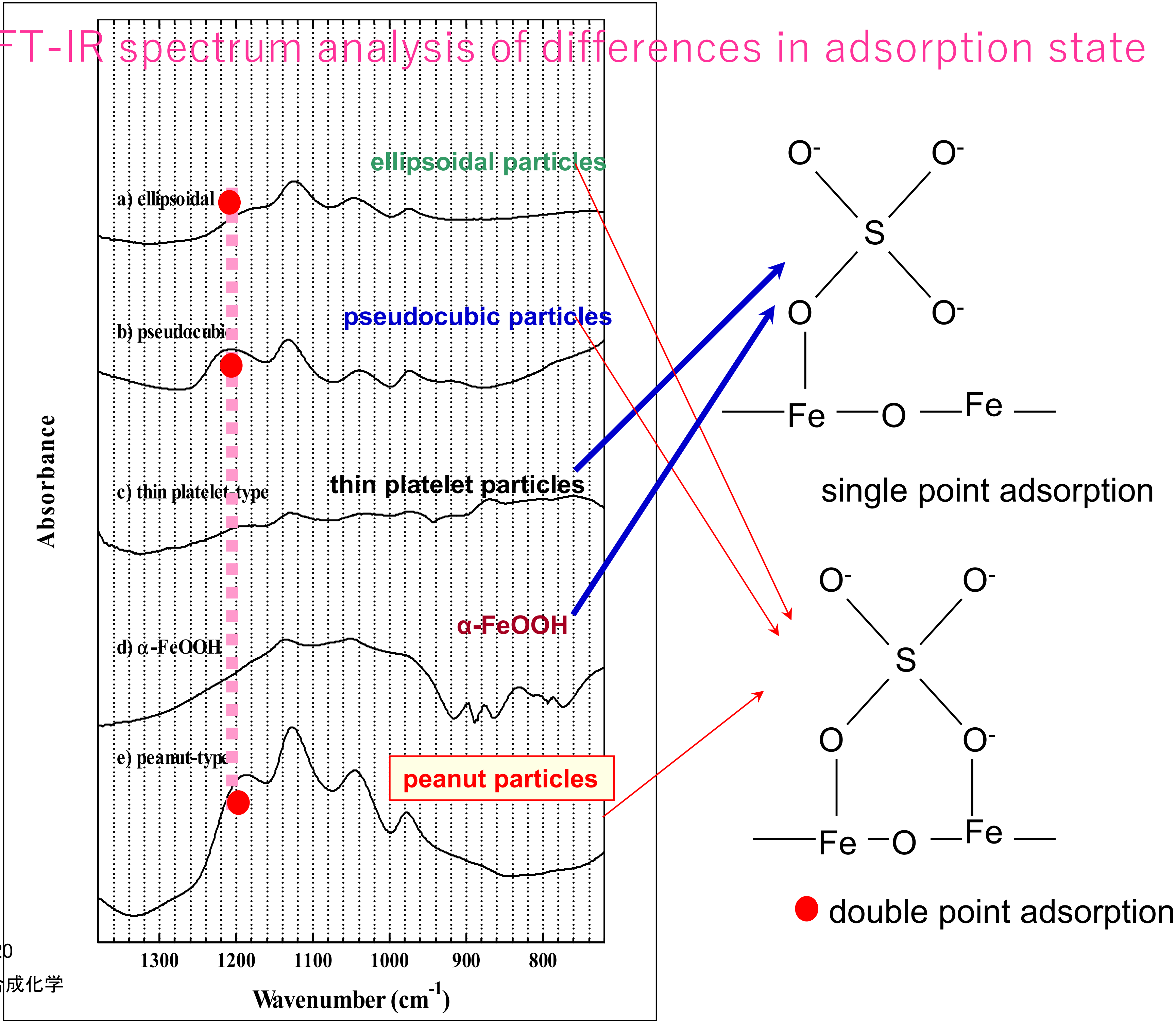
Sulfate strongly adheres to the plane parallel to the c-axis.

Adsorption force to c-plane is low.

peanut particles

The reason why the amount of adsorption to the thick flat plate is larger may be that the {012} plane is developed.

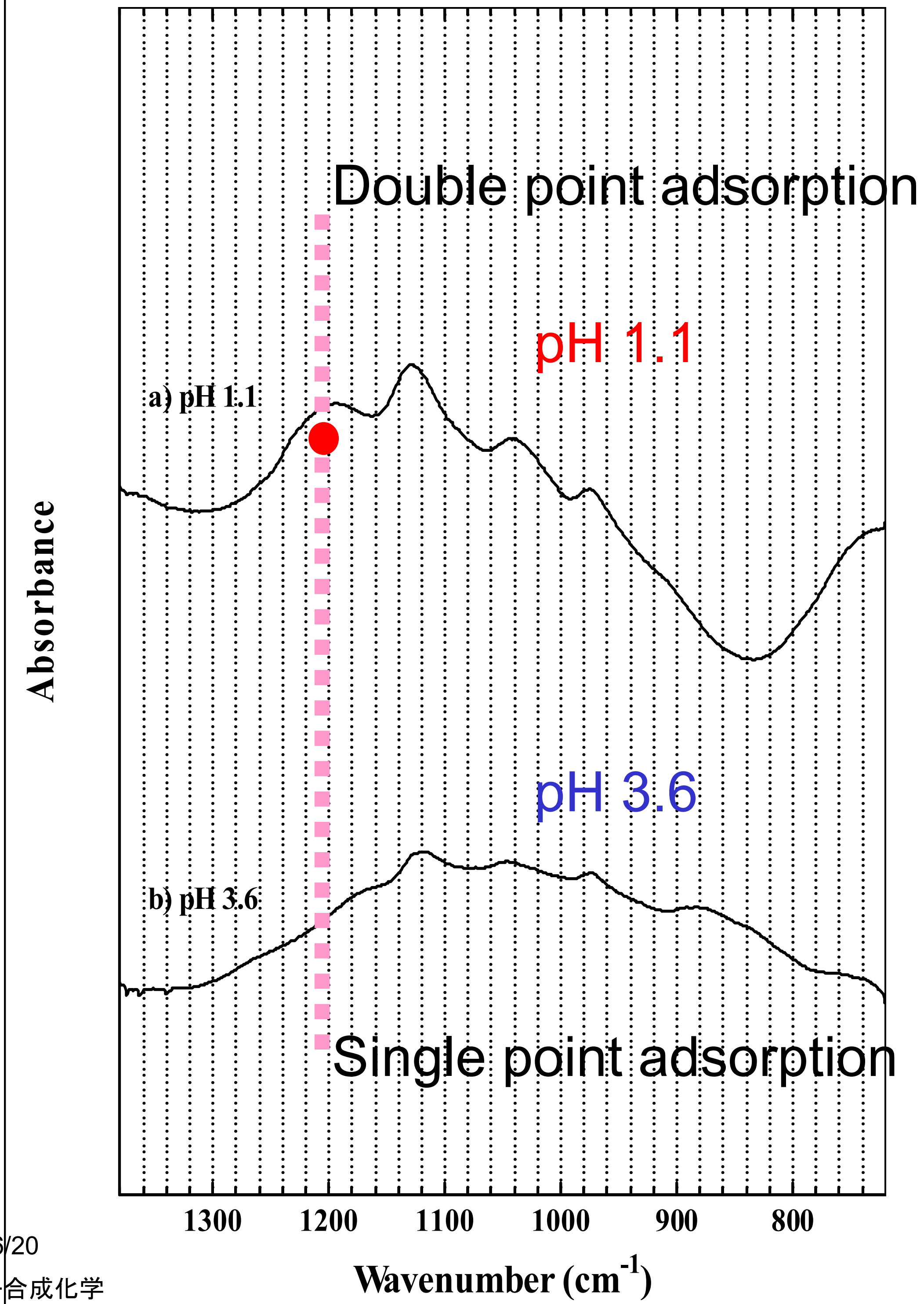
FT-IR spectrum analysis of differences in adsorption state



Adsorption to the sides and the {012} plane is overwhelmingly stronger than the c-plane {001} plane.

Since the O-O distance (2.45 Å) of SO_4^{2-} is closer to that of the lateral side (2.29 Å) than the Fe-Fe distance (2.91 Å) of the c-plane, SO_4^{2-} is adsorbed at single point on the c-plane. It is considered that the {012} plane has double-point adsorption.

The Fe-Fe distance (3.15 Å) on the side surface of α-FeOOH (needles) is farther than the O-O distance of SO_4^{2-}, resulting in single-point adsorption.



As the pH decreases, the single-point adsorption changes to a double-point one. adsorption.

It is speculated that at low pH, the hematite surface has a high positive charge, and the desorption of OH- ions creates an environment in which sulfate ions can be strongly adsorbed.

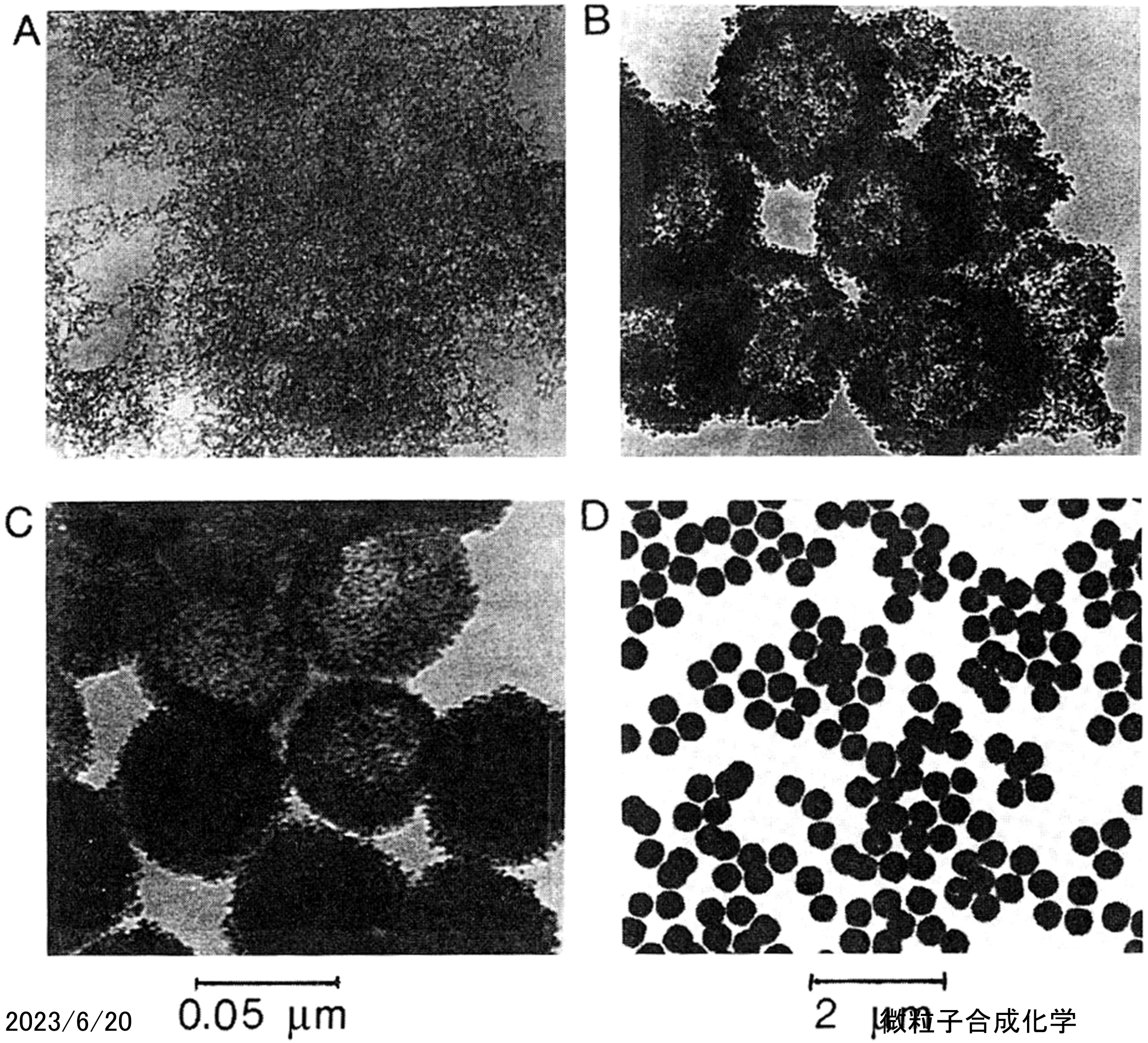
Particle Growth Mechanism

2023/6/20

never aggregation mechanism

Originating from CeO_2particles formation

If as-formed particles are polycrystalline, they will seem to grow aggregatively.

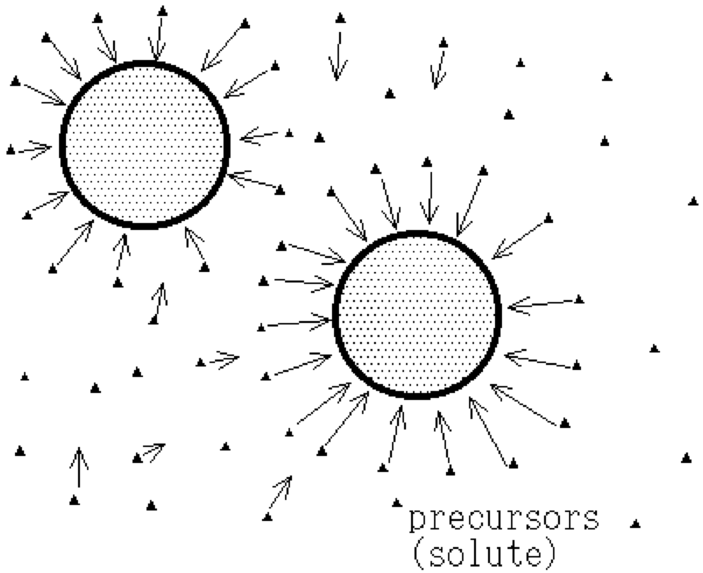


$1.0x10^{-3}$ mol/l $Ce(SO_4)_2$
$4.0x10^{-2}$ mol/l H_2SO_4
90 °C

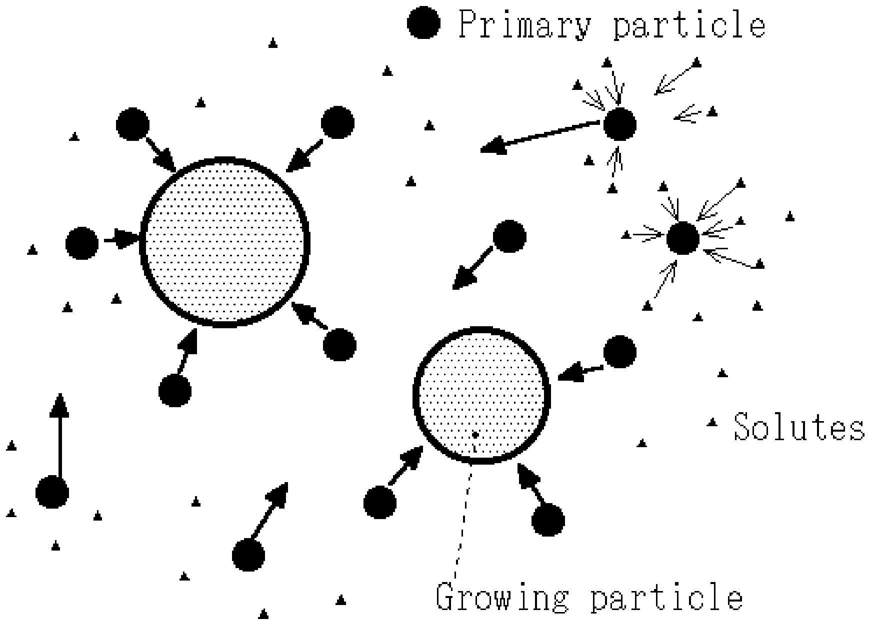
A is several hours later. B and C are aged.
In B, the primary particles seem to gather together to form aggregates.

Comparison of growth mechanism

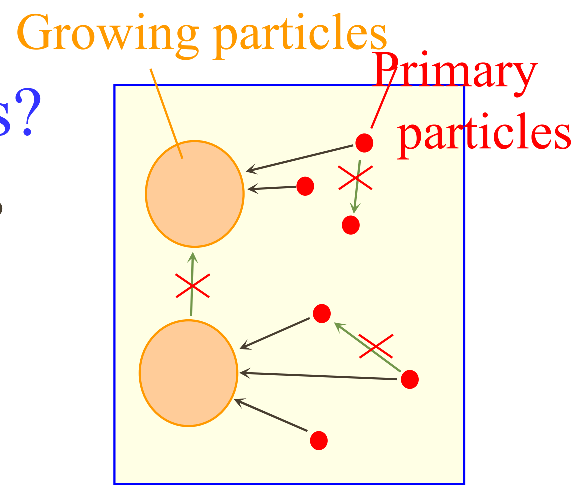
LaMer mechanism due to direct deposition of solute



Aggregative growth mechanism

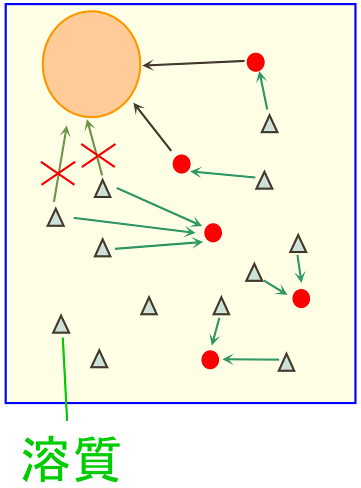


Problems of aggregative growth mode



1．Selective Aggregation into Only Growing Particles?

Why is there no coagulation between primary particles and between growing particles?
(If these coagulation occur, monodisperse particles cannot be obtained)



2．Isn't the generation of primary particles caused by the direct deposition of solutes?

The mechanism, by which primary particles and nuclei are generated, is the direct deposition of solutes.
Assuming that primary particles are generated during the growth, it means that the formation of the primary particles is due to direct deposition of the solute and the growth of the particles is due to aggregation.

Uniform hematite fine particle synthesis in dilute system

Although this hematite is single crystalline, some researchers interpret that it grew by an aggregative growth mechanism.
We deny it based on experimental facts.

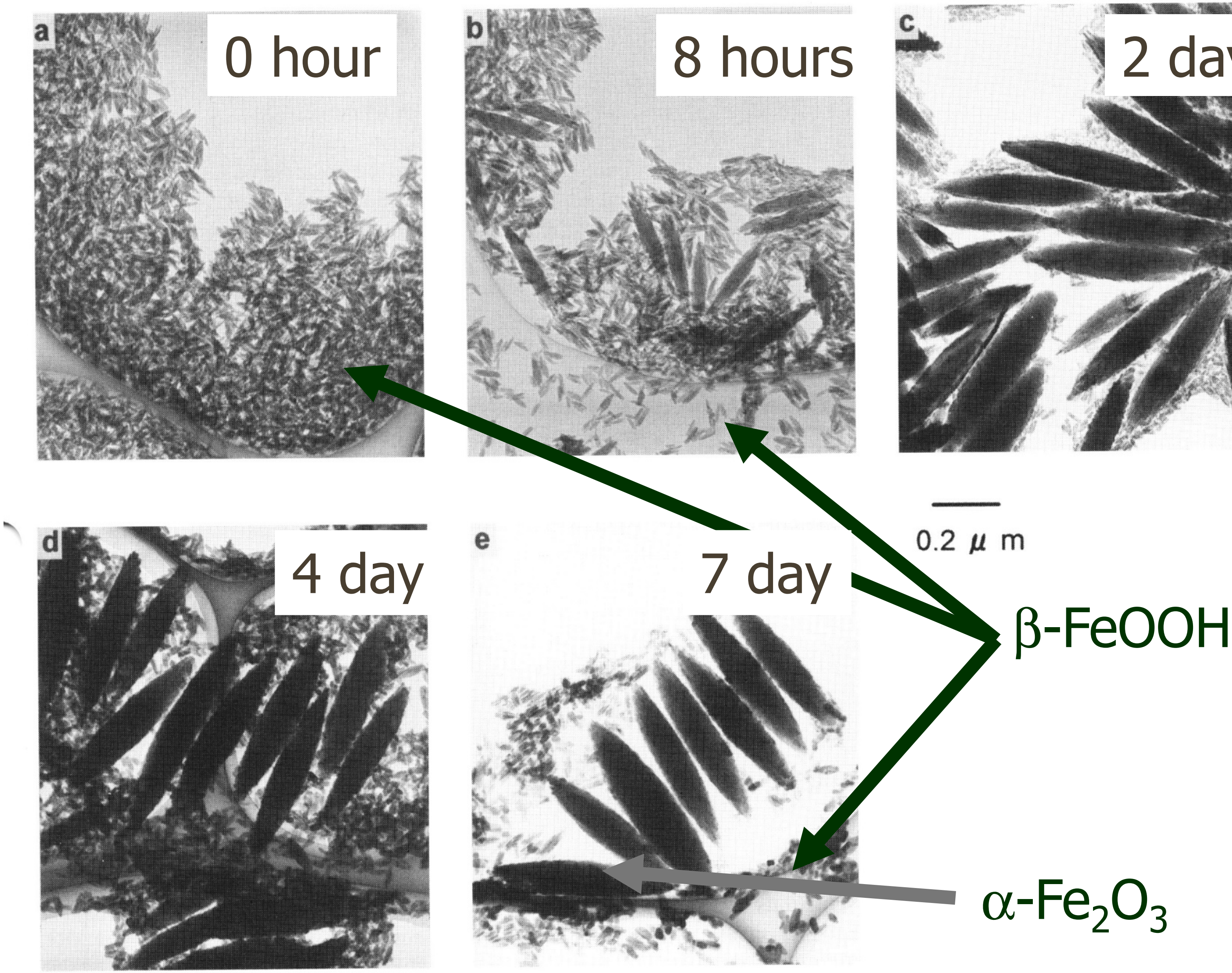
Synthesis conditions

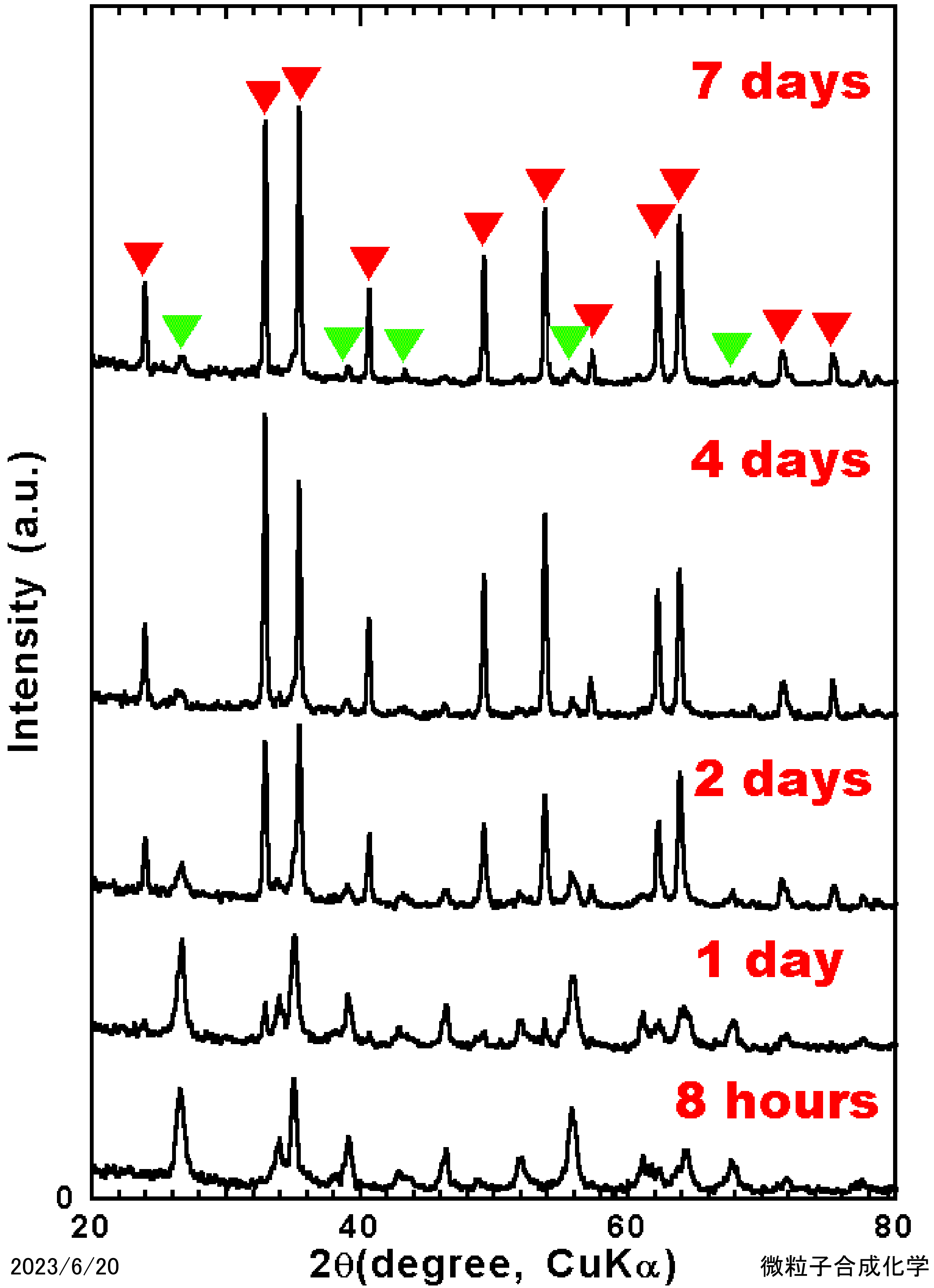
2.0×10^{-2} mol dm^{-3} $FeCl_3$ and 4.5×10^{-4} KH_2PO_4 at 100 °C

There are many papers supporting the aggregative growth mechanism.

M. Ocana, M. Morales, and C.J. Serna: J. Colloid Interface Sci. 171 (1995) 85.
M. Ocana, R. Rodriguez-Clemente, C.J. Serna: Adv. Mater. 7 (1995) 212.

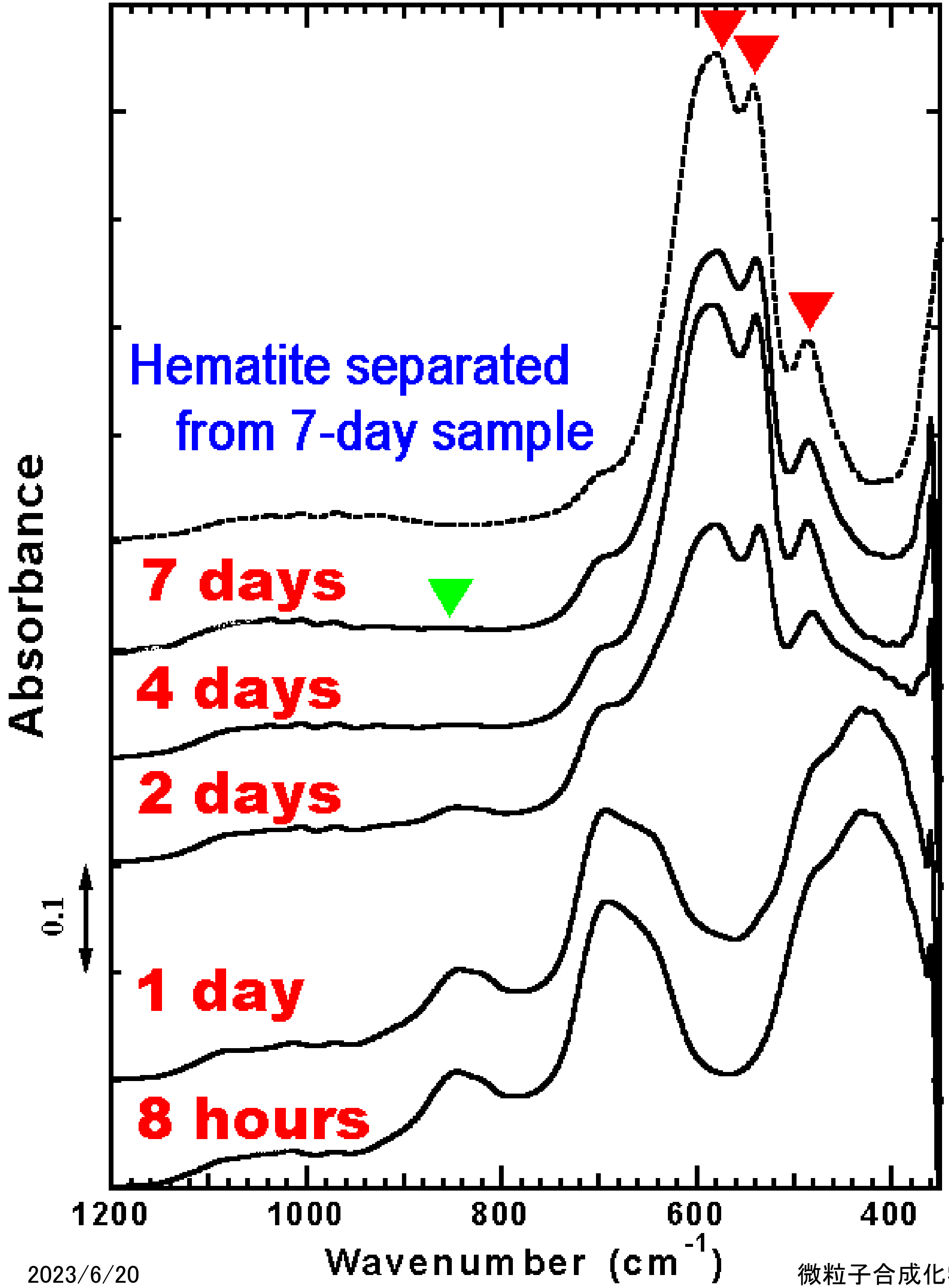
Time evolution





XRD

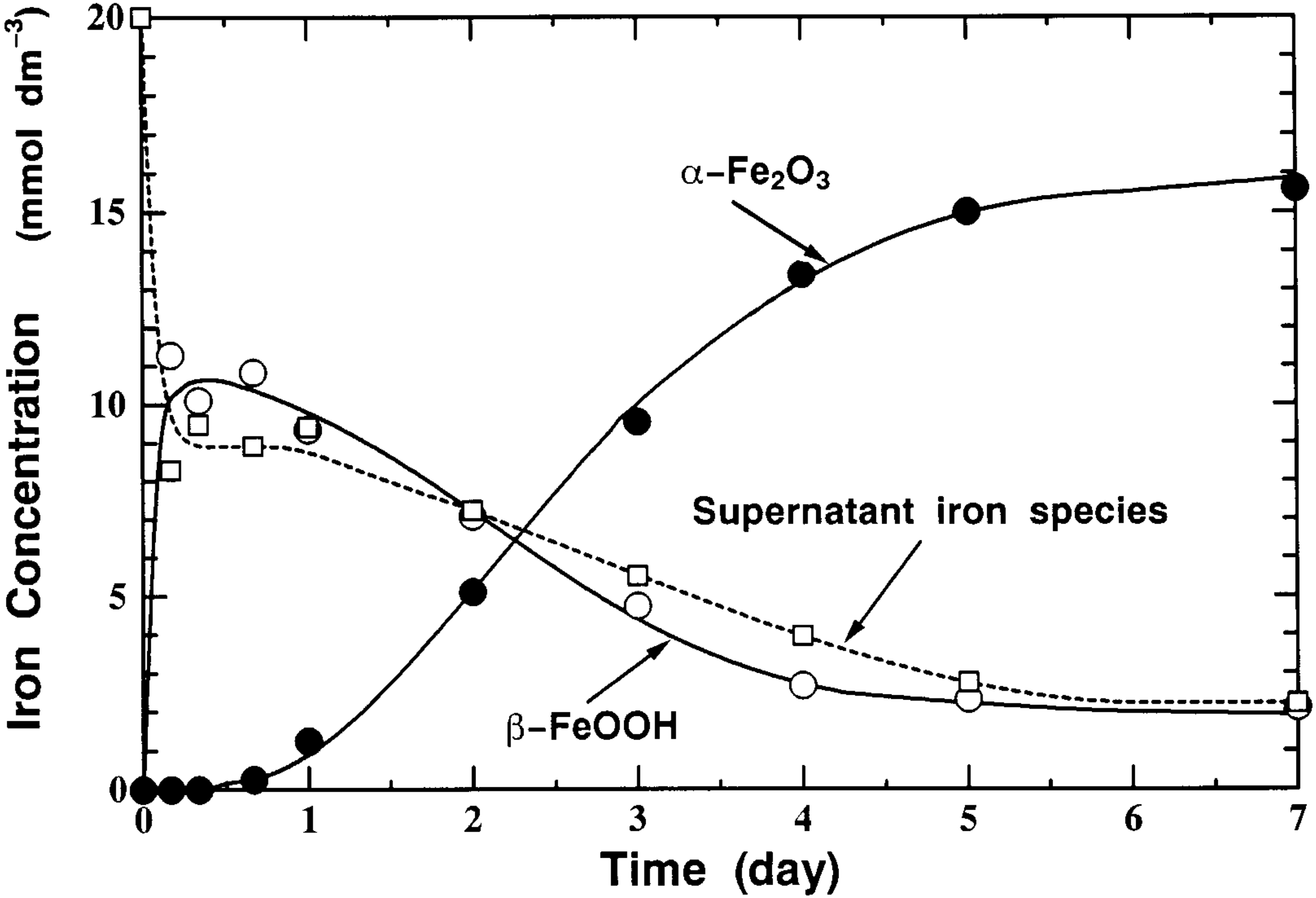
- β–FeOOH was first formed.
- α–Fe_2O_3 was formed at the expense of it.



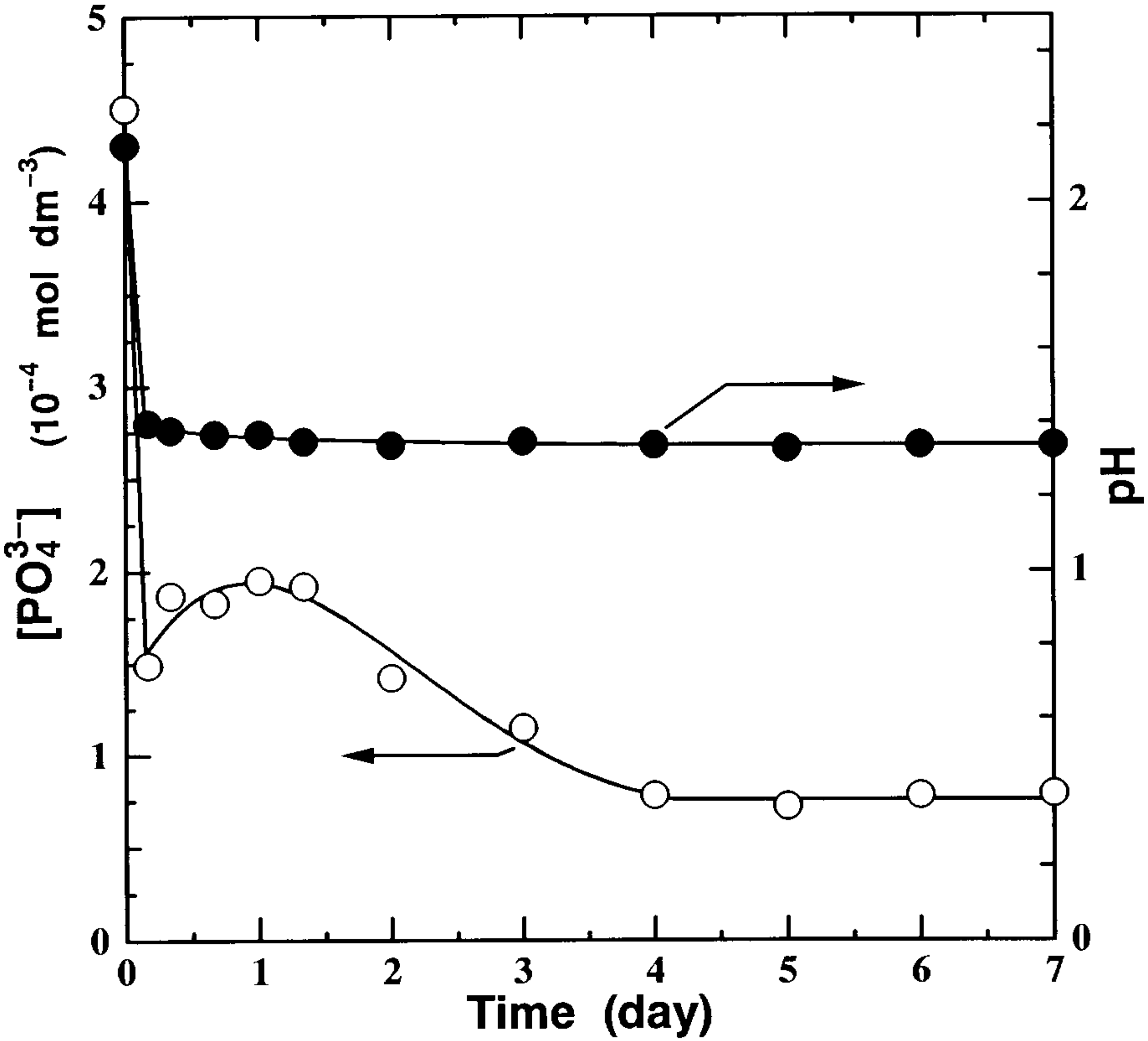
FT-IR

- Even after 7 days, β-FeOOH remained.

Solid concentration

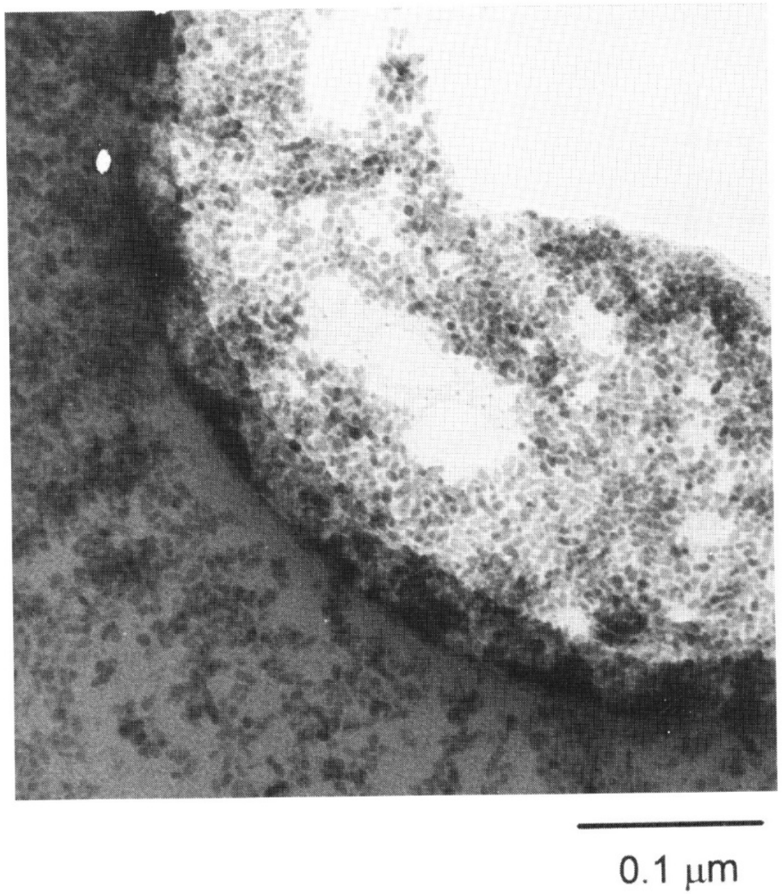


Soluion



- First, pH was rapidly decreased.
- PO_4^{3-} conc. was gradually decreased.

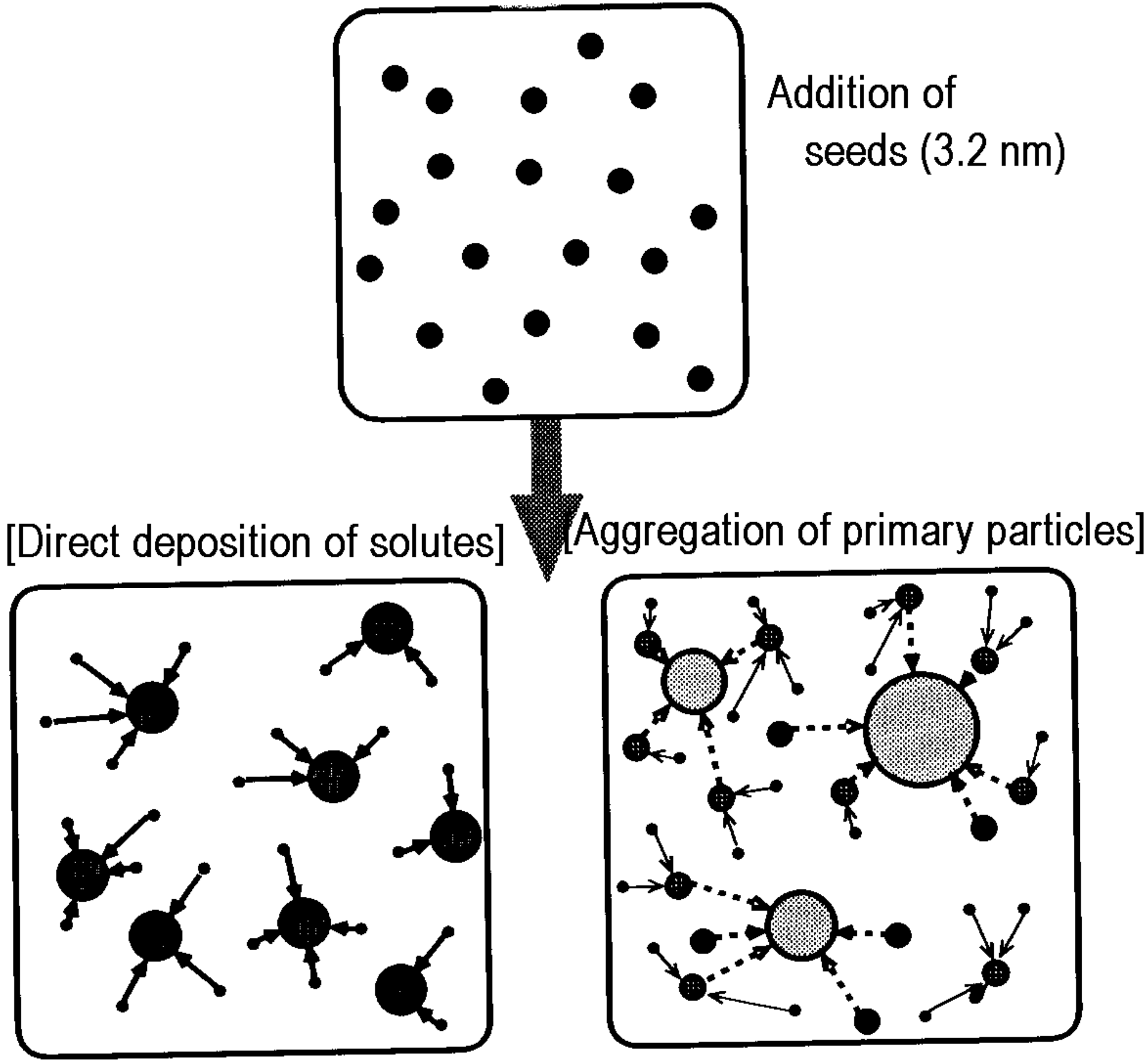
Elucidation of growth mechanism by seed addition



Seed addition

- For aggregative growth mechanism, the overall reaction rate does not change, because the primary particles in equilibrium are responsible for the particle growth rate.
- If the solute is precipitated directly, the seed addition increases the total surface area, so that the growth rate is increased.
- The number of particles depends on the number of seeds and original nuclei.

Seeds effect



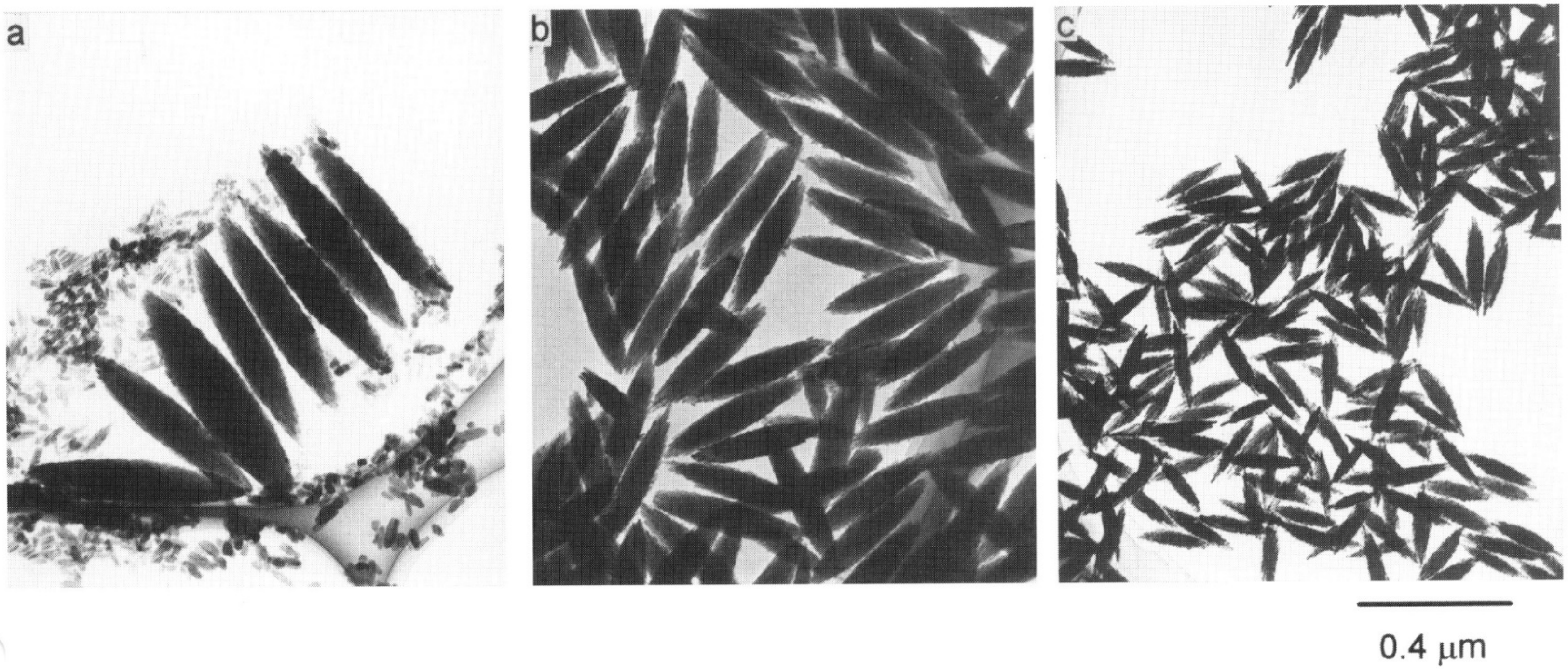
Promoting growth rate
due to the increase in total surface area

No effect of seeds

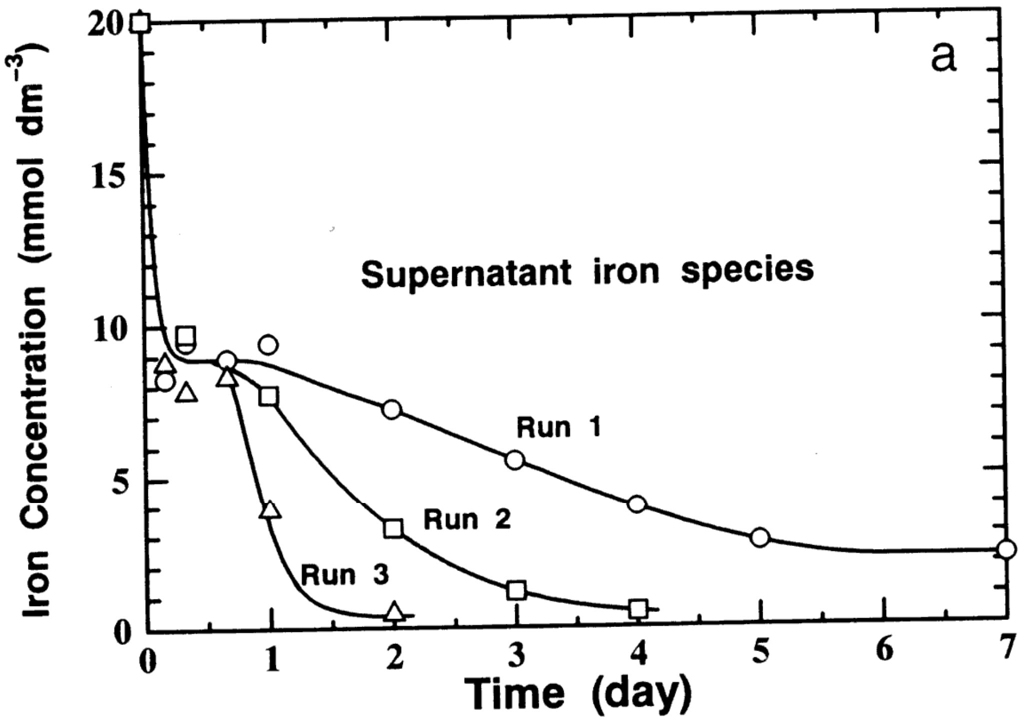
Number: particles = seeds + nuclei

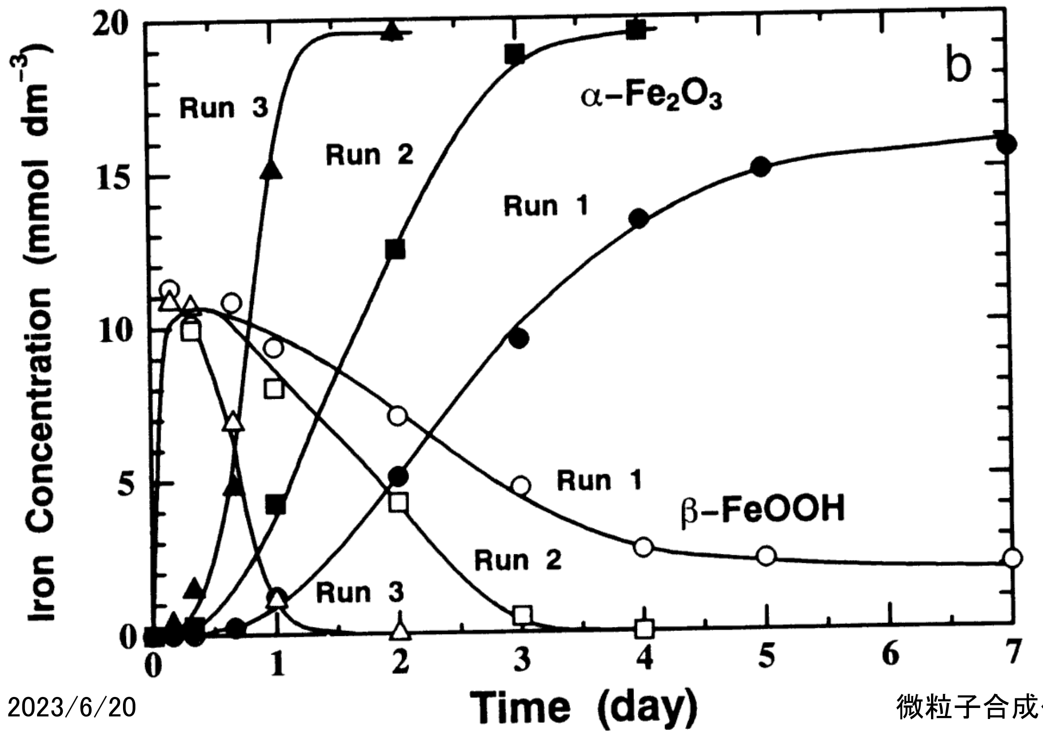
Seeds addition

Run 1 no seeds Run2 Seeds small Run3 Large



Effect on the rate





The apparent growth rate increases as the amount of seed added increases. ⇒
Therefore, no aggregative growth mechanism is possible.
In addition, it was decided that the product should be single crystalline and that no primary particles should be observed in the formation pathway.

Particle growth =
direct deposition of solute
≠ aggregative growth mechanism

Nucleus number is almost the same as particle number

Run No.	Aging time (day)	Nucleus number (dm^{-3}): Seeds	Nucleus number (dm^{-3}): Spontaneous nuclei	Nucleus number (dm^{-3}): Total	Products: Yield (mol%)	Products: Size (μm)	Products: Aspect ratio	Products: Particle number (dm^{-3})
Run 1 (a)	7	0	$8.4x10^{13}$	$8.4x10^{13}$	77.8	0.67	6.7	$8.4x10^{13}$
Run 2 (b)	4	$2.7x10^{14}$	$8.4x10^{13}$	$3.5x10^{14}$	94.2	0.46	6.5	$2.9x10^{14}$
Run 3 (c)	2	$2.7x10^{14}$	$8.4x10^{13}$	$2.8x10^{15}$	97.7	0.22	6.3	$2.5x10^{15}$

Monodispersed Hematite Particles

2023/6/20

Systematic control of size, morphology and internal structure

Monodispersed Hematite Particles Synthesized by the Gel-Sol Method

Na_2SO_4 or NaH_2PO_4
Addition of shape controller

When the temperature during mixing is changed, the supersaturation state of the solution changes, and the number of nuclei generated in hematite particles changes.

2 mol dm^{-3} $FeCl_3$

↓ ← 4.8 – 5.8 mol dm^{-3} NaOH

$Fe(OH)_3$

Seeds are added here, and the size is controlled by the seed growth method.

↓ **100℃ closed container**

β-FeOOH

Intermediate

↓ **100℃ closed container**

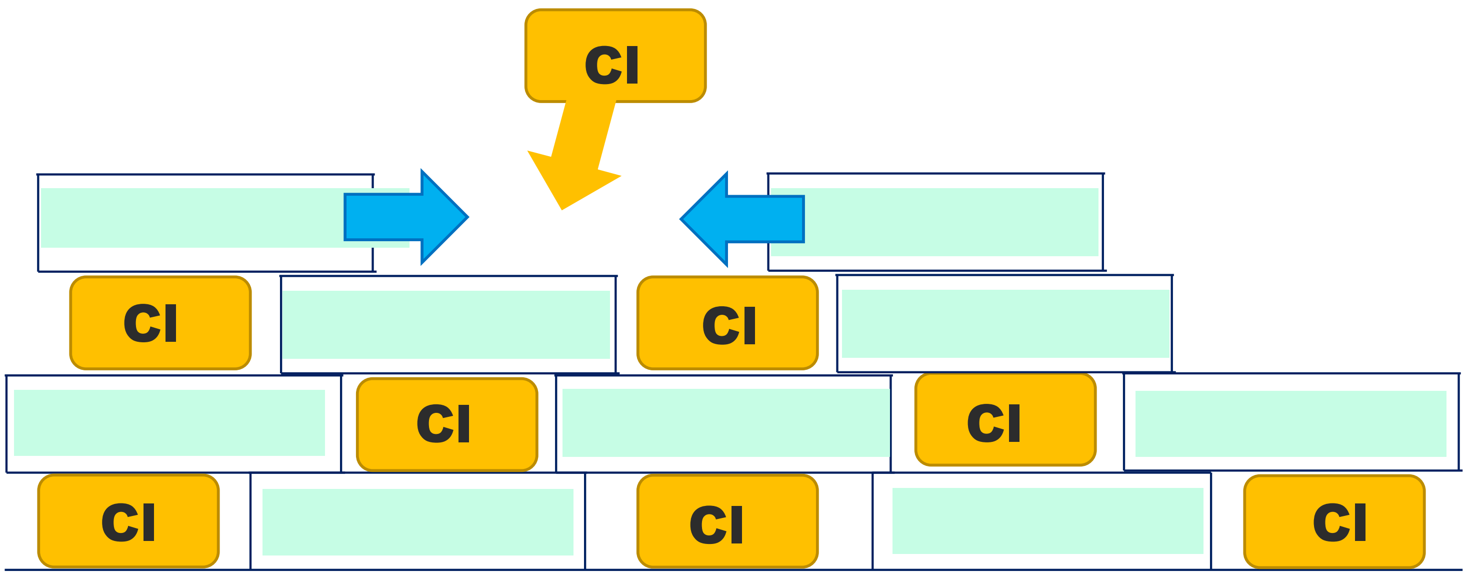
α-Fe_2O_3

Since Cl inhibits crystallization during the growth, if the Cl is removed here, the crystallinity increases.

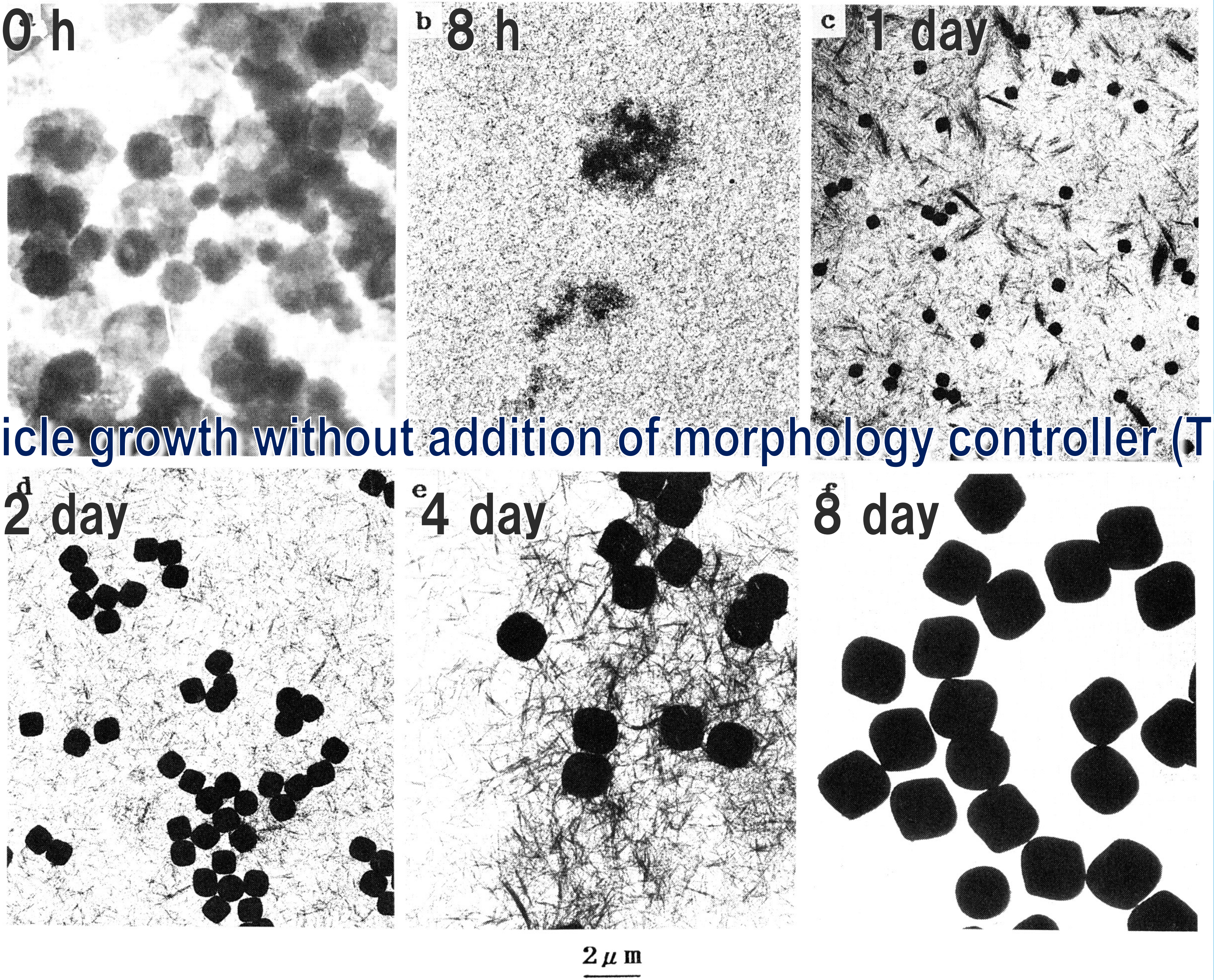
The highly viscous ferric hydroxide gel and the intermediate product Akaganite protect the particles from coagulation.

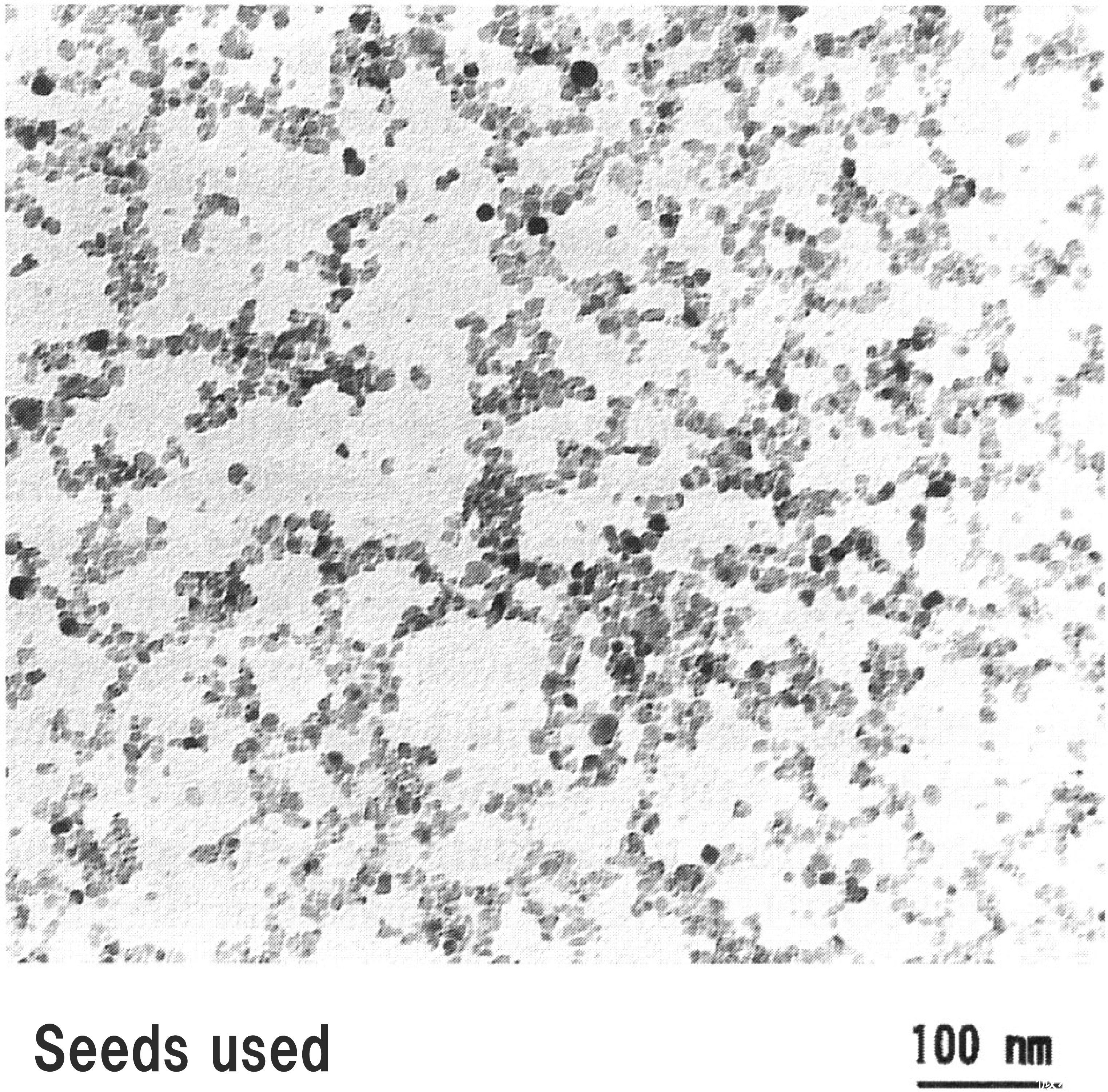
Crystallization inhibition by residual chlorine Cl

It should be a single crystal, but it turns out to be a polycrystal.



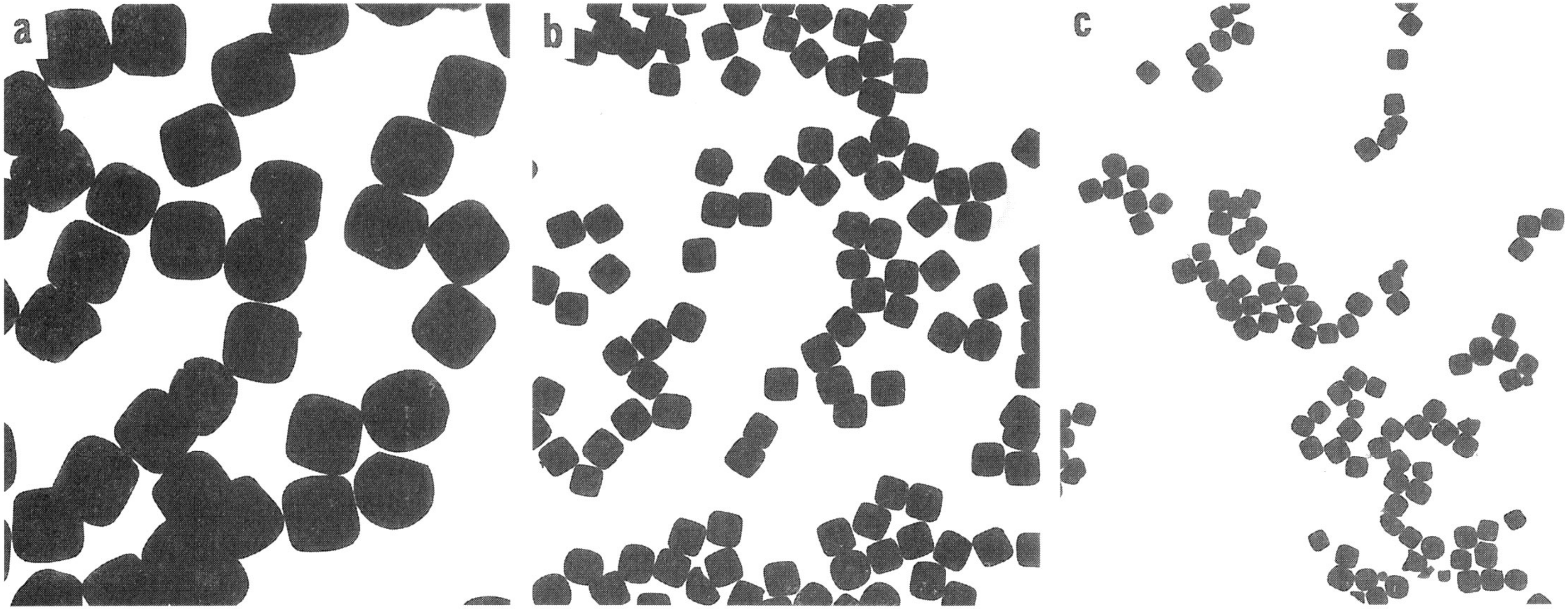
Particle growth without addition of morphology controller (TEM)




Seeds used
100 nm

Size control by the number of generated nuclei

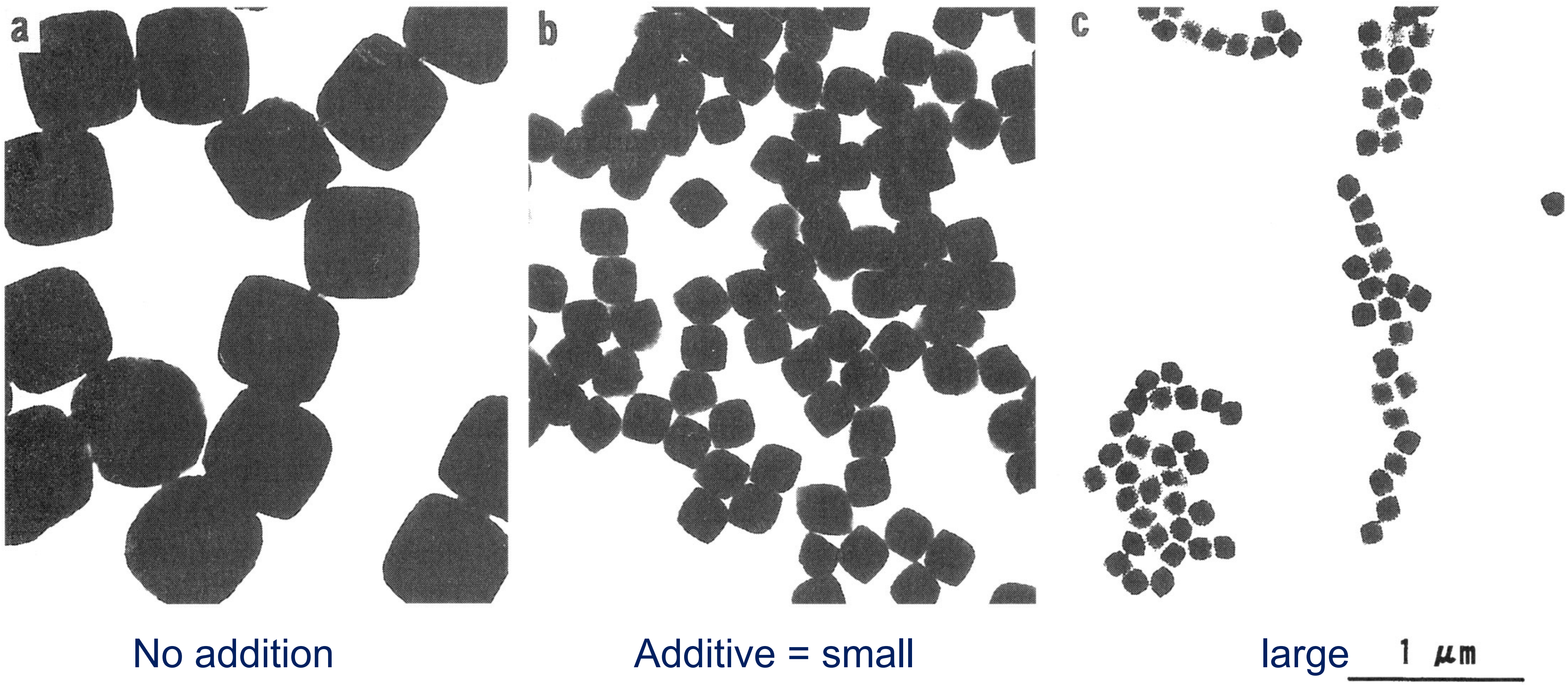
Control the solution temperature when $FeCl_3$ and NaOH are mixed (TEM)



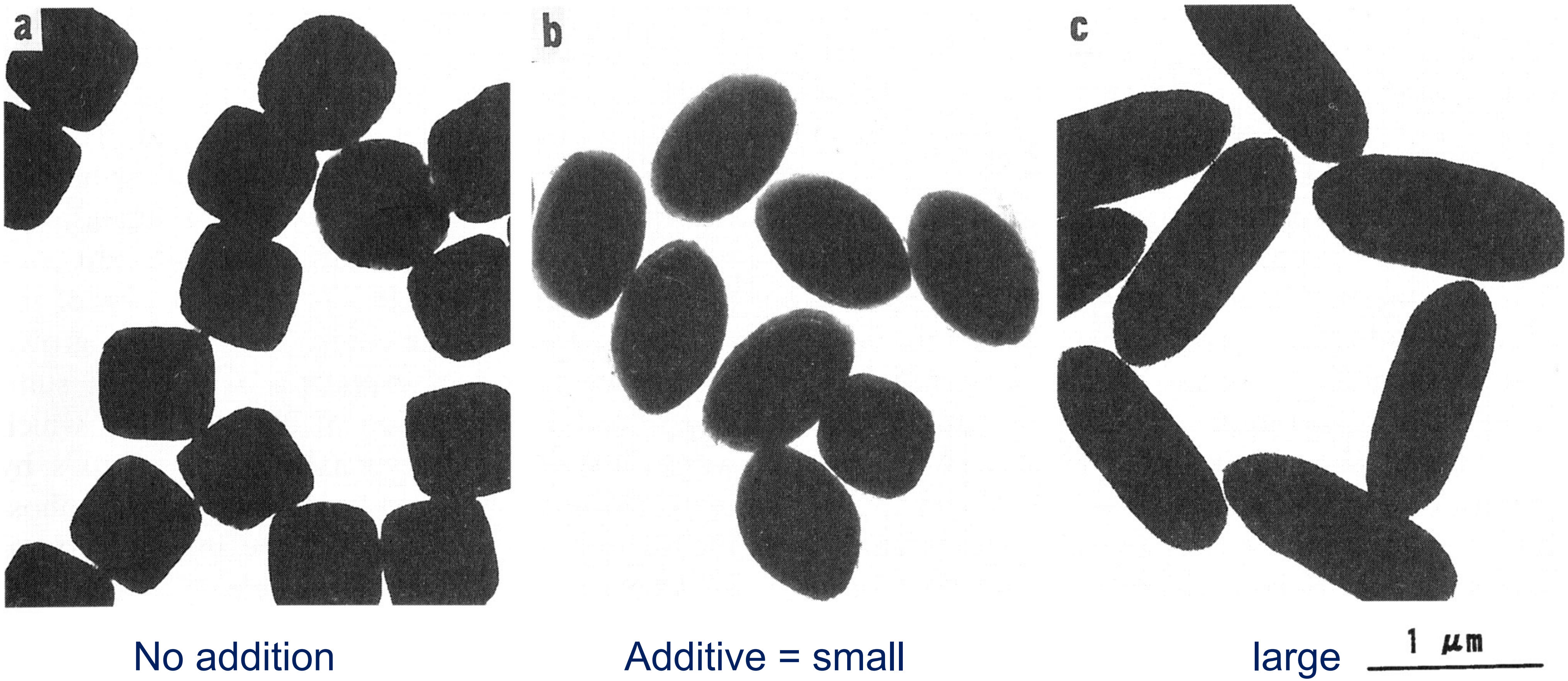
Normal (R.T.)　　ca 70℃　　ca 90℃

Size control by using seeds

Size control by seeds addition（TEM)

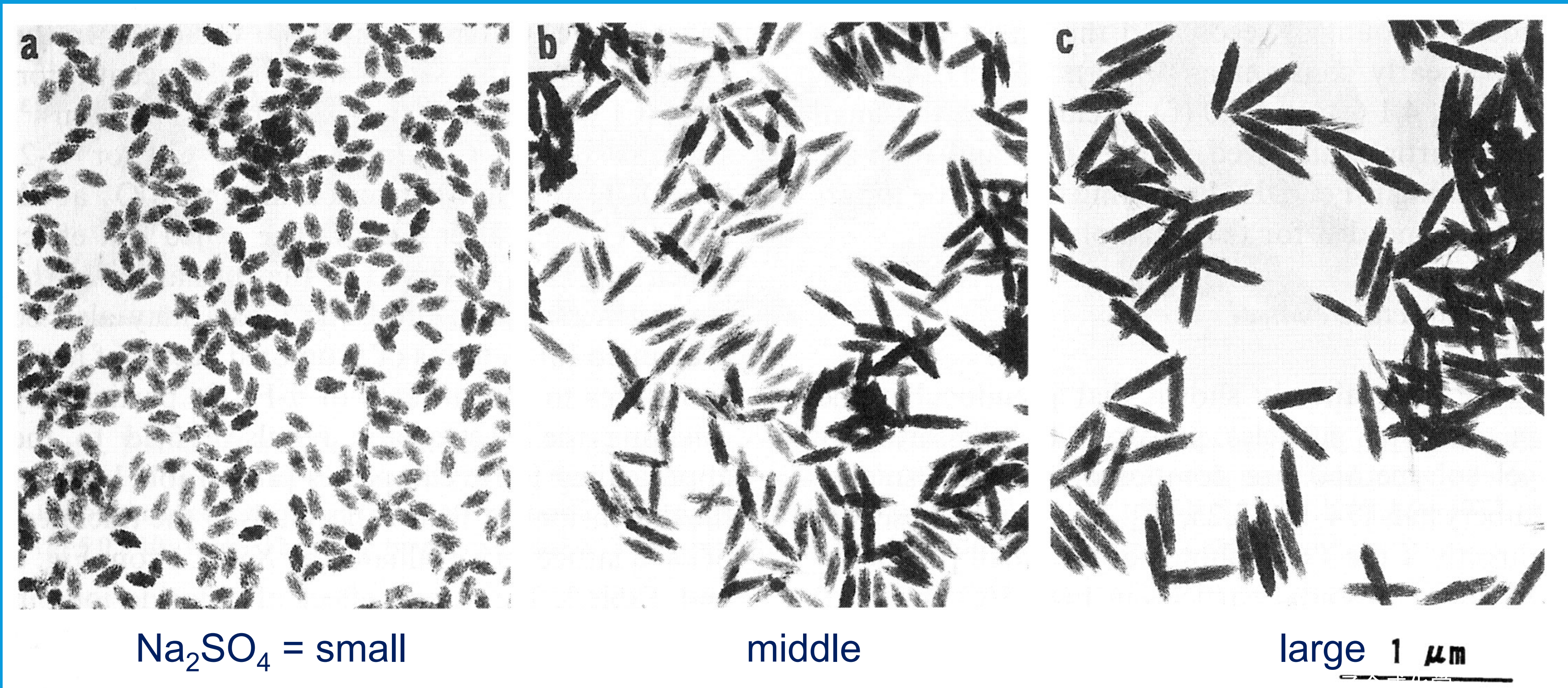


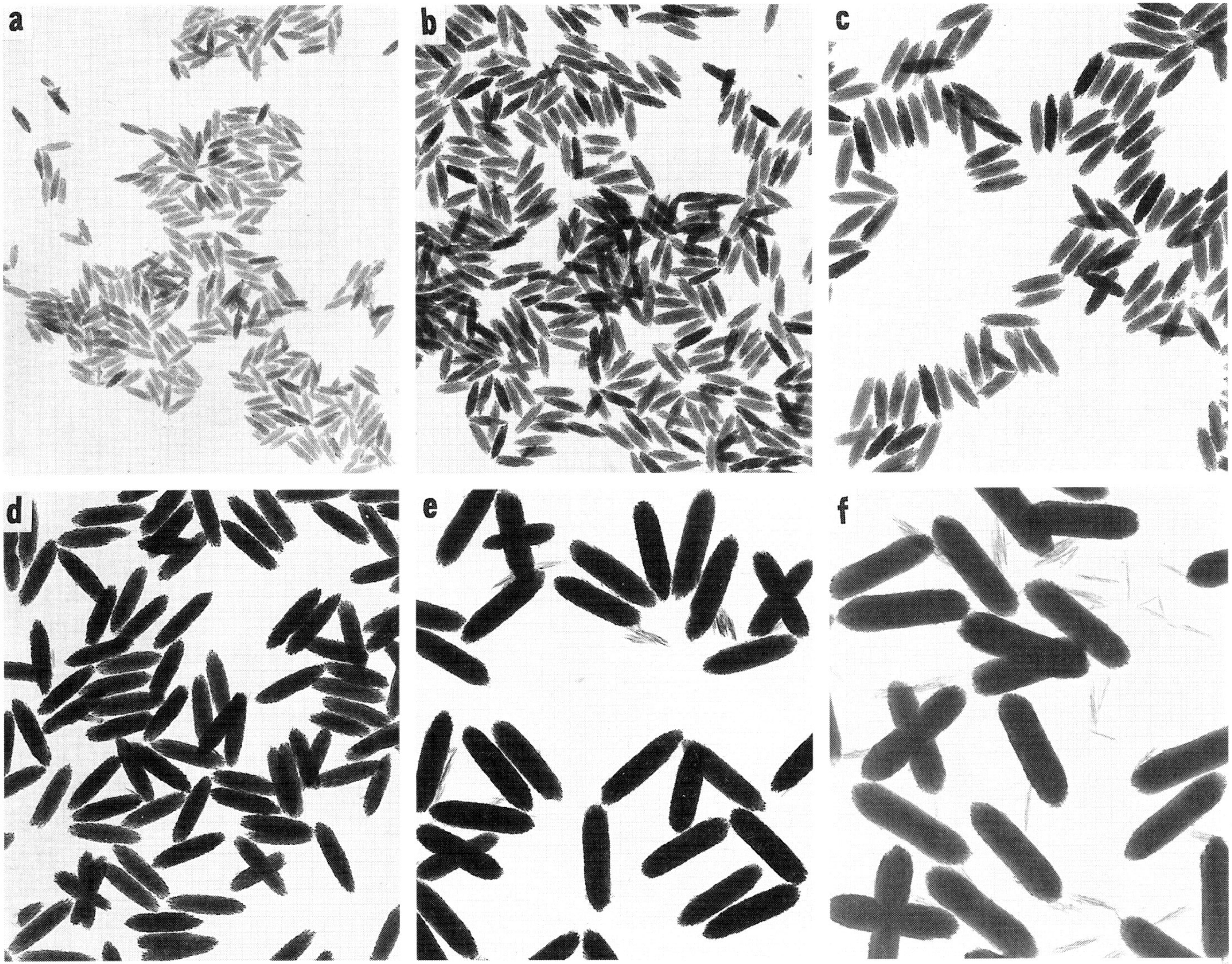
Shape controller /Phosphate Na_2HPO_4



No addition   Additive = small   large

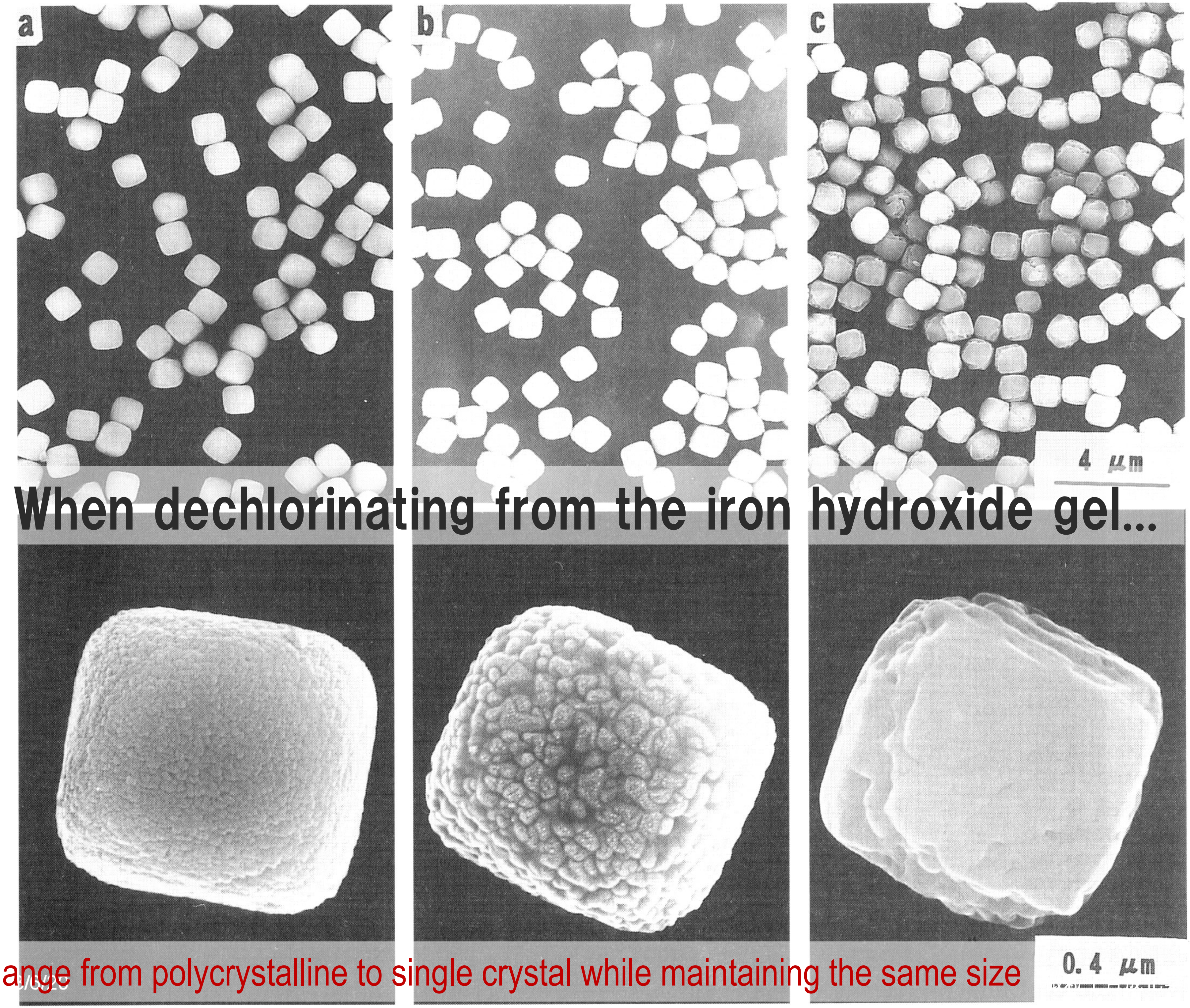
Seeds amount is constant.
Shape controller/sulphate amount changes.





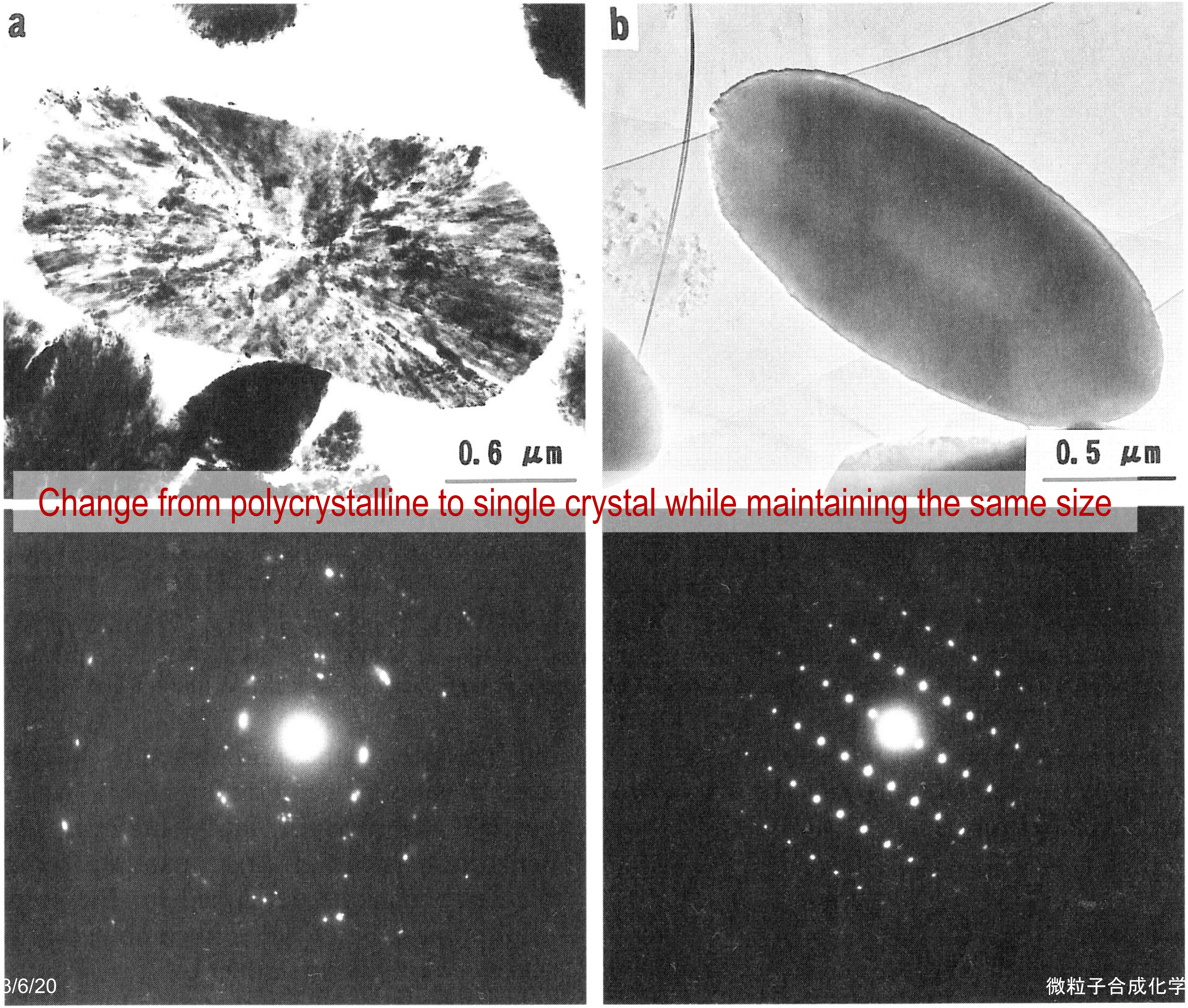
Sulfate concentration is constant, seed amount change

1 μm

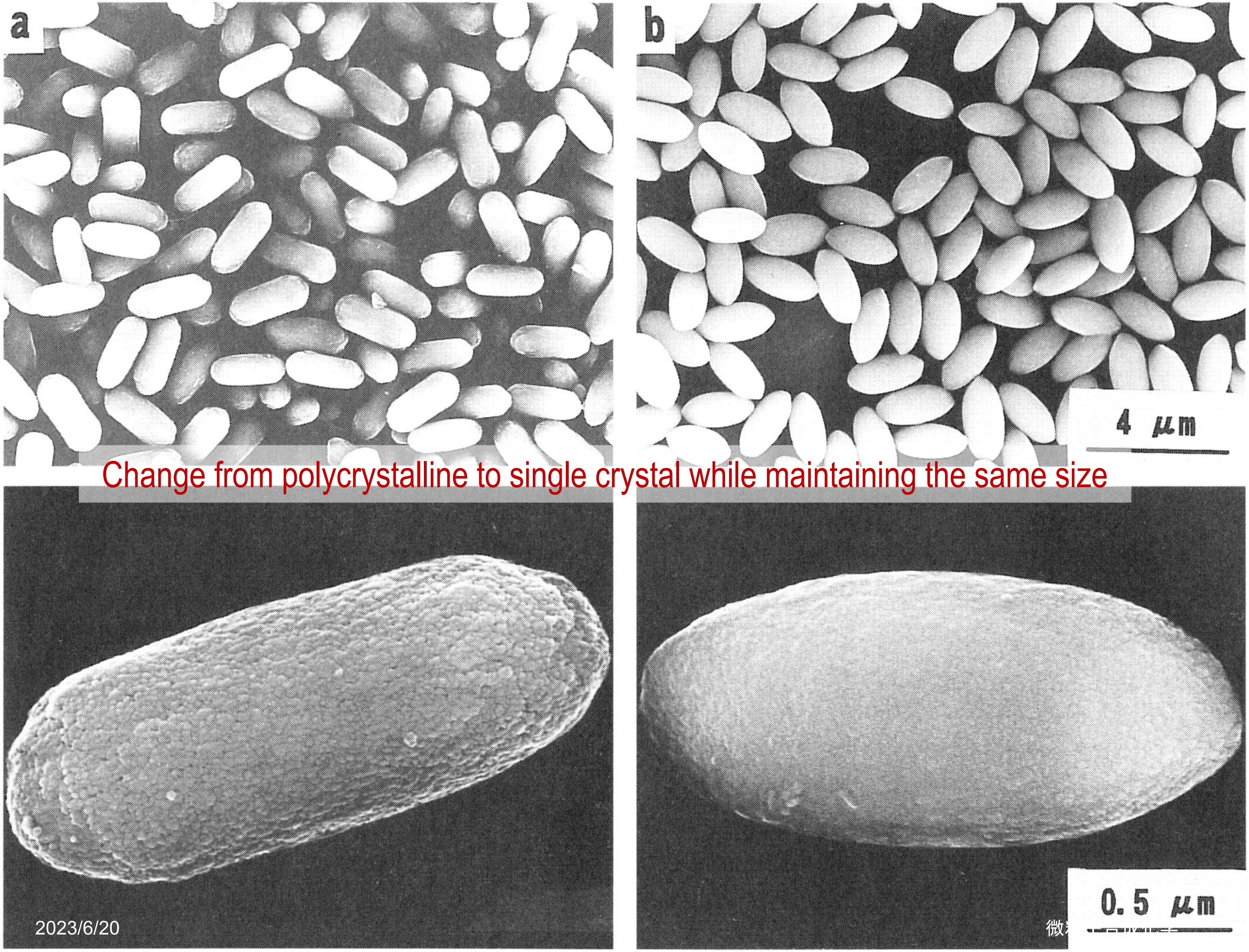


When dechlorinating from the iron hydroxide gel...

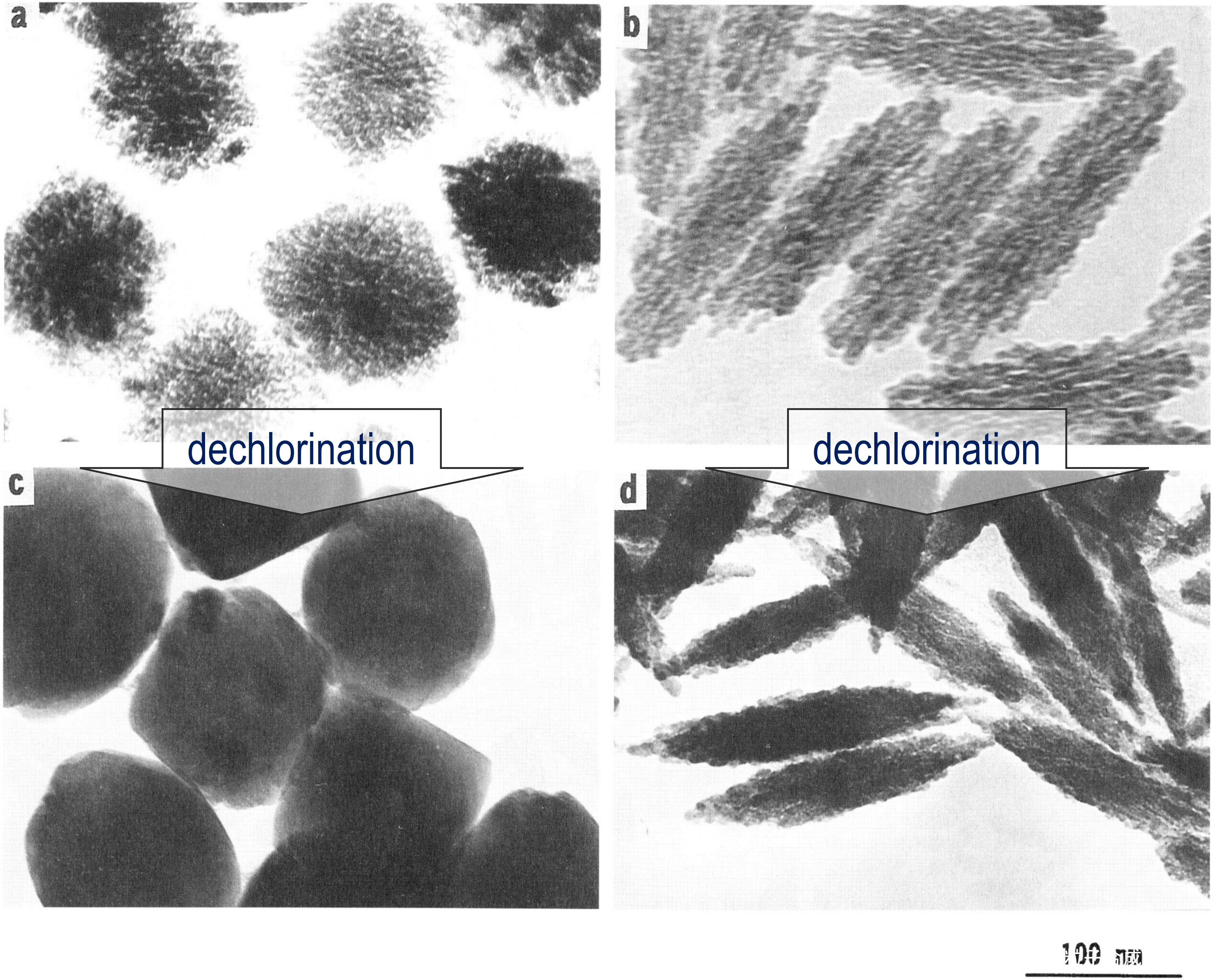
Change from polycrystalline to single crystal while maintaining the same size

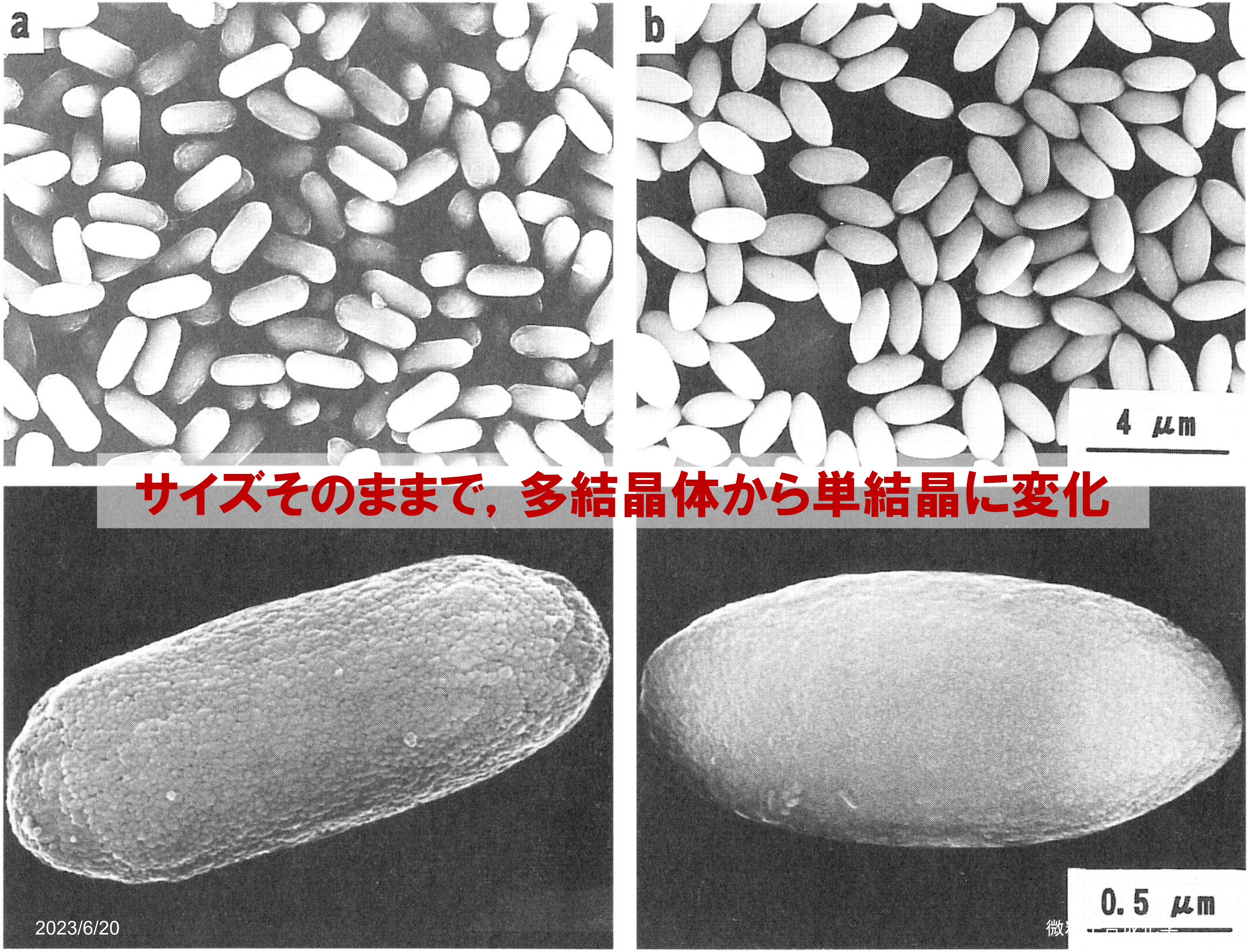


Change from polycrystalline to single crystal while maintaining the same size

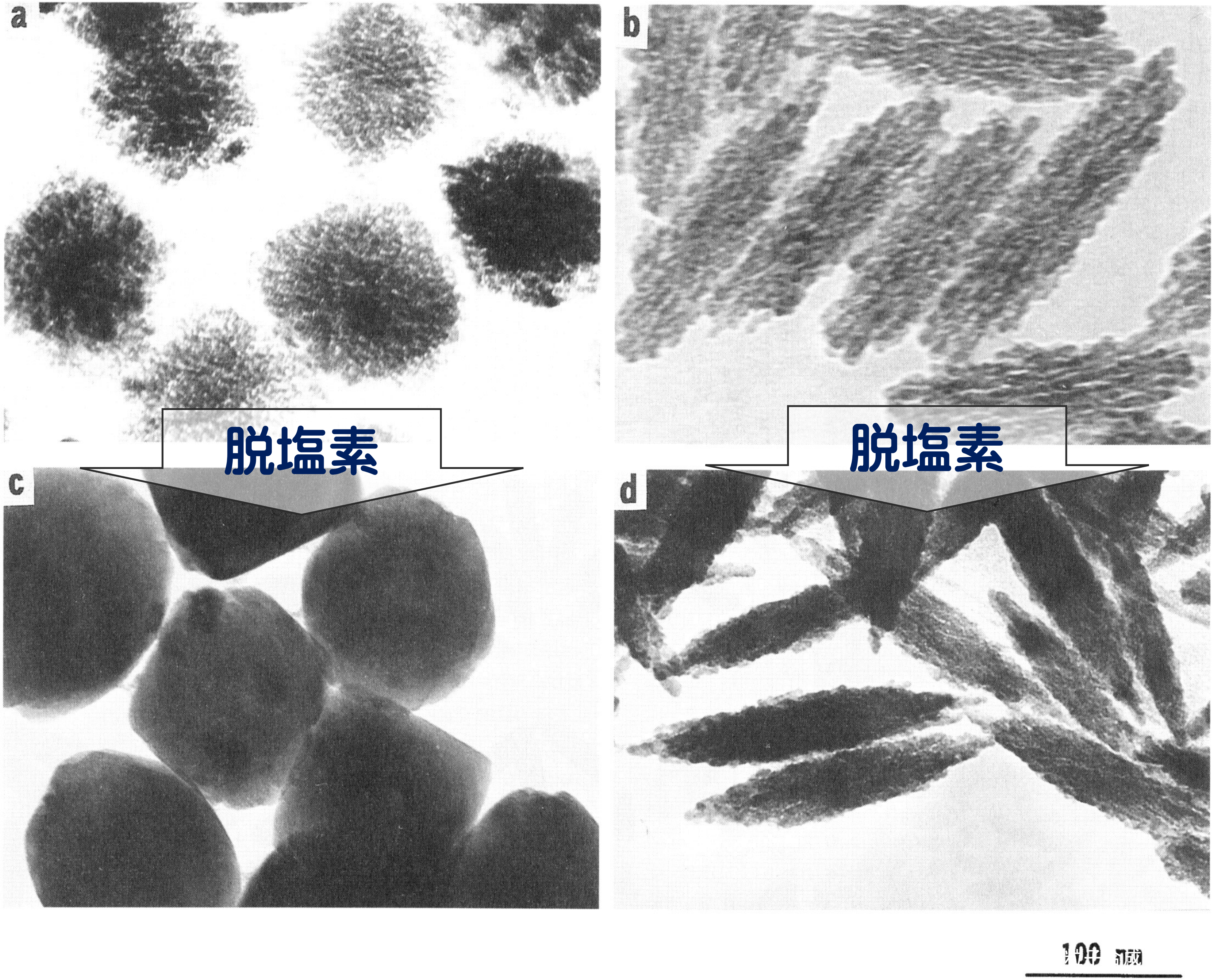


Change from polycrystalline to single crystal while maintaining the same size


a
b
dechlorination
dechlorination
c
d
100 nm



サイズそのままで，多結晶体から単結晶に変化


a
b
脱塩素
脱塩素
c
d
100

Zirconia

BACKGROUNDS

1 General Requirements for the Preparation of Monodispersed Particles

1. Separation between nucleation and growth stages
2. Inhibition of coagulation
3. Reserve of monomers

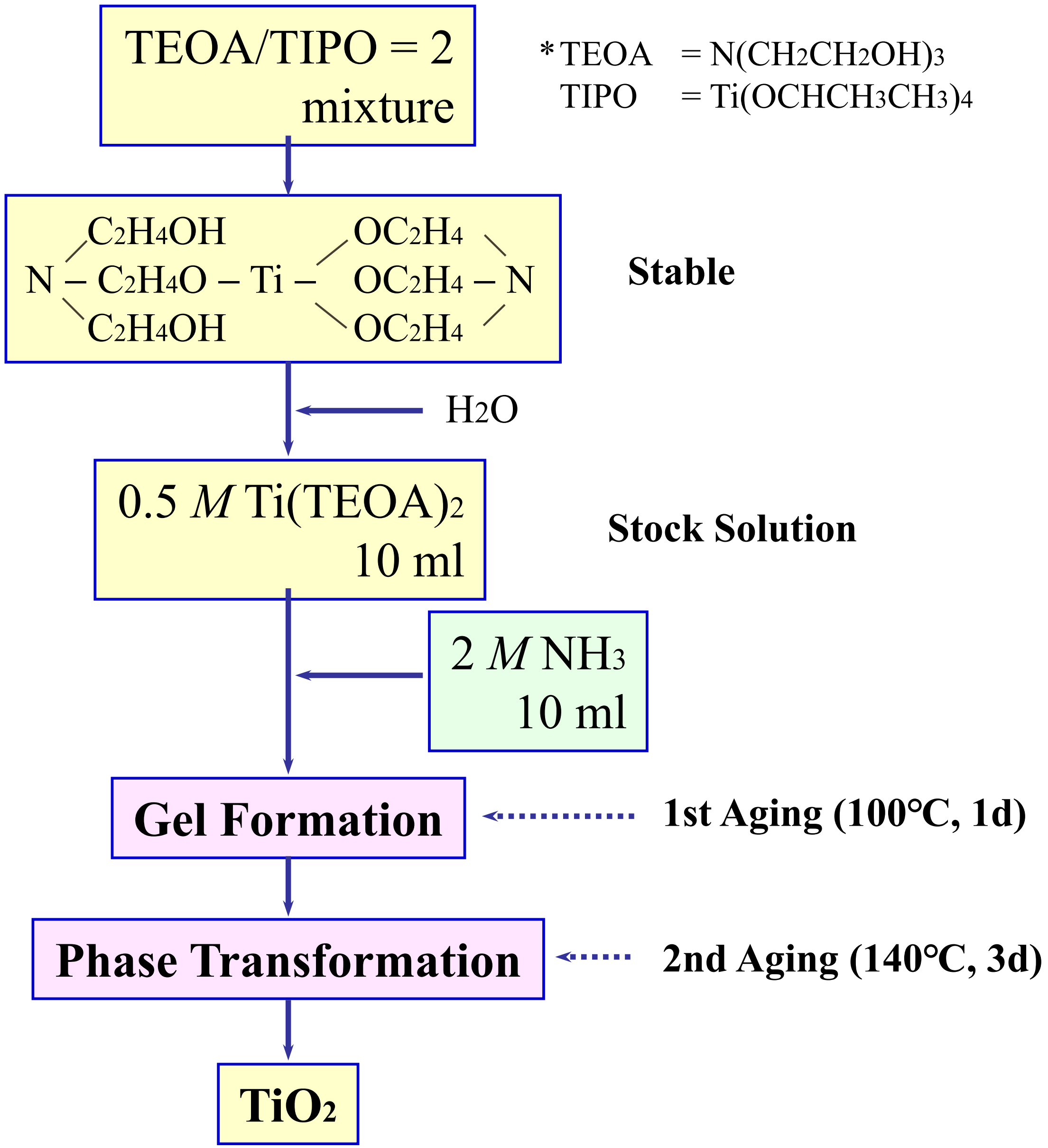
(T. Sugimoto, Adv. Colloid Interface Sci. 28, 65 (1987).)

"We need a new method to overcome the essential problem of coagulation so as to achieve a high productivity."

↓

"Gel-Sol Method"

2 Preparation of Monodispersed TiO_2



3

Role of Each Component to prepare ZrO_2 particles

- **TEOA = triethanolamine**
  - as a complexing agent with Zr propoxide to make stable complex, releasing ZrO2 monomers gradually
- **Ammonia**
  - as an inhibition of anisotropic growth

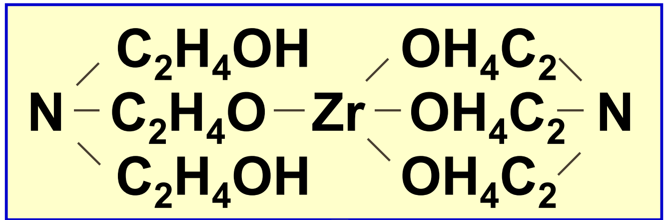
4

Standard Procedure

TEOA/ZNP = 3
mixture

TEOA = $N(CH_2CH_2OH)_3$
ZNP = $Zr(OCH_2CH_2CH_3)_4$

Agitation (24 h, room temp.)



Stable Zr complex against hydrolysis at room temperature

H_2O

5

Fig. 1 FT-IR spectra of TEOA-ZNP mixture

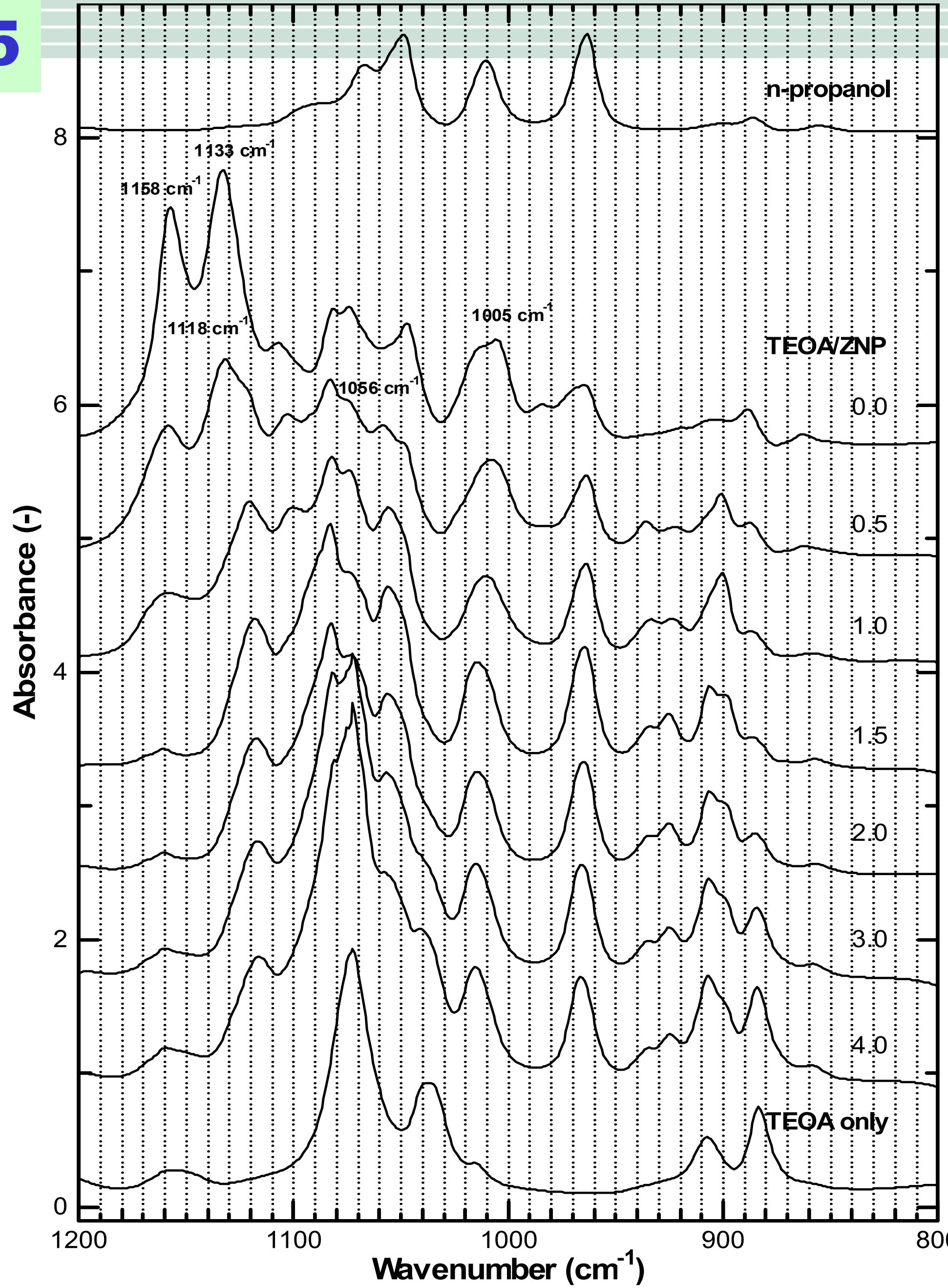
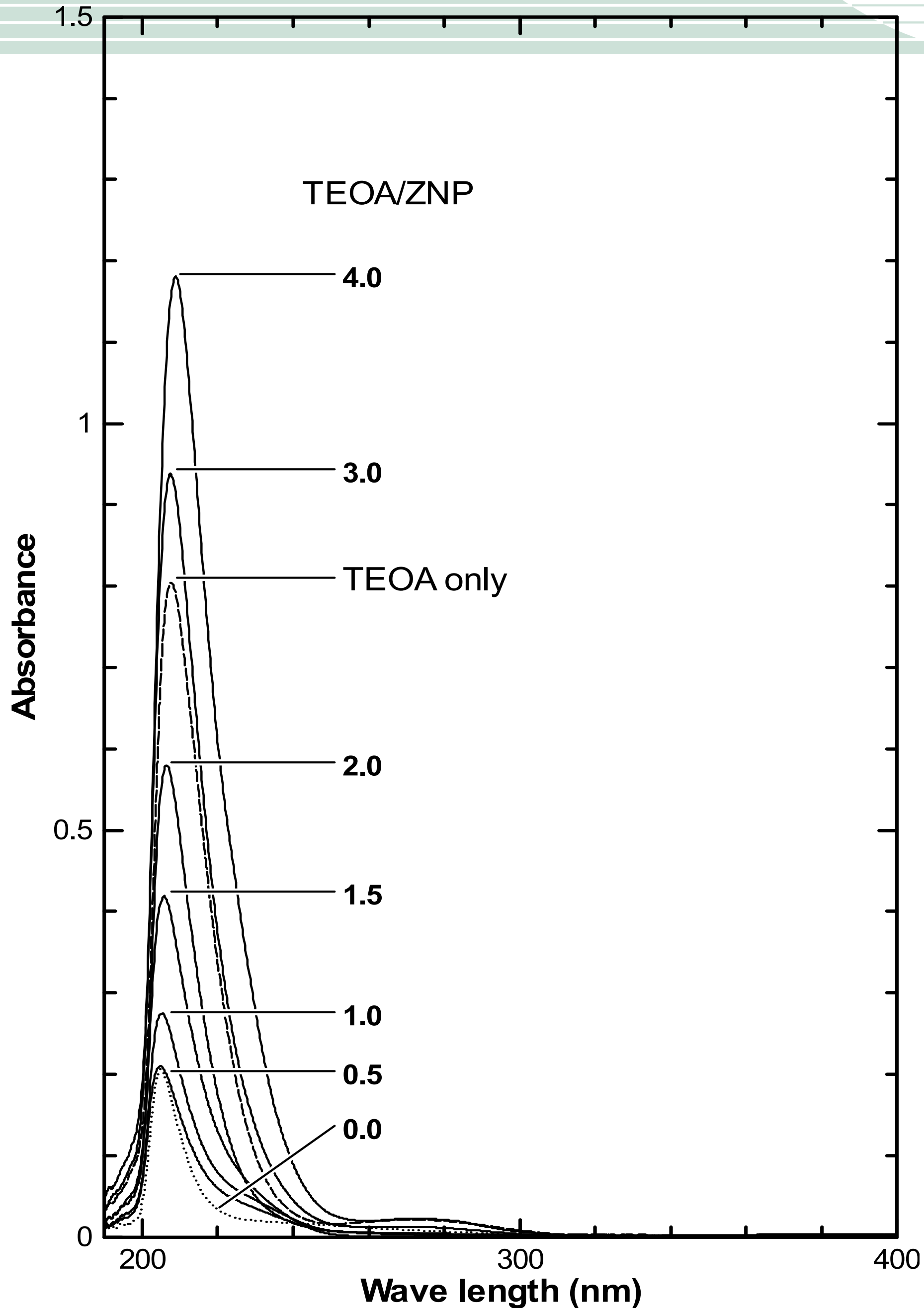


Fig. 2 UV spectra of TEOA-ZNP mixture



NH_3

0.5 *M* $Zr(TEOA)_2$
1 *M* NH_3

pH 10.7

Transparent solution

Aging

200℃, 3 days

Gelation and phase transformation

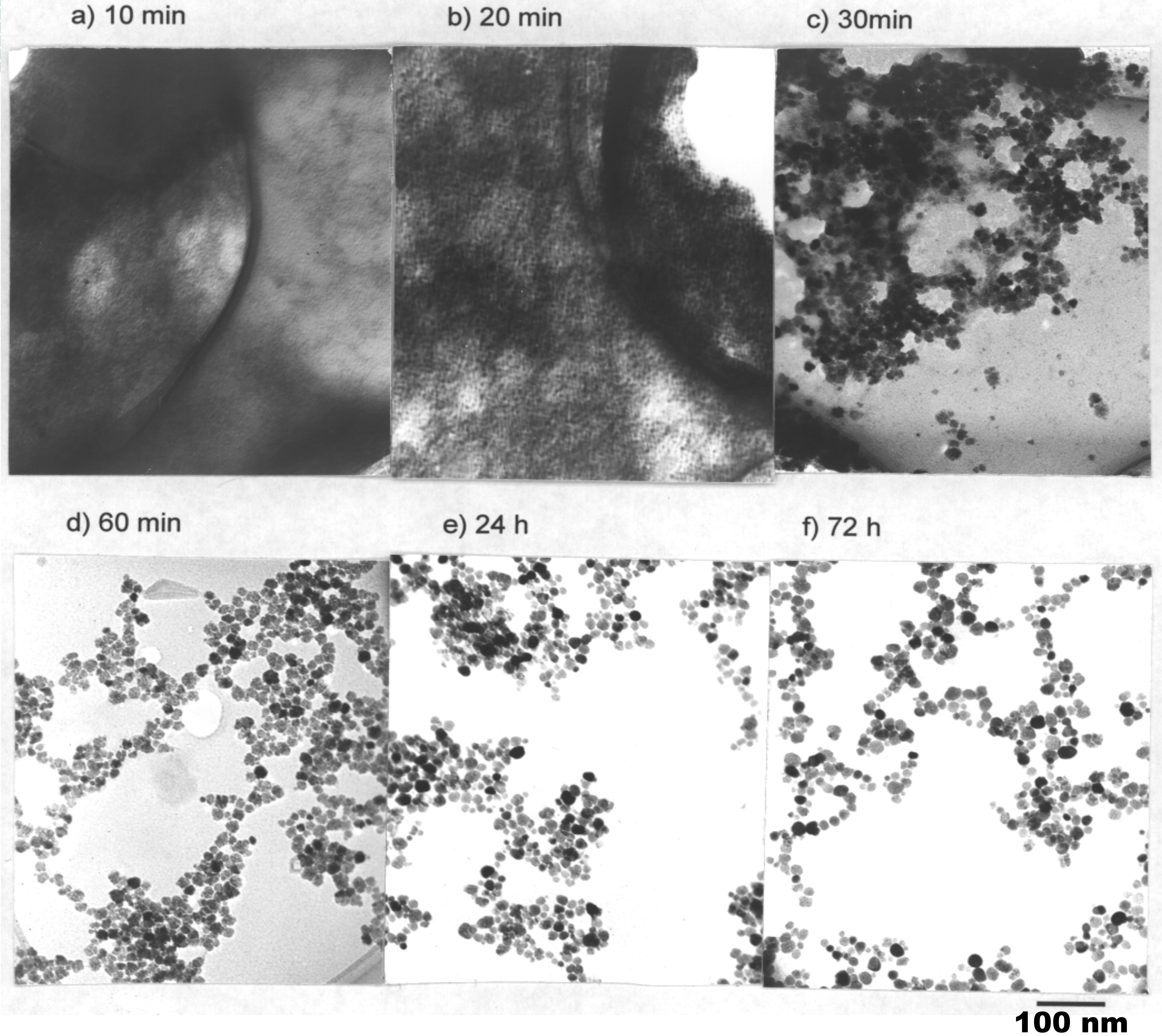
ZrO_2

Uniform crystalline nanospheres of ZrO_2 (~15 nm)

Fig. 3

7

Time evolution of ZrO_2 particle growth



8

Fig. 4 Change in FT-IR spectra with aging time

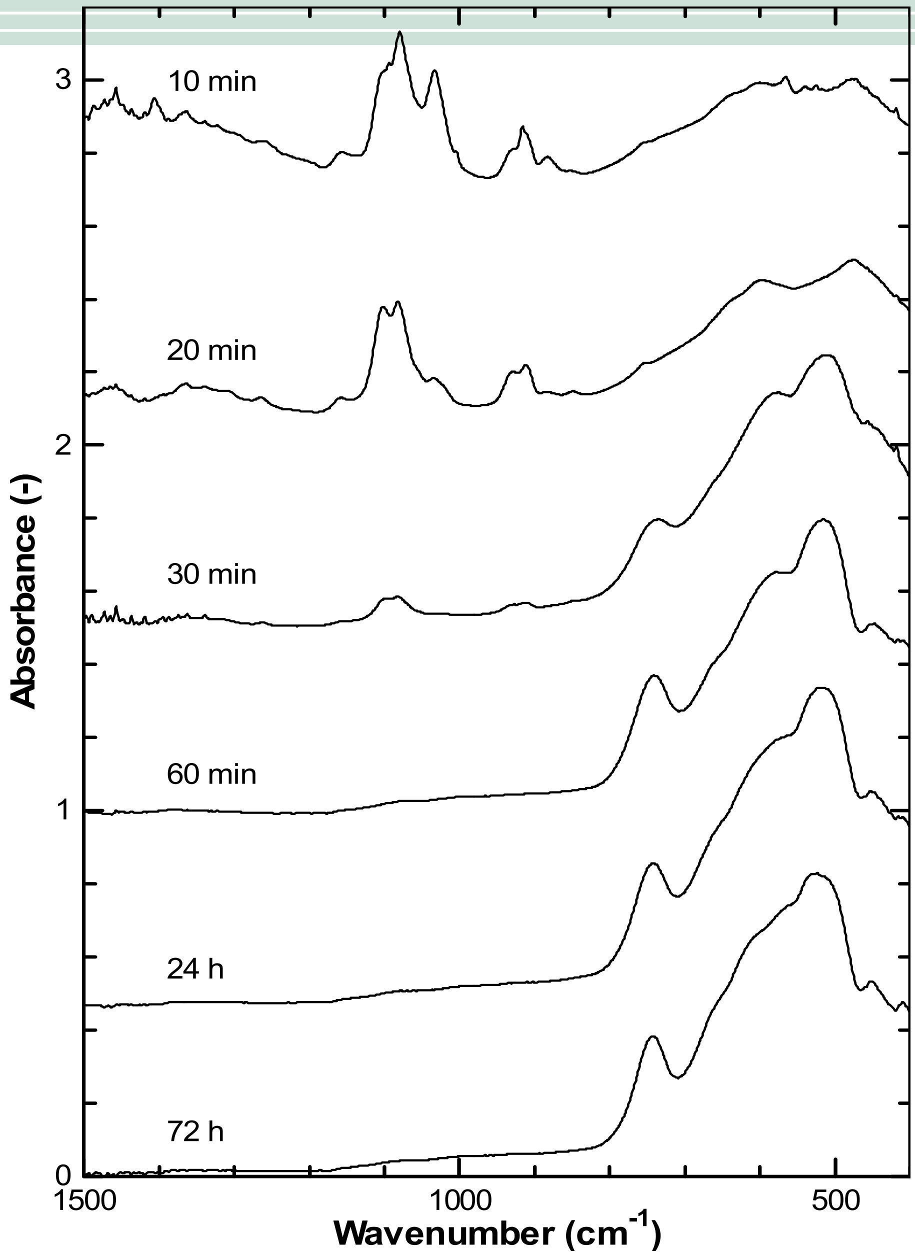
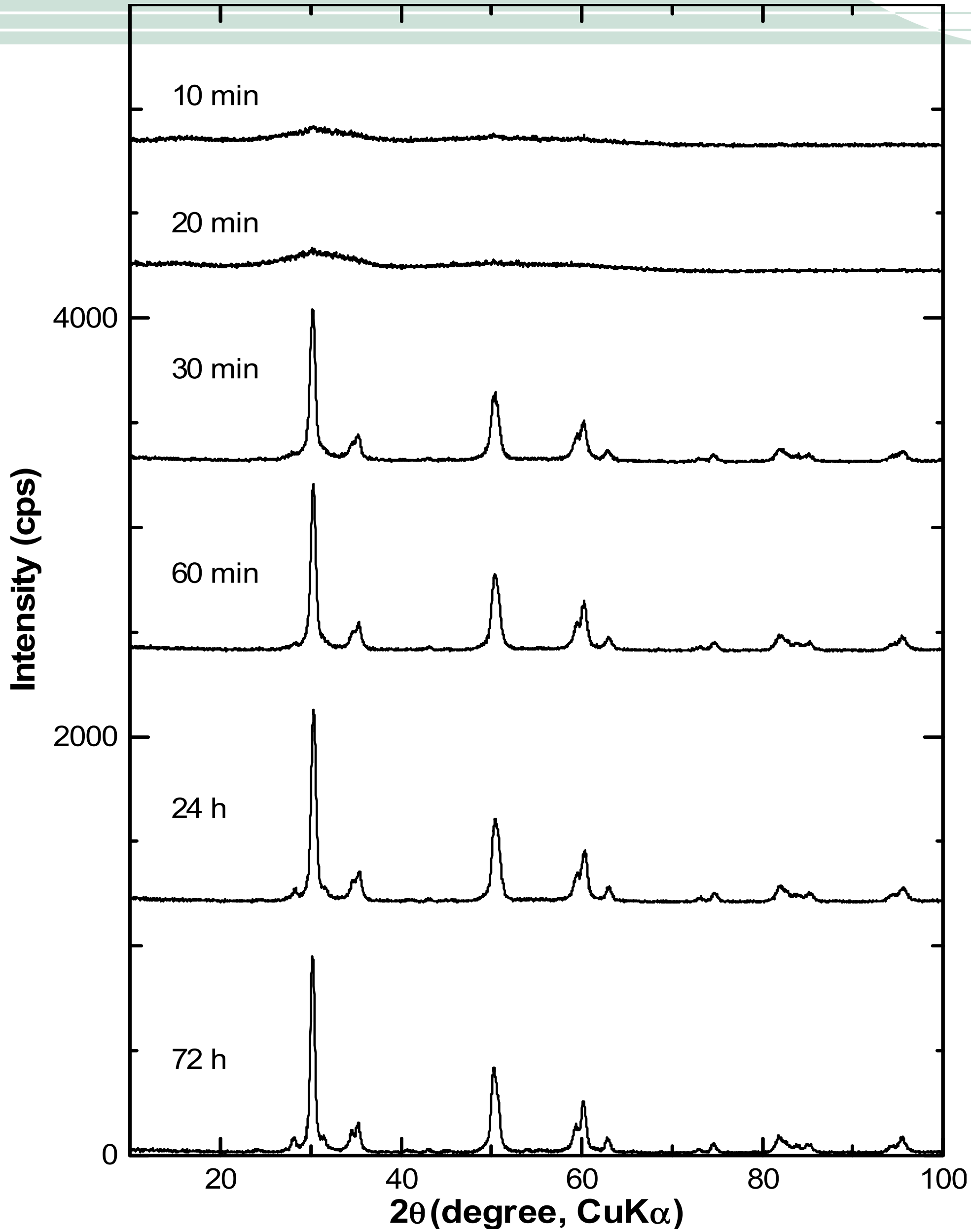
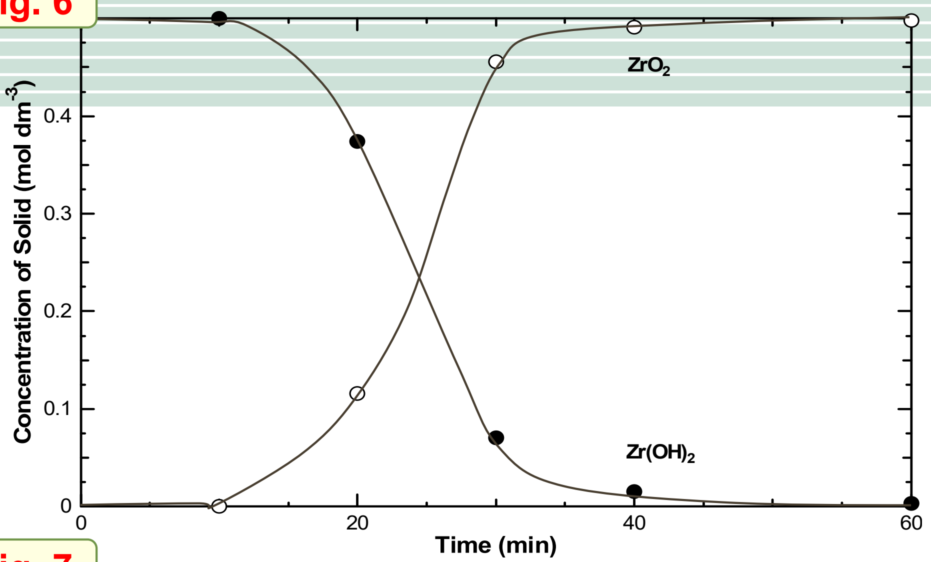


Fig. 5 Change in UV spectra with aging time



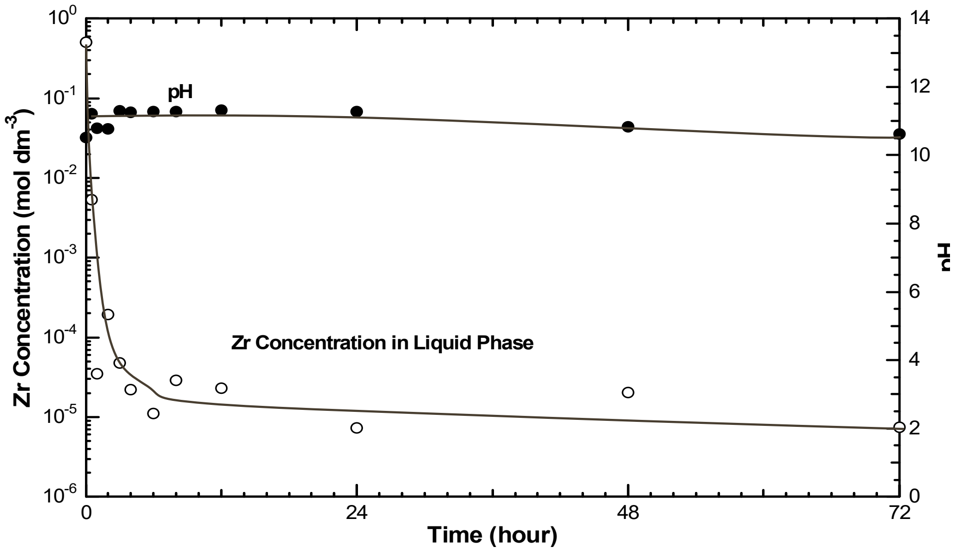
9

Fig. 6



Transformation from Zr(OH)$_2$ to ZrO$_2$ virtually finished within 1 hour.

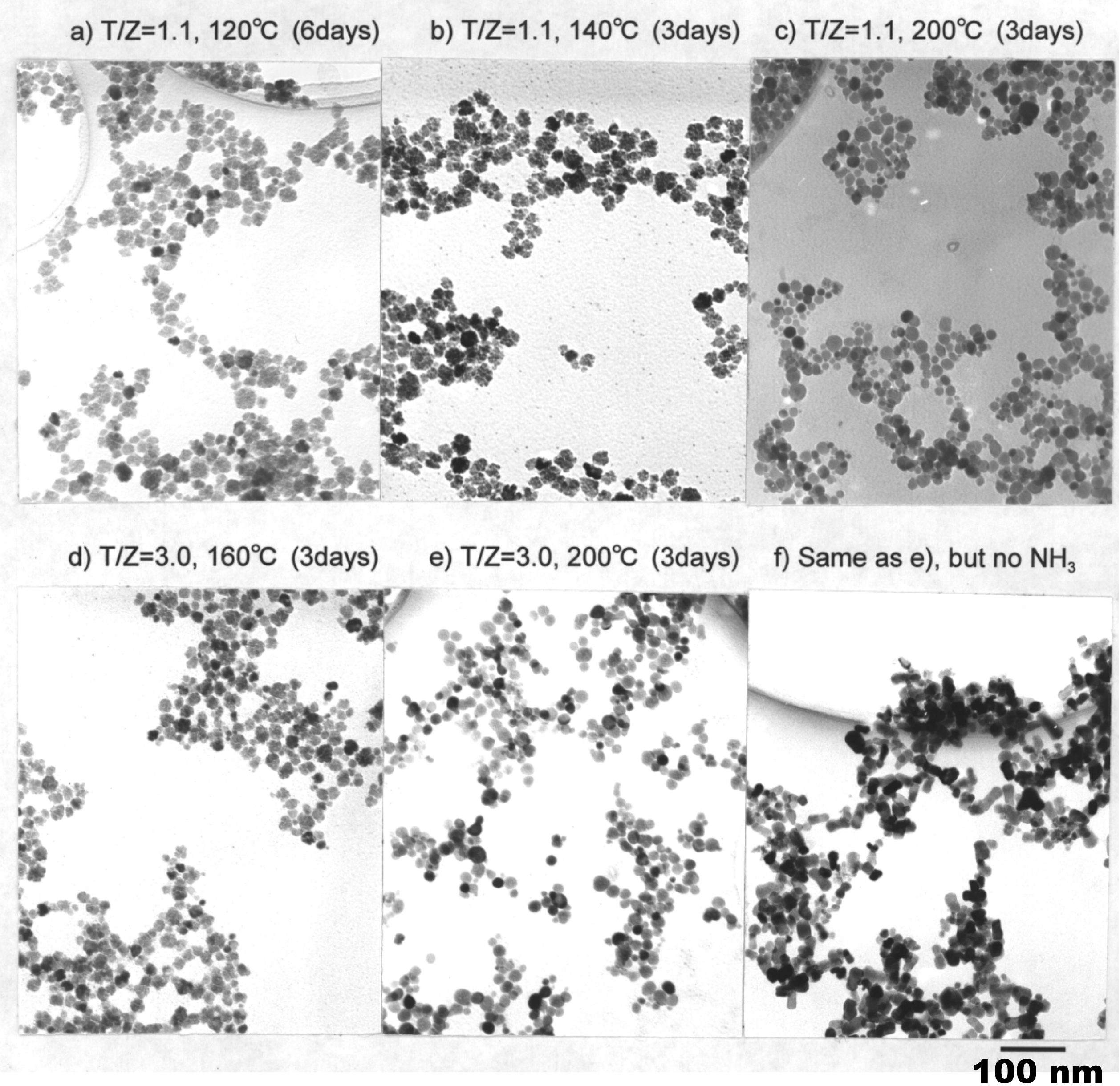
Fig. 7



Though the particles at 60 min were of rough surfaces, they became spherical by degrees with further aging. This morphological change seems to be due to the intra-particle recrystallization, but the ordinary Ostwald ripening concurrently proceeds.

10 Effects of TEOA/ZNP ratio, temperature and concentration of NH_3

Fig. 8



T/Z = TEOA/ZNP

TEOA/ZNP

As TEOA/ZNP increases, the uniformity is improved.

Temperature

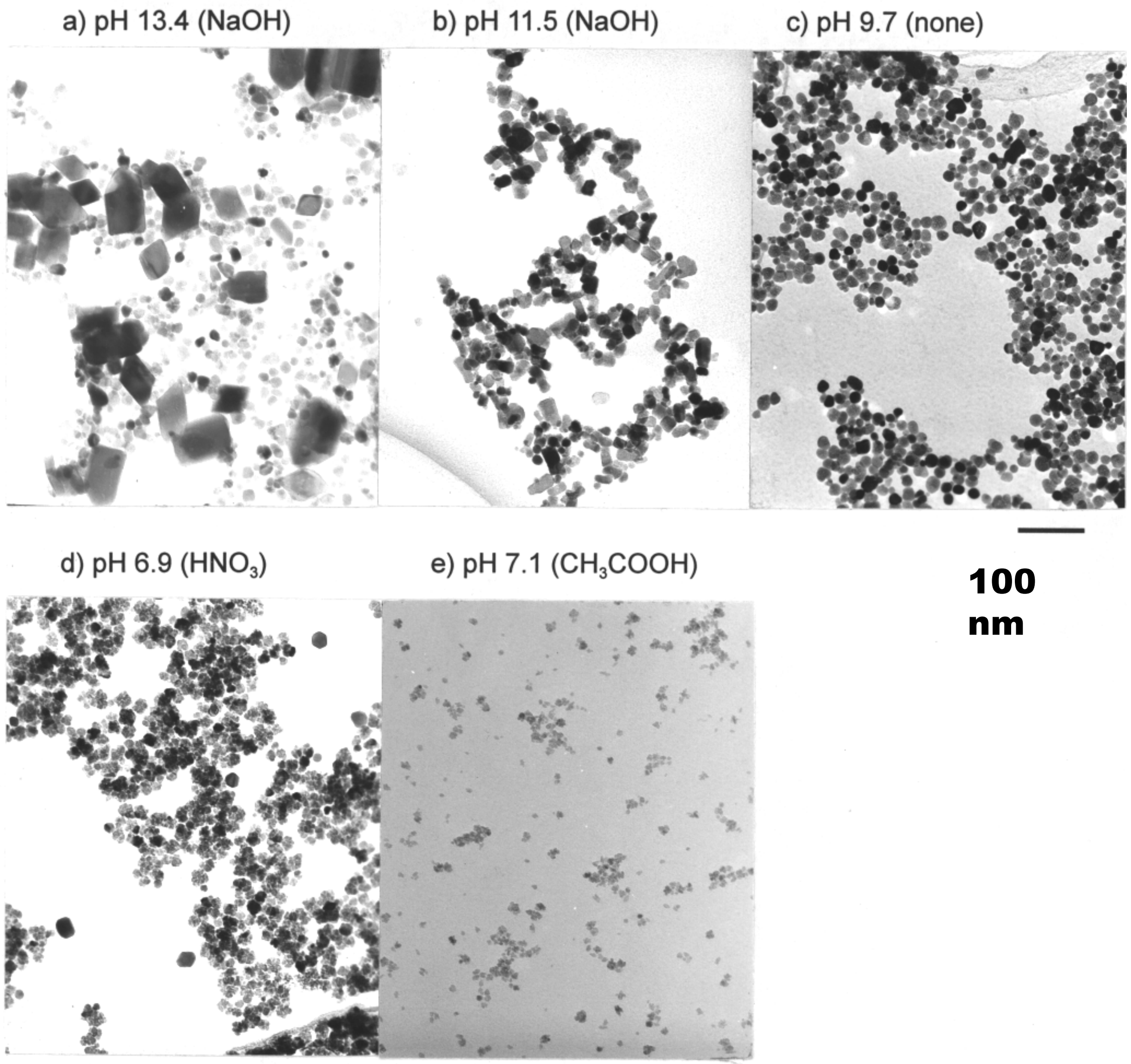
As temperature is elevated, the uniformity is improved, the mean size is decreased, and surfaces become smoother.

Ammonia

As $[NH_3]$ increases, shape of ZrO_2 changes from rectangular parallelepiped to spheroid at pH 10.7.

11 Effects of pH and acetate without NH_3

Fig. 9



High pH (13.4) >>
- very large
- sharp-edged
- size distribution: large

pH: decrease >>
- size: decrease
- size distribution: narrow
- shape:
  - irregular polyhedra
  - rods
  - smooth-surface spheroids

Acetate (pH 7.1)
- >> ultrafine in size

↓

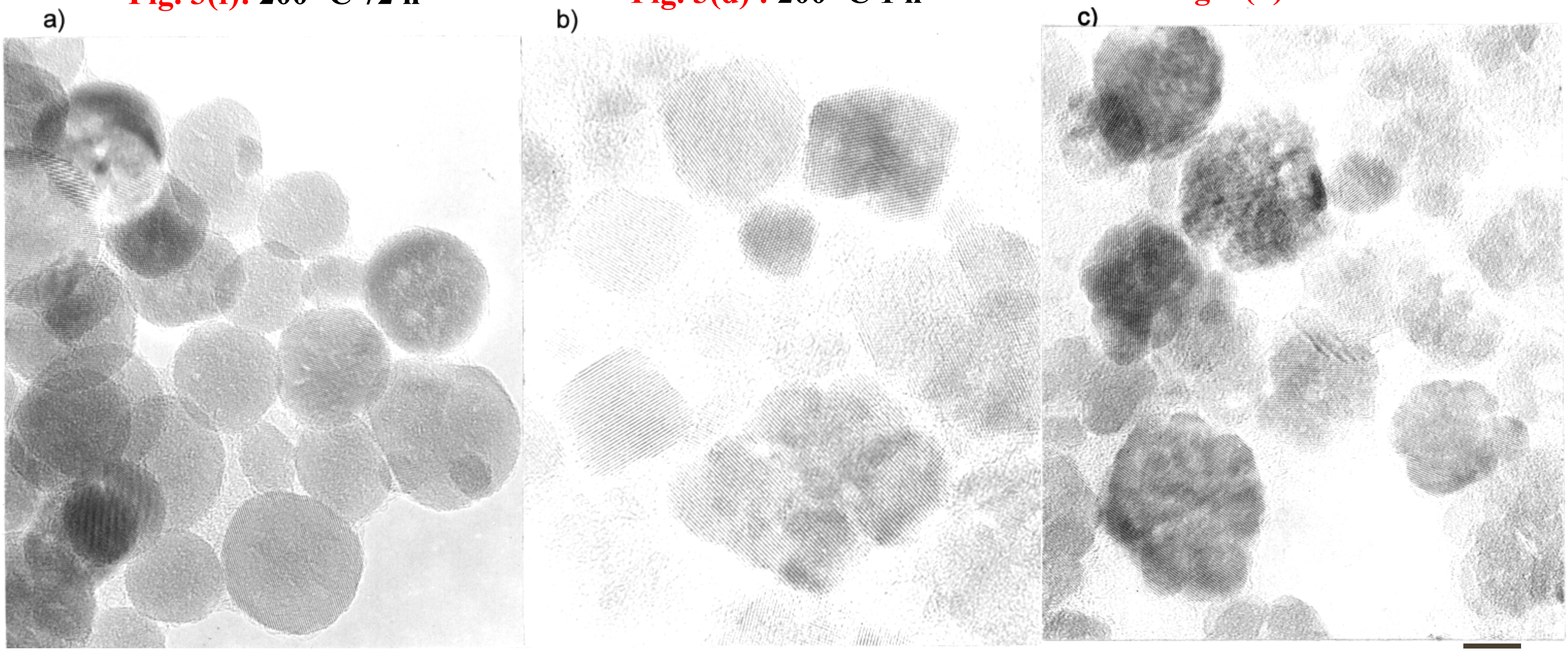
Reduction of the growth rate of ZrO_2 nuclei with descending pH, due to the decreasing concentration of hydroxide complexes

12

Characterization of ZrO_2 particles

Fig. 10

Fig. 3(f): 200 °C 72 h   Fig. 3(d) : 200 °C 1 h   Fig. 8(b) : 140 °C 72 h



All particles are basically single crystals, even if they are irregular in shape. The spherical particles of sample (a) are formed by intra-particle recrystallization of irregular-shaped particles like those of samples (b) and (c)

ITO

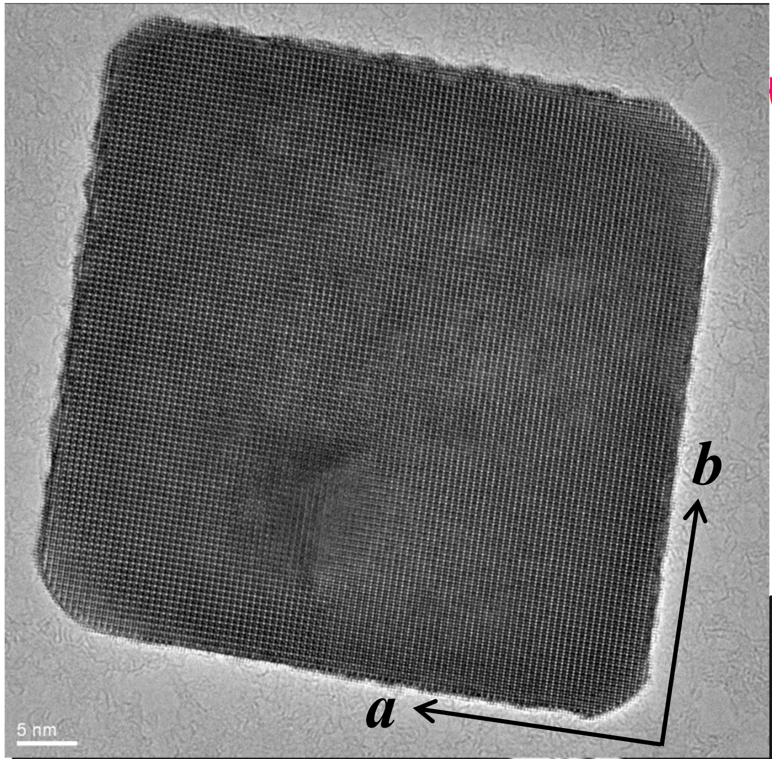
2023/6/20

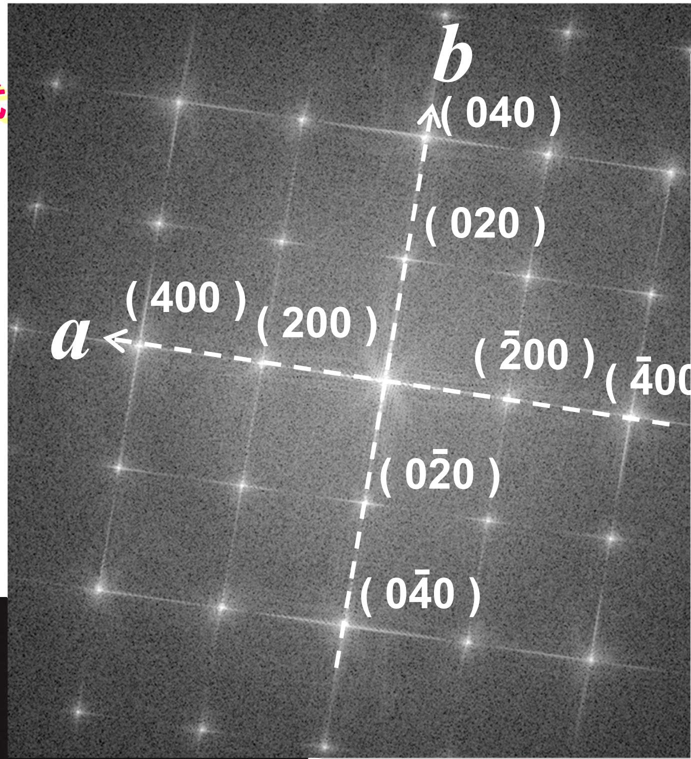
Monodisperse particles put to practical use in the field of advanced materials

Examples of cutting-edge nanomaterials ･･･

ITO （ tin-doped indium oxide ）

Materials necessary for smartphones, tablet PCs, and next-generation solar cells





薄型テレビ画面の材料「ITO」

安定微粒子合成に成功

東北大など 希少金属 節約可能に

東北大多元物質科学研究所の村松淳司教授（工業物理化学）のグループはDOWAエレクトロニクス（東京）と共同で、液晶ディスプレーなどの透明導電膜に利用されるインジウム・スズ酸化物（ITO）の安定した微粒子合成に成功した。生成手法は希少金属のインジウム使用量も抑えられ、効率的な塗布成膜法への応用が期待される。

ITOは、液晶やプラズマなど電子ディスプレーの透明導電膜の材料として広く普及。透明導電膜のほとんどは、電子を利用してITO分子をガラス基板に堆積（たいせき）させるスパッタリング法で生成されている。

スパッタリング法は導電性に優れた薄い膜ができる一方、基板以外にもITOが付着するなどの難点があり、省インジウム成膜法としてITO微粒子の塗料を使う塗布法が注目されている。

従来の塗布法では、十ナノメートル(ナノは十億分の一)以下の粒子を使用することから分散剤が必要となり、塗料の質低下による塗りムラや導電性の維持が課題となっていた。

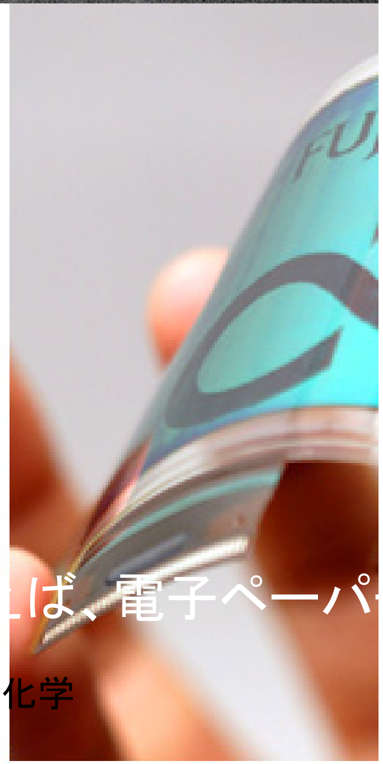
グループは、多元研が開発した単分散粒子合成法「ゲルーゾル法」を用いて、五十—百ナノメートルの立方体ITO微粒子の合成を実現した。

粒子のサイズ、形態、構造がそろっているため扱いやすく、水やアルコールなど溶媒への分散性が高いのが特長。基板に薄く均一に塗布できる上、ノズルから塗料を飛ばすインクジェットでも目詰まりしにくいという。

粒子の表面電位を制御することで導電性も確保し、生成過程ではインジウム含有率を減らすことも可能だという。

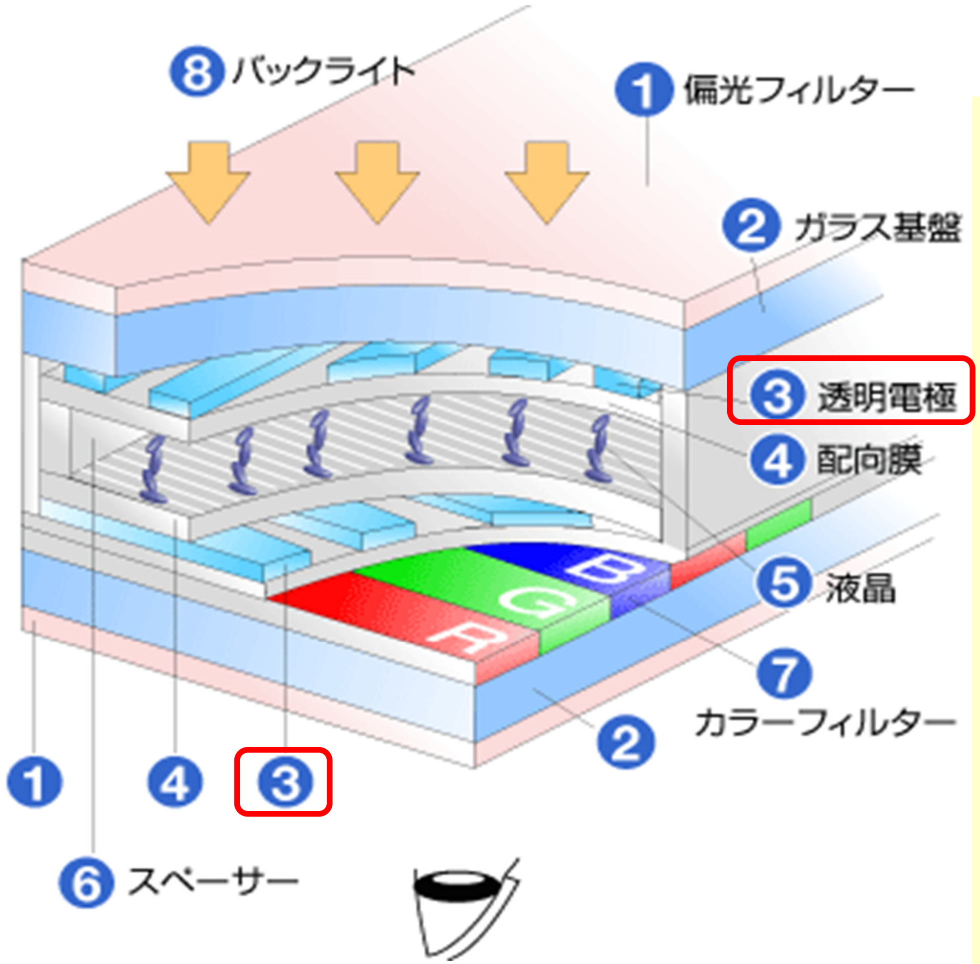
中国などからの輸入に依存しているインジウムは、薄型テレビの大型化に伴い需要が急増。将来的には供給不足も懸念され、消費量の低減や代替物質の開発が急務となっている。

村松教授は「小さな液晶用の透明導電膜に向く手法。実験室規模で大量に合成できるので、資源の無駄を減らし、生産性の向上も図れる」と話している。



たとえば、電子ペーパ

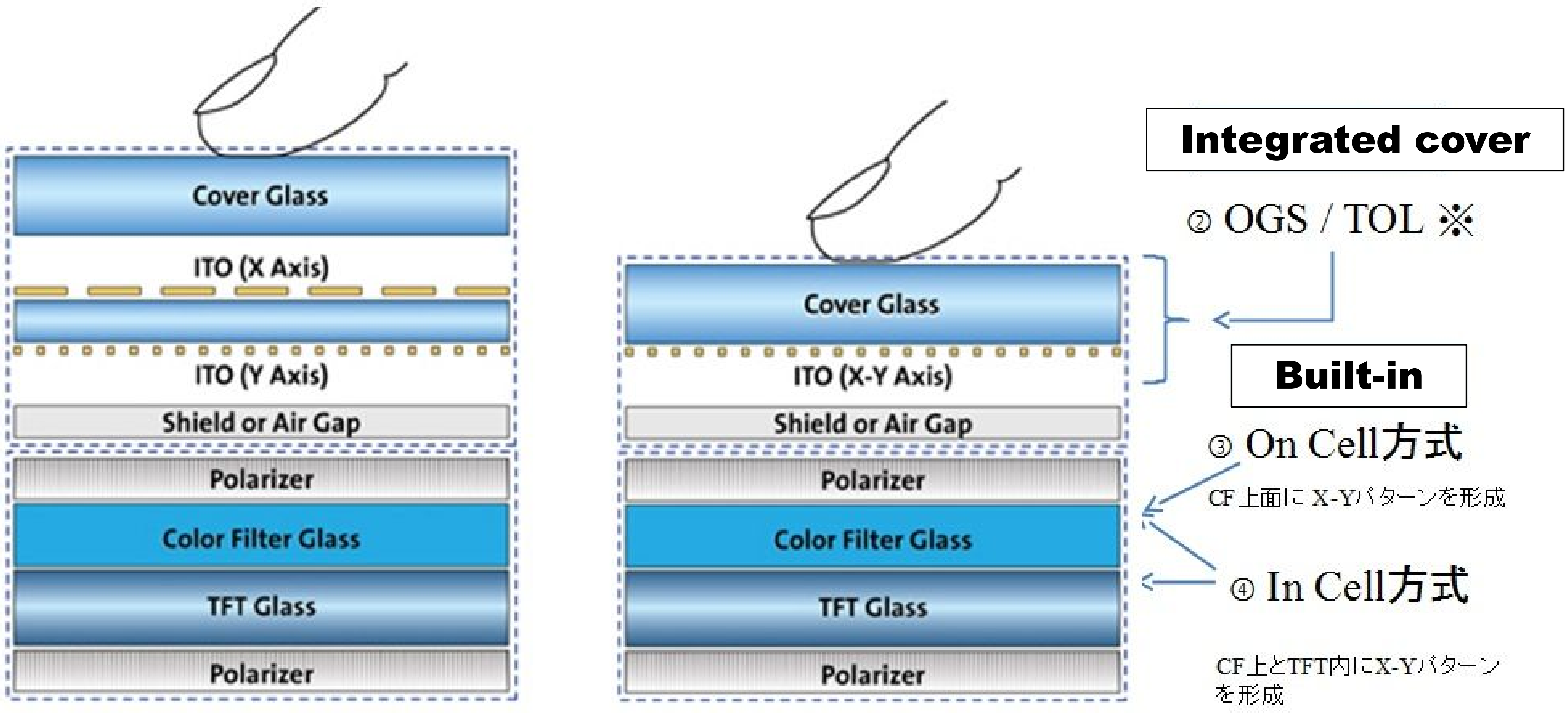
Liquid crystal display and transparent conductive film



1) Polarizing filter
Control the incoming and outgoing light.
2) Glass substrate
Prevent electricity from leaking from the electrode to other parts.
3) Transparent electrode, transparent conductive film
Electrodes for driving the liquid crystal display. Use highly transparent materials so as not to interfere with the display.
4) Alignment film
A film for aligning liquid crystal molecules in a certain direction.
6) Spacer
A uniform space is secured between the two glass substrates that sandwich the liquid crystal material.
7) Color filters
Apply each RGB filter to display the color.
8) Backlight
Shine light from behind the display to brighten the screen. Some monochrome liquid crystal displays use a "reflector" instead of this to make it visible in natural light.

Structural variation of touch panel

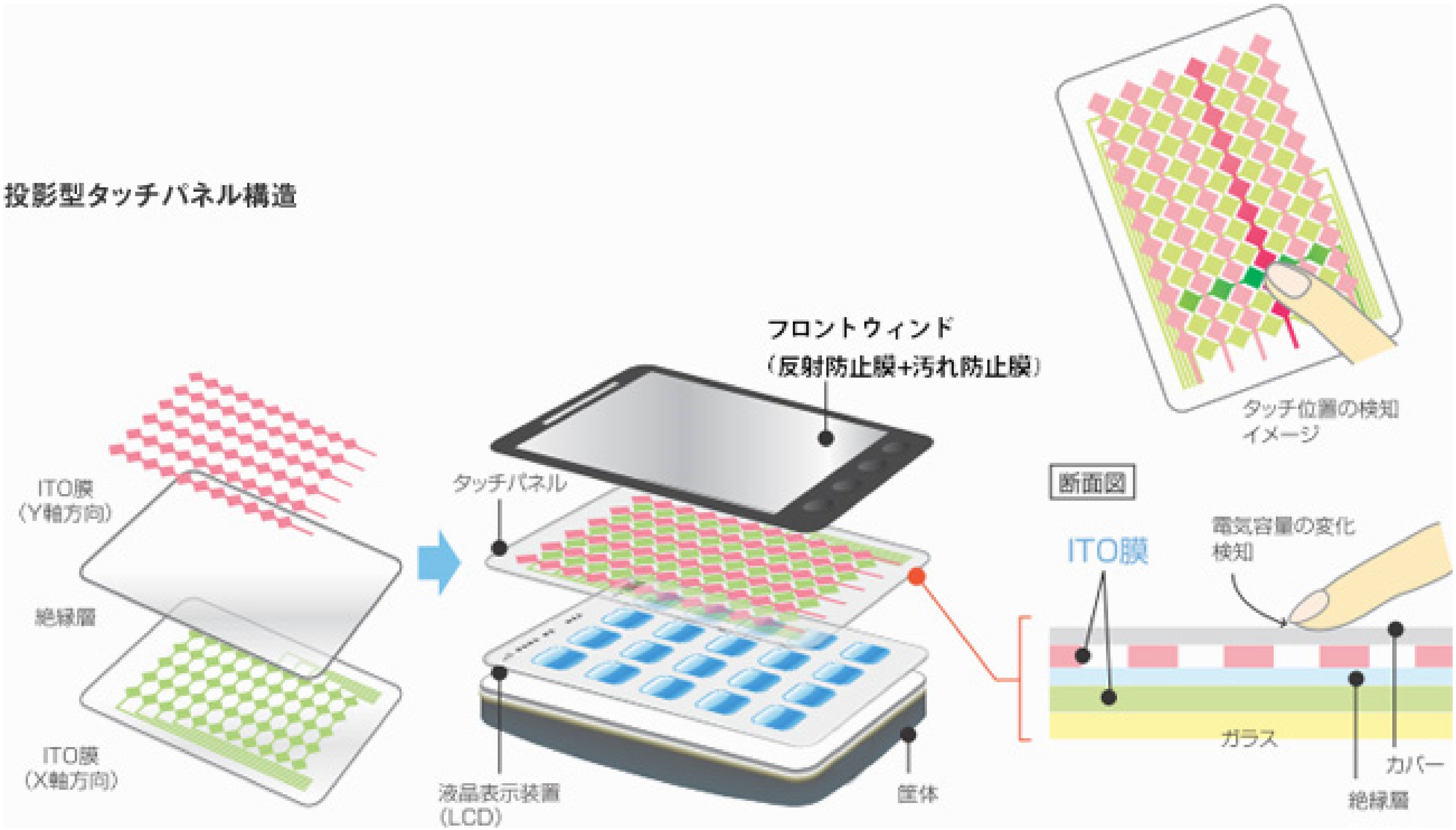
smartphone conductivity



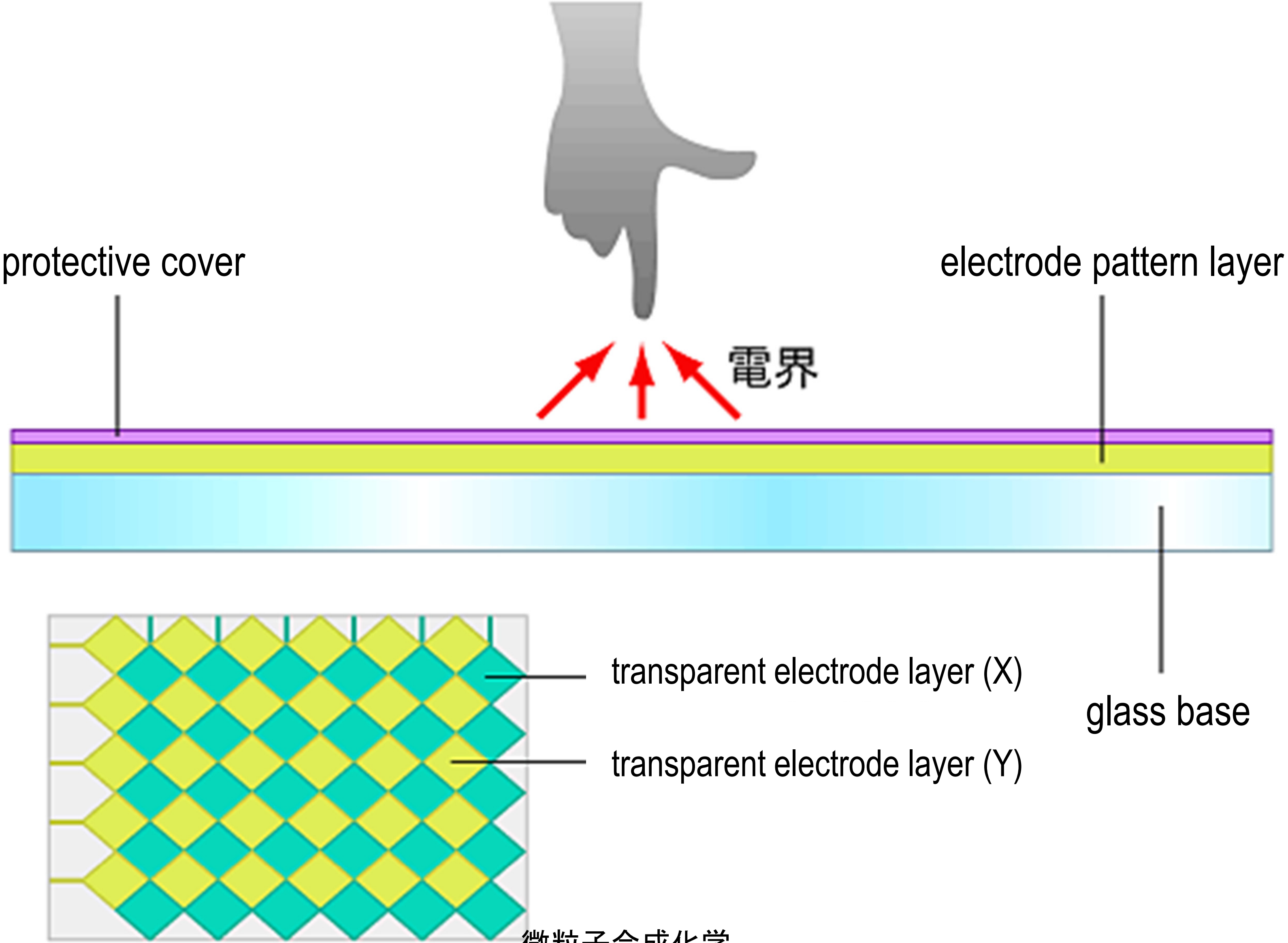
General method

Integrated cover, built-in touch panel function

※ OGS (One Glass Solution: コーニング), TOL (Touch On Lens) smartphone conductivity



Projected capacitance method



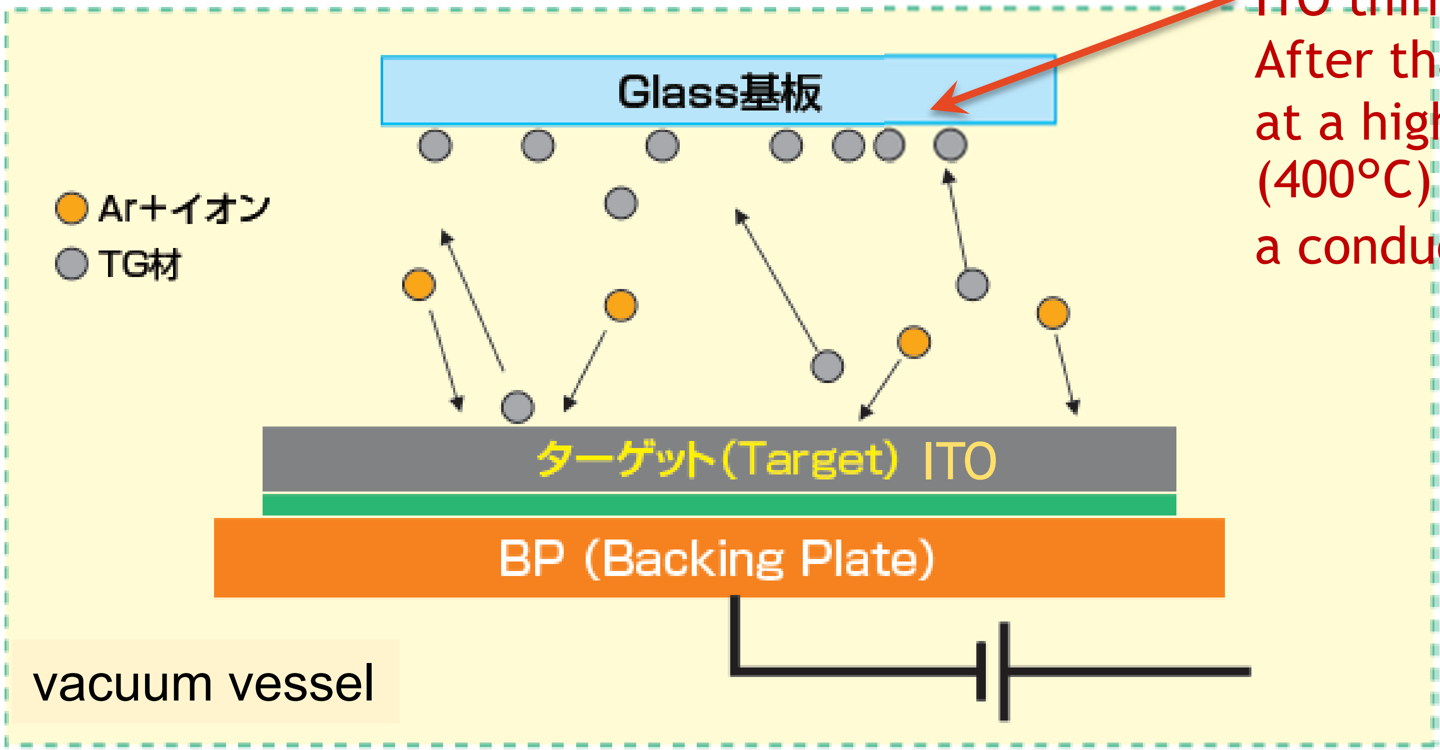
Scolded by Chico chan !

Why does the touch panel respond to touch?
→I'm getting an electric shock

Why smartphones are hard?

Thin film formation by sputtering

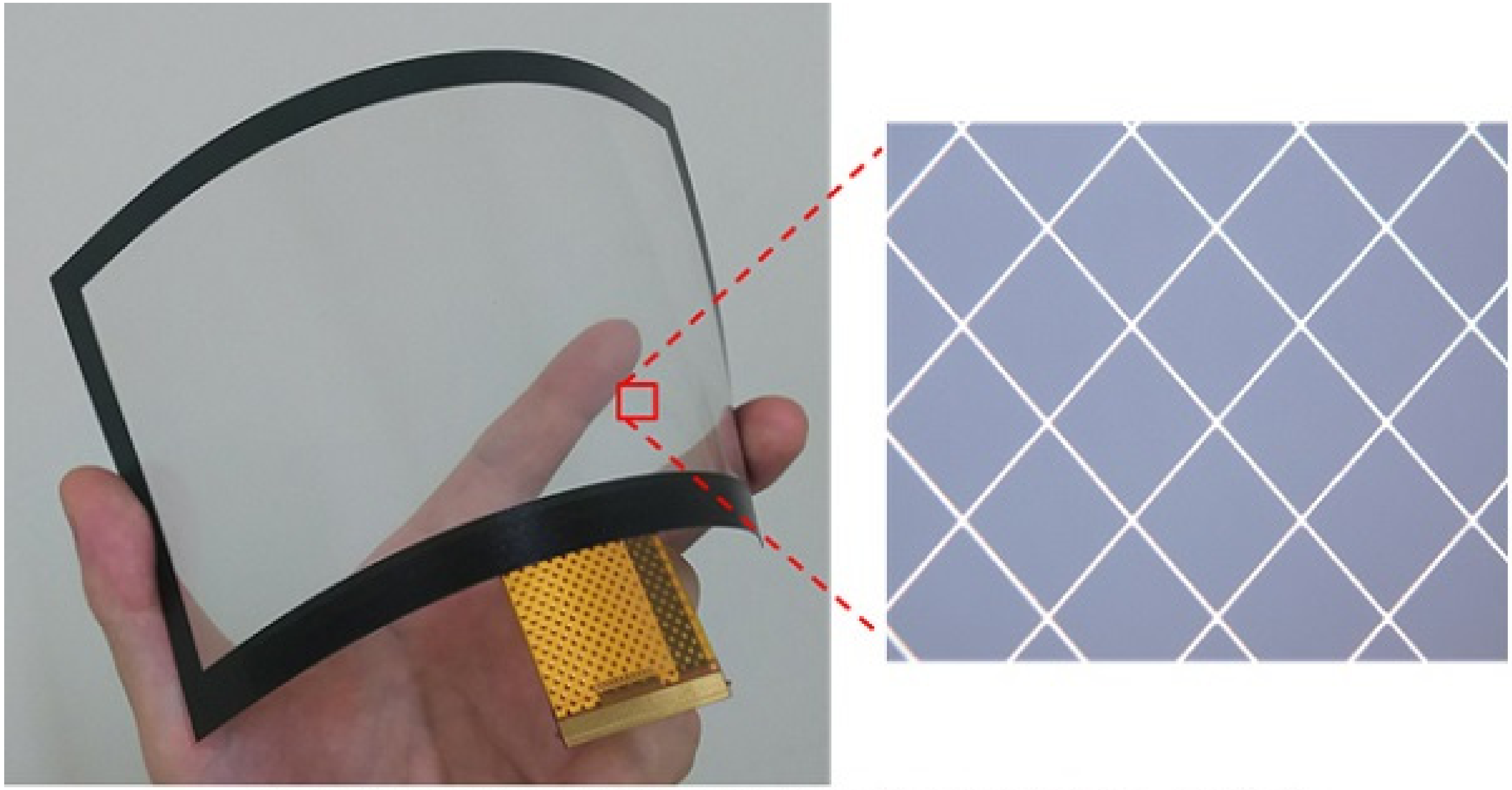
スパッタリング=Sputter…はじきとばす
基板上に薄膜を形成することができる技術



ITO thin film formation
After that, it is treated at a high temperature (400°C) to make it into a conductive film.

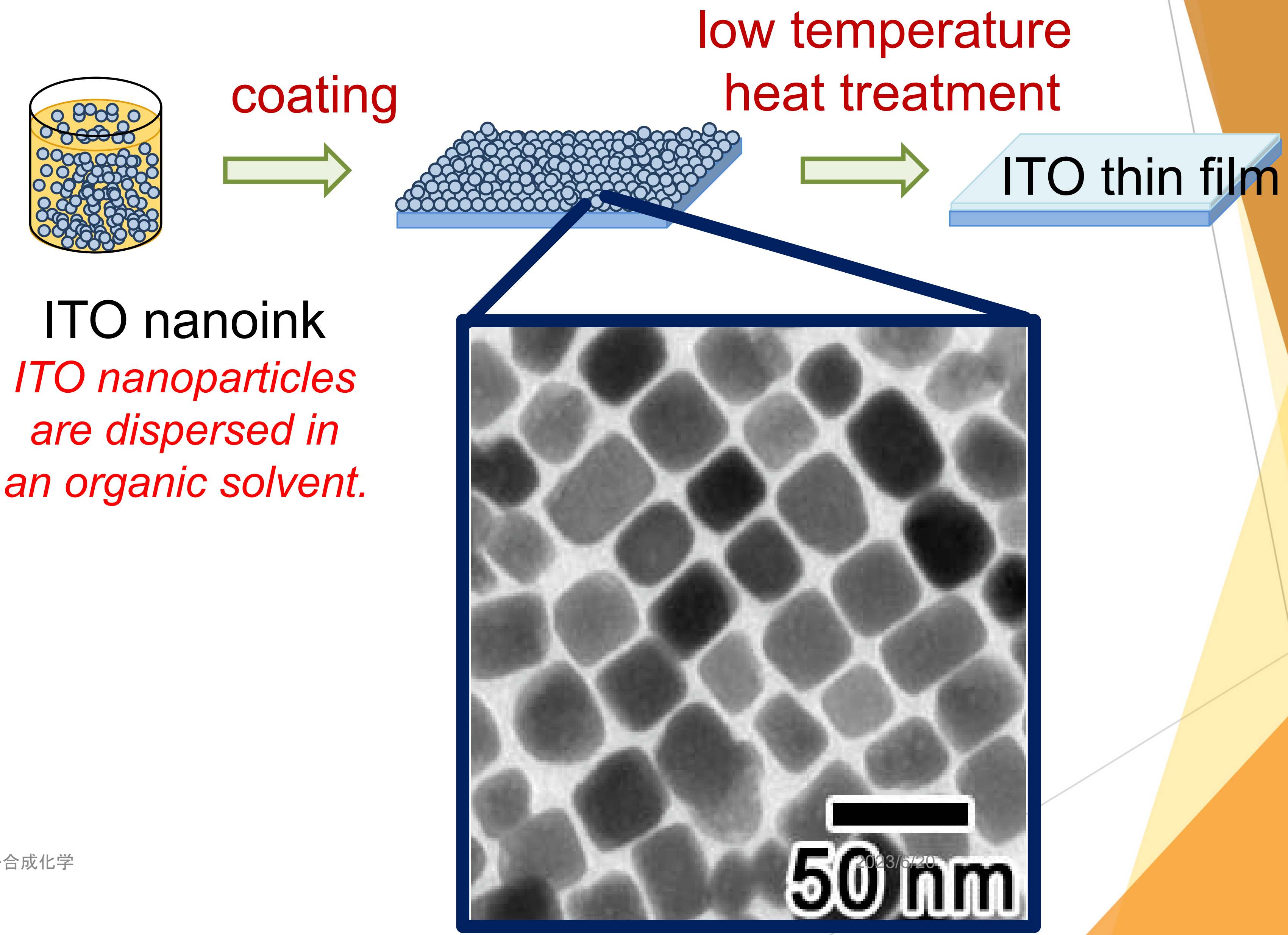
You can't use soft plastic because you can't apply heat.
In order to use easily bendable plastics, a new method that is not the conventional sputtering method is indispensable.

Soft liquid crystal display with plastic film + ITO nano ink

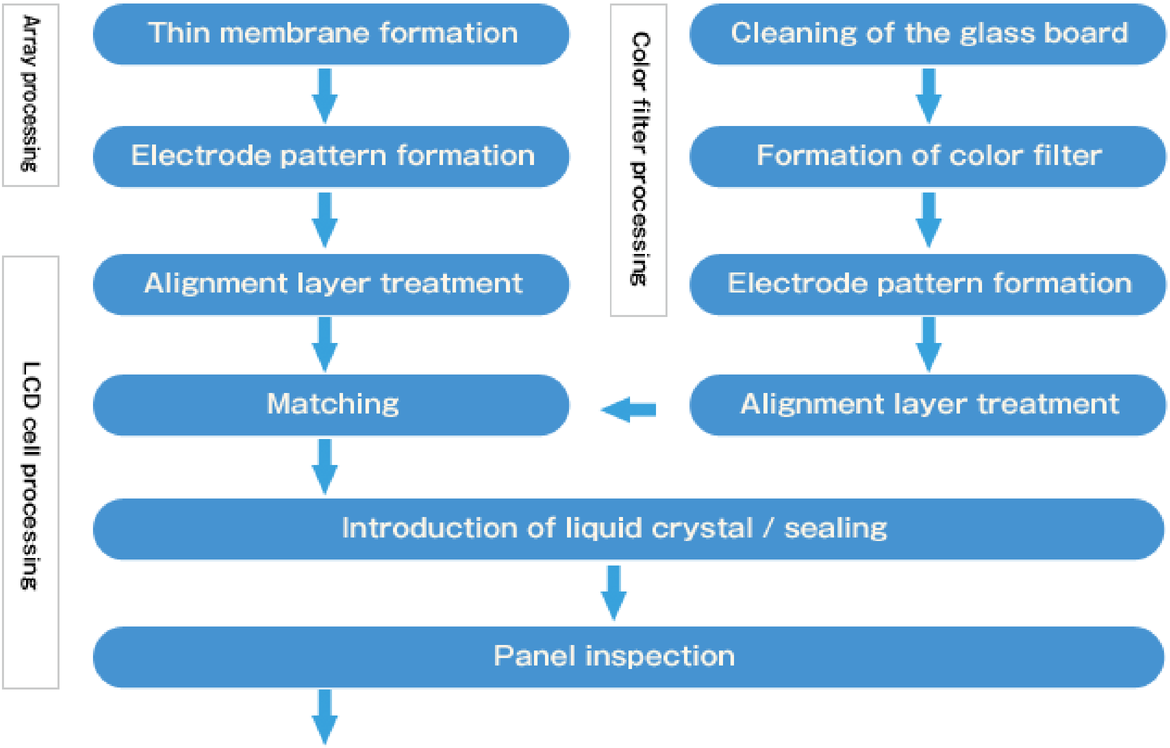


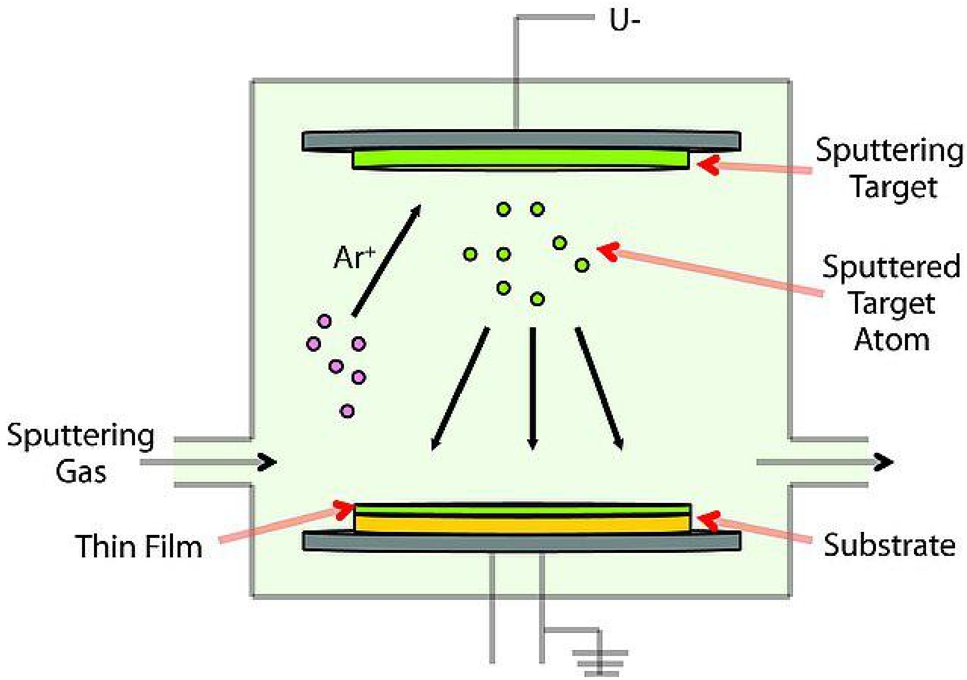
印刷微細配線形成技術を応用したアプリ例：タッチセンサー・パネル
（全光線透過率：85％以上、ヘーズ：2.0％以下、表面抵抗：35Ω/□）

Just use ITO nano ink!



Liquid crystal cell manufacturing process

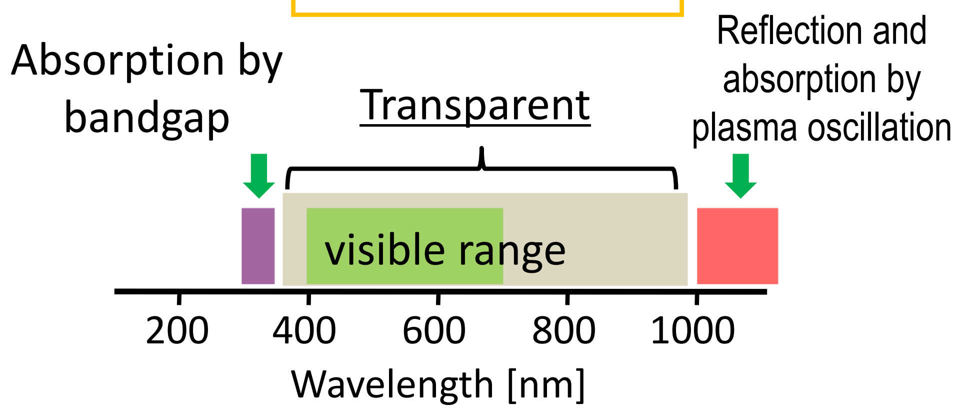




The PVD method is used to create the current transparent conductive film (ITO film).
A glass substrate is essential for high-energy and high-temperature processing.
It cannot be applied to polymer films.
⇒ Impossible with soft film

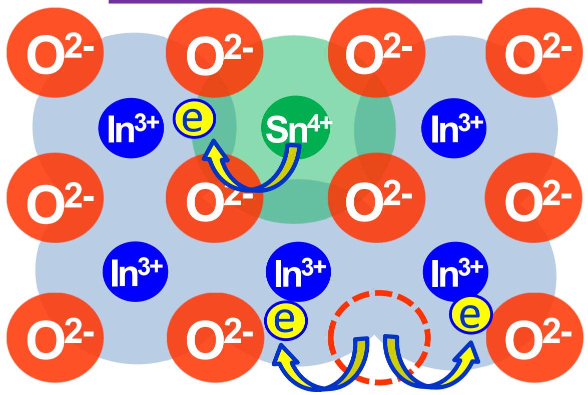
tin-doped indium oxide（ITO）

Transparency



Band gap = 3.5～4.0 eV (310～350 nm)
Wavelength of plasma oscillation = more than 1000 nm

Conductivity



Generation of carriers by Sn^{4+} doping and/or oxygen defects

transparent conductive material
･･･**ITO**、SnO_2、ZnO、AZO etc.

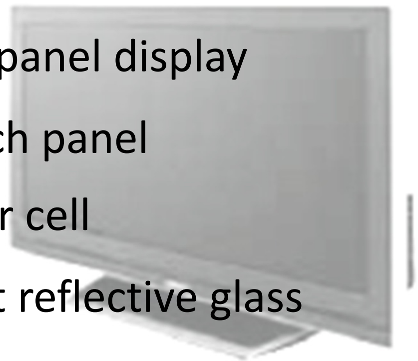
Transparency | Conductivity | workability

the best one

ITO

thinning

Used as a transparent electrode

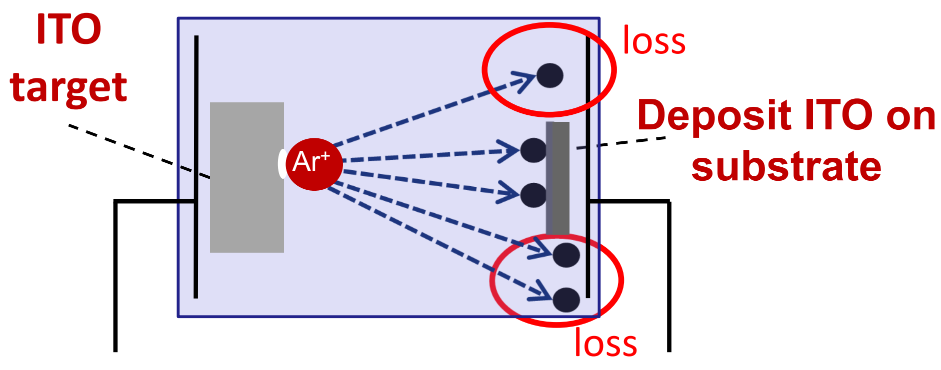


・flat panel display
・touch panel
・solar cell
・heat reflective glass

Transparent conductive films are dominated by ITO.

Problems with the sputtering method

Sputtering



Merit : High conductivity, transparency

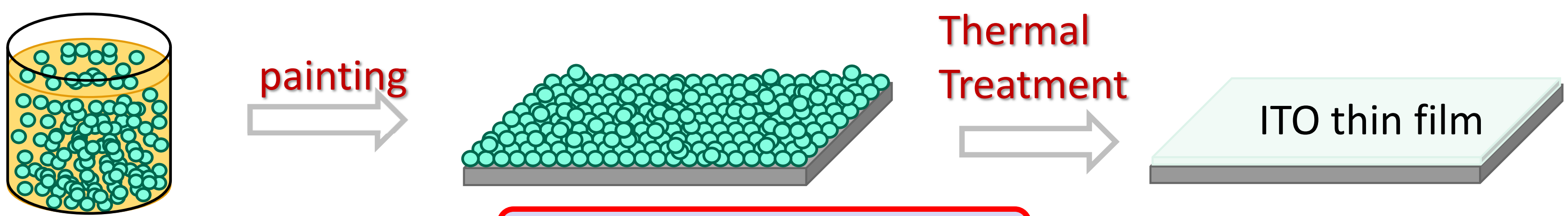
Resistivity $10^{-5} \sim 10^{-4}$ Ω·cm

Problems: High indium loss, high temperature

Adhesion of ITO inside equipment, etching loss

ITO Usage efficiency only10 % **Very wasteful!**

Ink painting



ITO ink
(ITO particles + binder)

Advantage: High efficiency of use

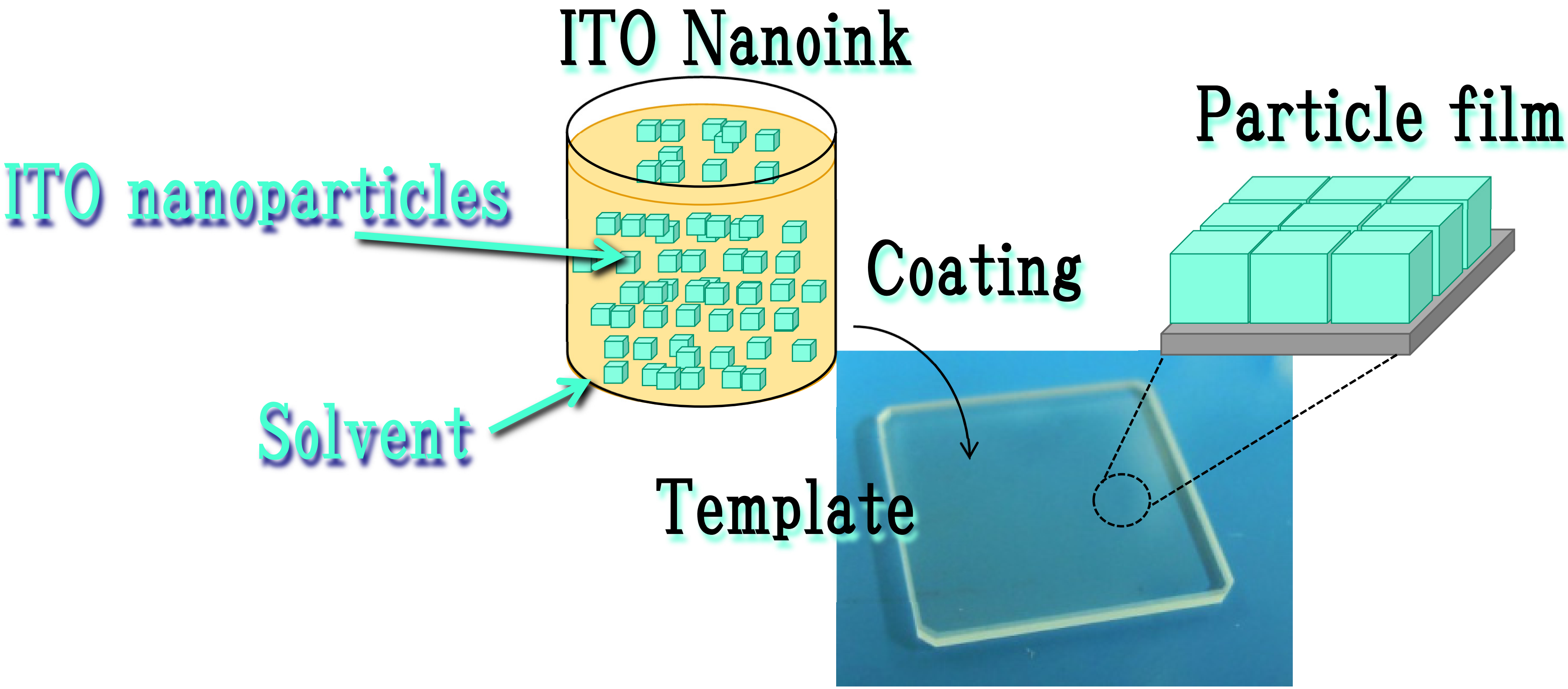
ITO efficiency 100 %

Problem: Low conductivity

Resistivity $10^{-3} \sim 10^{-1}$ Ω·cm

In order to solve this problem, it is essential to develop a technology that makes the particles 10 to 20 nm in size, cubic in shape, arranges the particles neatly, and processes them at low temperatures!

Production of ITO nanoink coating film



ITO particles were not obtained directly from the aqueous solution.

Gel formation

In^{3+} initial conc. **0.25 mol dm^{-3}**

Nucleation
- ← **0.50 mol dm^{-3} $In(NO_3)_3$**
- ← **8.0 mol dm^{-3} NaOH**
- ← **100 °C, 24 h**

↓

Hydrothermal synthesis

Particle growth
- ← **250 °C, 3 h**
- ← Centrifuge, washing
- ← Freeze drying

↓

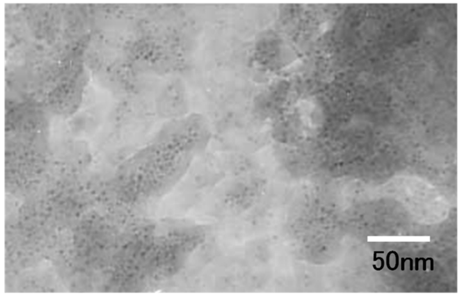
Uniform $In(OH)_3$ fine particles

- ← $SnCl_4$ (5% to In)
- ← Thermal treatment at 300°C for 3h

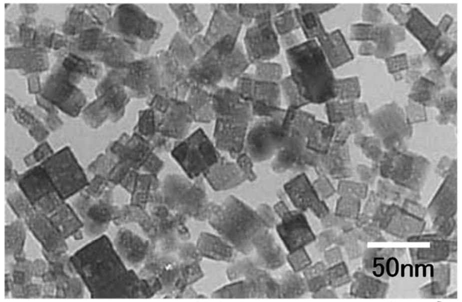
↓

Uniform ITO fine particles

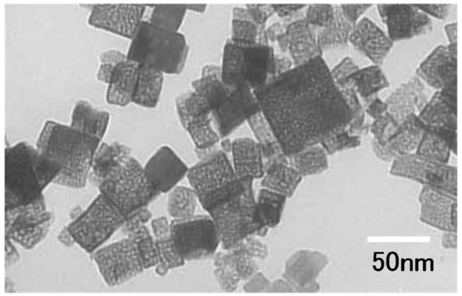
ITO particles are obtained by heat treatment and dehydration.



Amorphous $In(OH)_3$ gel formation



Crystalline $In(OH)_3$ fine particles formation

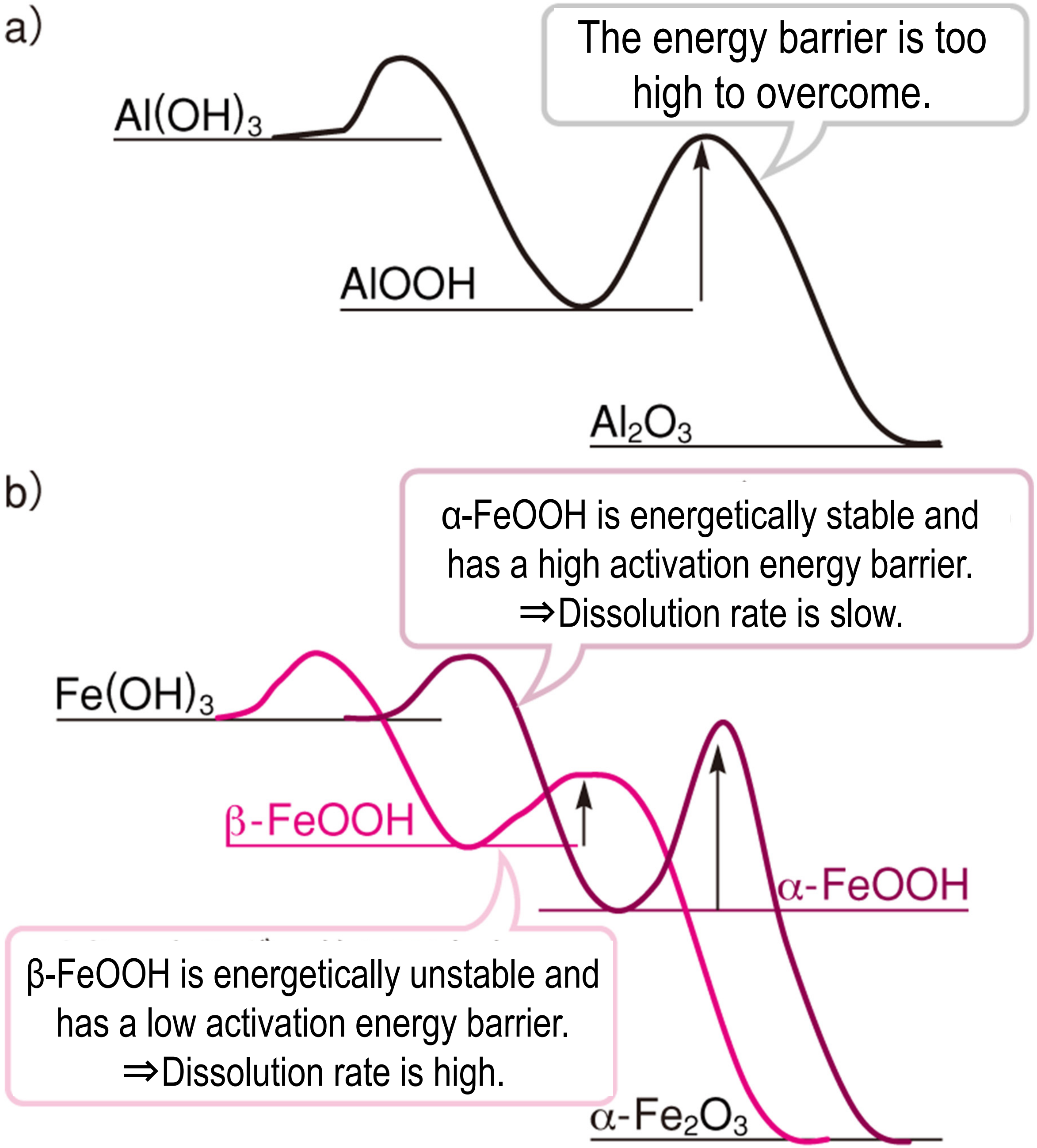


ITO fine particles formation

Synthesis of ITO particles by Gel-Sol method and heat treatment

Why can't aluminum oxide particles be formed by hydrolysis reaction from aqueous aluminum solution?

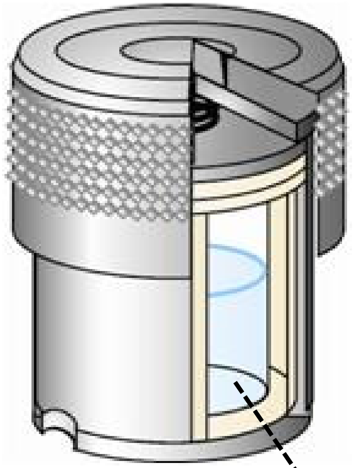
The production of hematite depends on intermediate products.



Limitations of synthesis of oxide particles by hydrolysis method

Direct ITO nanoparticles synthesis

Particle synthesis using an autoclave



Thermal treatment
at 250 ℃

Ethylene glycol solution

indium salts, tin salts, bases

First direct synthesis method ITO nanoparticles

Since no gel was formed at the beginning, aggregation could not be prevented and no monodisperse particles were obtained.

Experimental

Direct synthesis of ITO

0.50 M $InCl_3$ &
0.050M $SnCl_4$ EG solution $[In^{3+}]_T$ = 0.25 M

← 1.0 ~ 2.0 M NaOH EG solution
($In^{3+} : OH^- = 1 : 2 \sim 1 : 4$)

NaOH did not form a thick gel.

Stirring for 15 min

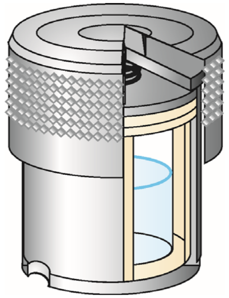
→ Put 10 ml of suspension to Autoclave

Aging at 200 ~ 250 ℃, ~ 8days

Washed by EtOH and centrifuged for 3 times

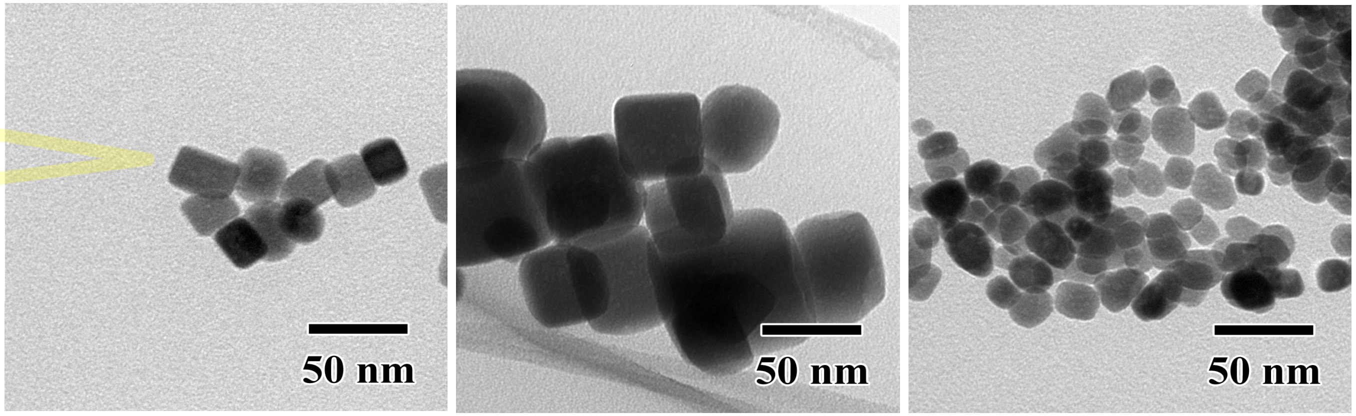
↓

ITO nanoparticles



Autoclave

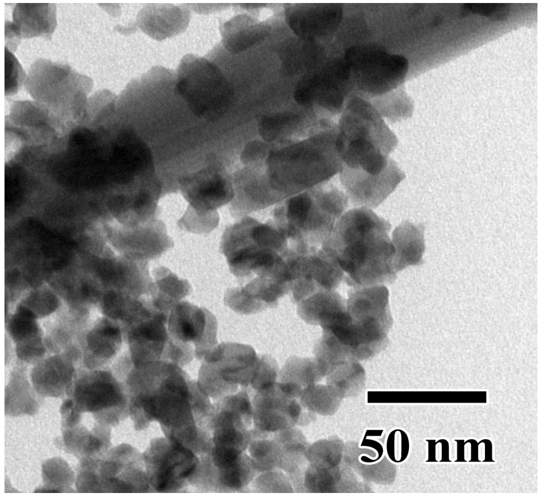
Therefore, the sizes did not uniform.



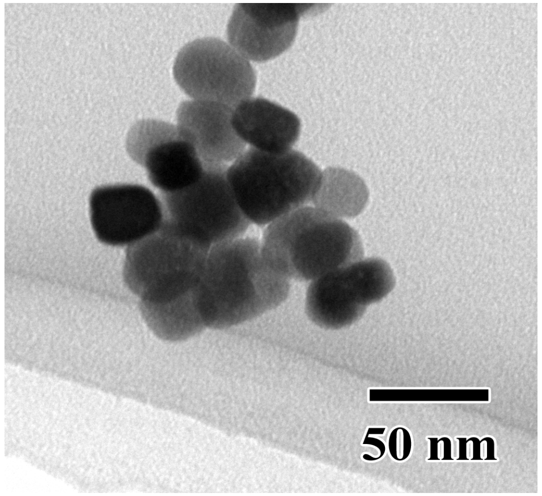
Solvent Effect

Solvent effect

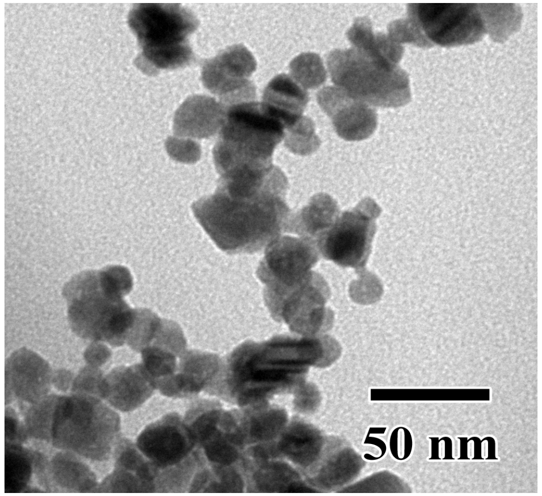
($In^{3+} : OH^{-}$ = 1 : 3、250℃、12 h)



BuOH



DEG

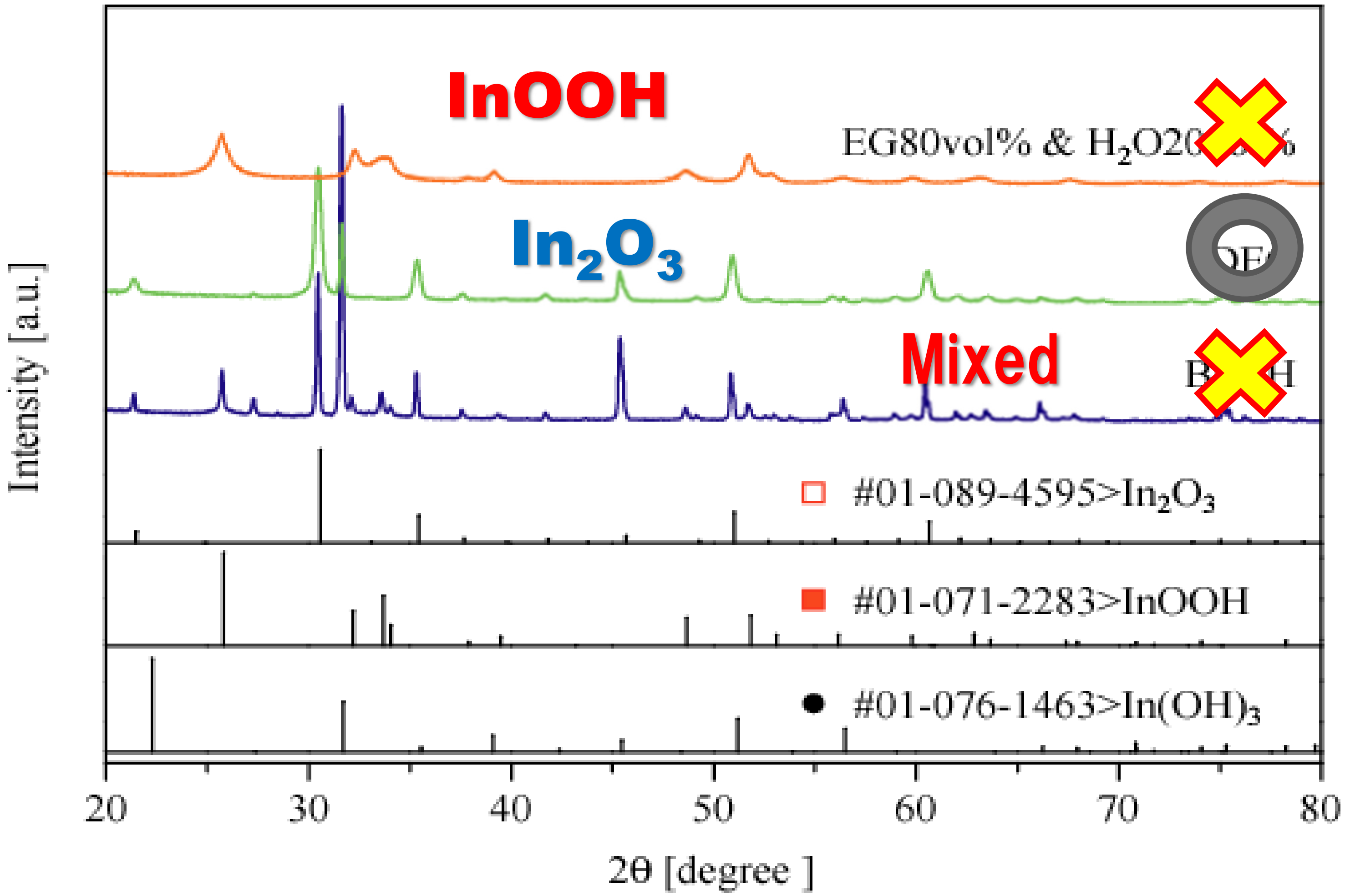


EG 80vol% + H_2O 20vol%

Solvent Effect

Solvent effect

(In^{3+} : OH^- = 1 : 3、250℃、12 hで合成)



Crystalline radius（Å）

150 (InOOH)

287

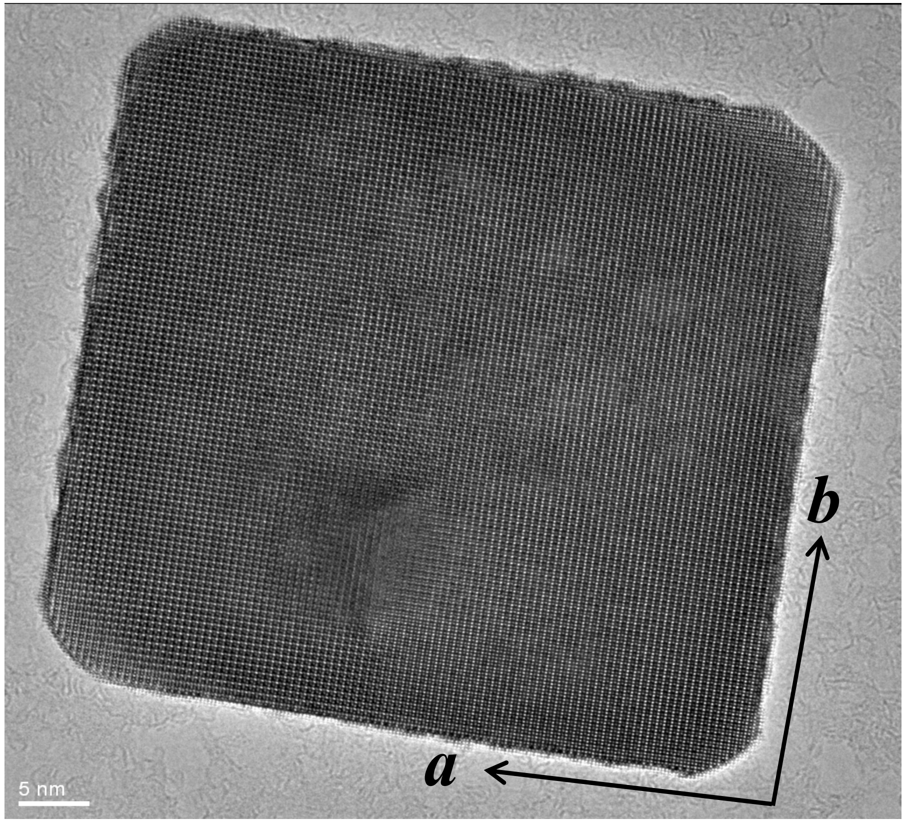
＞1000

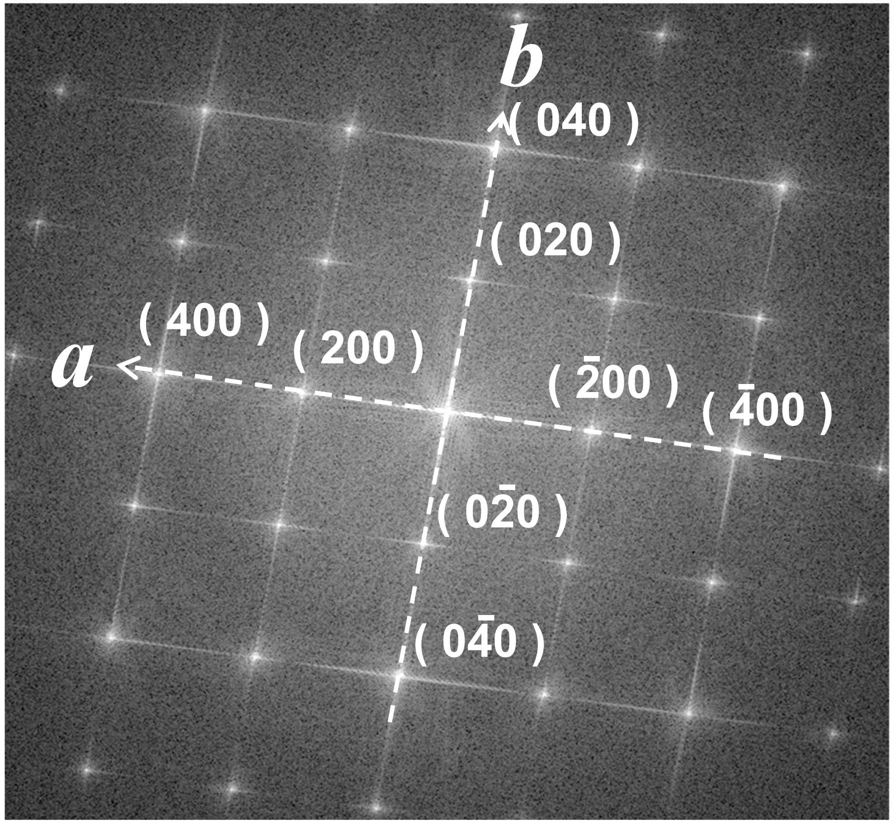
High resolution transmission electron microscope

- HR-TEM

T = 250℃, In^{3+} : OH^{-} = 1 : 2, 96 h

FFT





HR-TEM image ⇨ Grain boundaries not observed ⇨ **Single crystal**

FT image ⇨ ***Growing along the a, b, and c axes***

Streak **tin doping or oxygen defect**

Single-crystal ITO nanoparticles surrounded by (100) facet

Practical synthesis of ITO nanoparticles

This is the synthesis of particles for which sample shipment started in 2012.

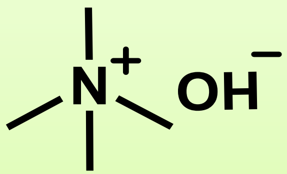
2023/6/20

微粒子合成化学

Experimental Procedure -Solvothermal synthesis-

Tetramethylammonium hydroxide (TMAH)

$(CH_3)_4N{\cdot}OH$



- OH^- ion resource

0.50 M $InCl_3$ &
0.050 M $SnCl_4$ in Ethylene glycol (EG) solution

← Stirred at 0 ^oC

← 1.5 M TMAH in EG solution
([TMAH] = 1.5, 2.0, 2.5)

← Stirred for 15 min

← Put 10 ml of suspension into autoclave

← Aged at 250 ^oC, 0 ~ 96 h

← Washed by EtOH, H_2O and centrifuged

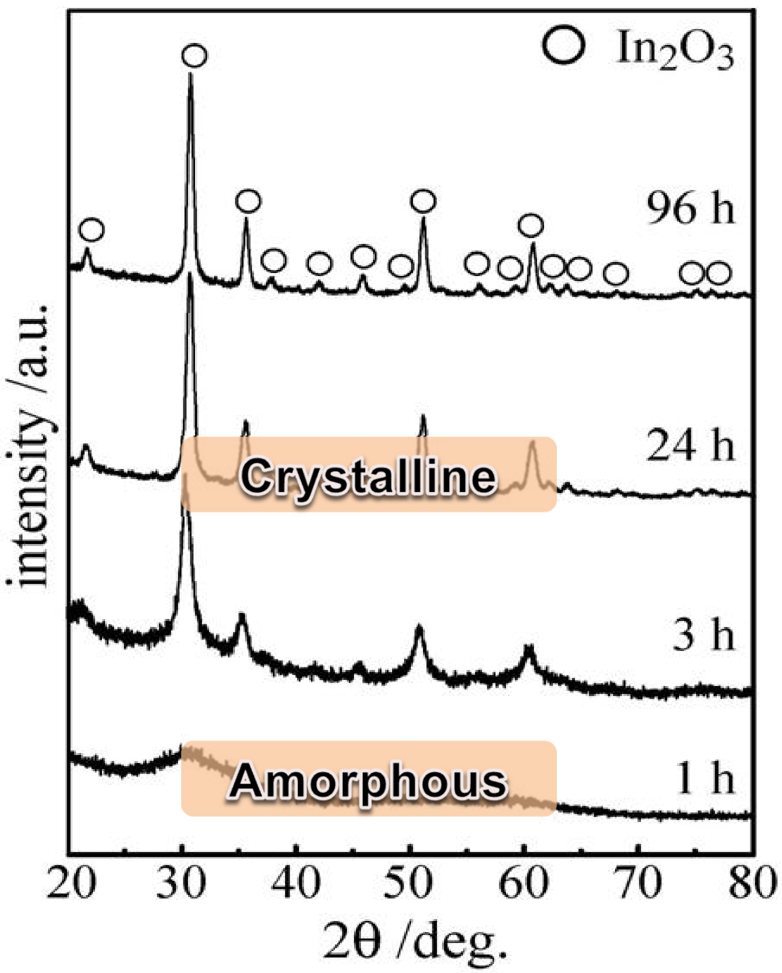
↓

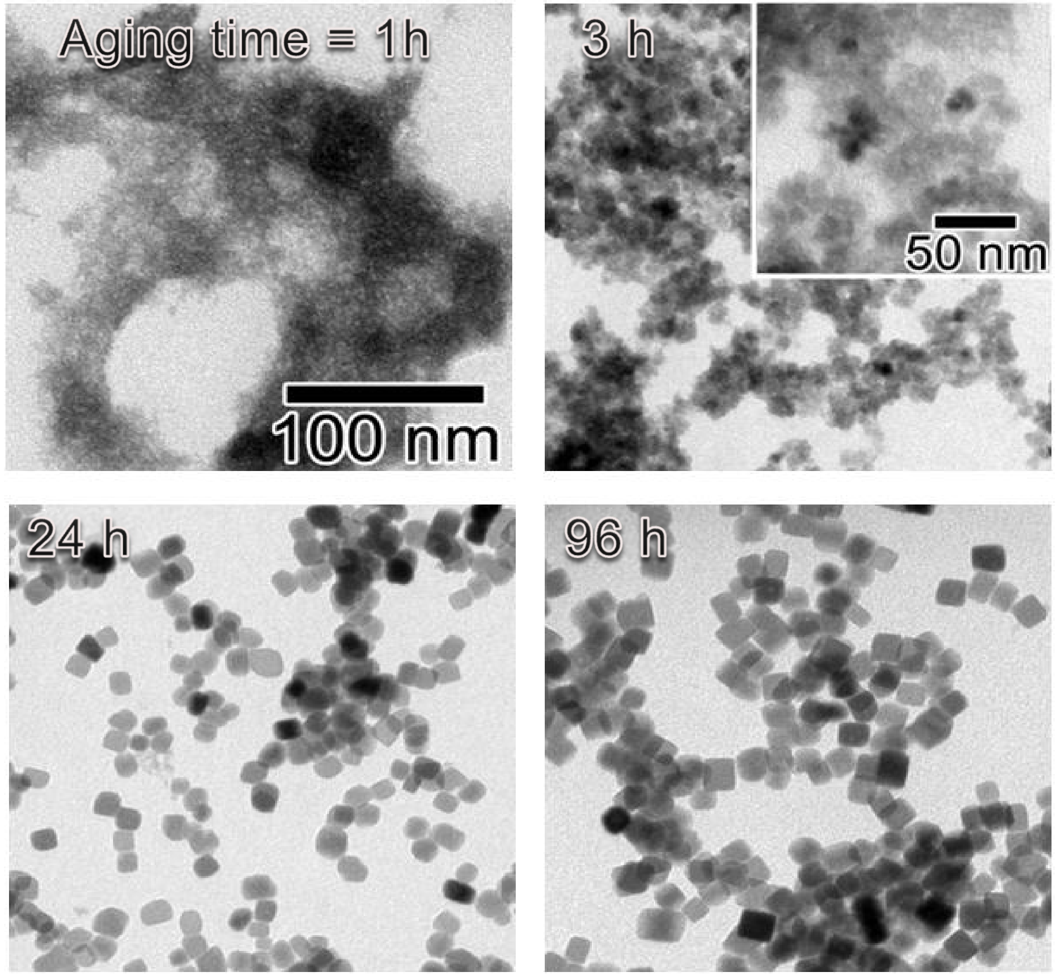
Products
(Analysis: XRD, TEM)

We have realized a system that causes only homogeneous nucleation, not heterogeneous one without any coagulation.

Time dependence of particles growth

Reaction condition: TMAH 2.0 M, 250 ^{o}C





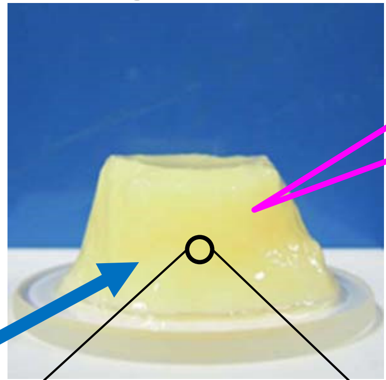
The particles grow at the expense of amorphous products initially fomred

Macroscopic change in particle synthesis

Synthesis conditions.: TMAH（Base） 2.0 M, 250 ºC

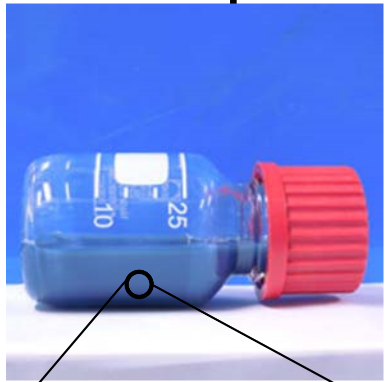
Initial solution | **yellow gel formation** | **ITO nanoparticles**

250 ºC
1 h

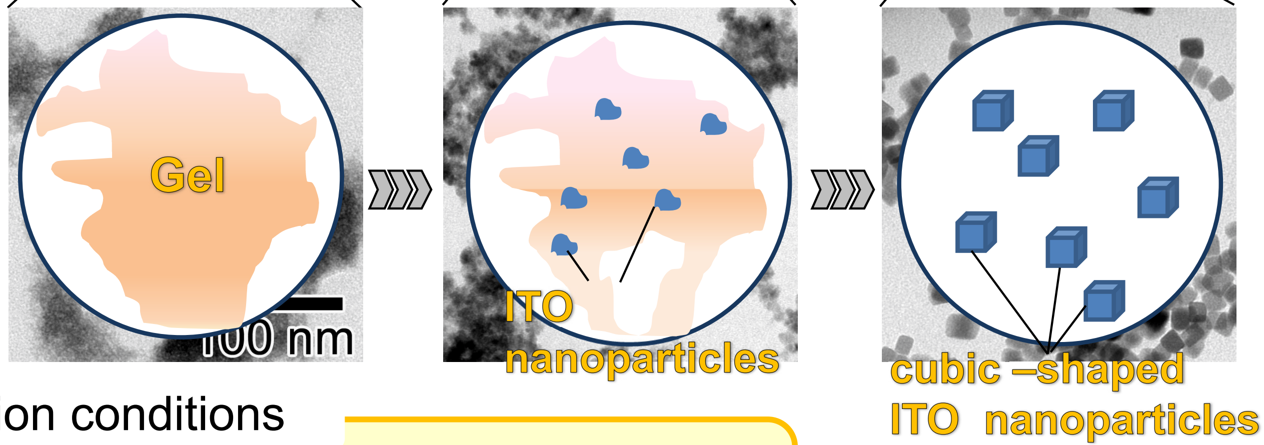


The particles are fixed in the gel network and do not coagulate.

250 ºC, 95 h



◆ Gel prevents particle coagulation
◆ Control the concentration of ions in solution ⇒ control of nucleation and particle growth



Homogeneous nucleation first, no renucleation!

Gel formation conditions

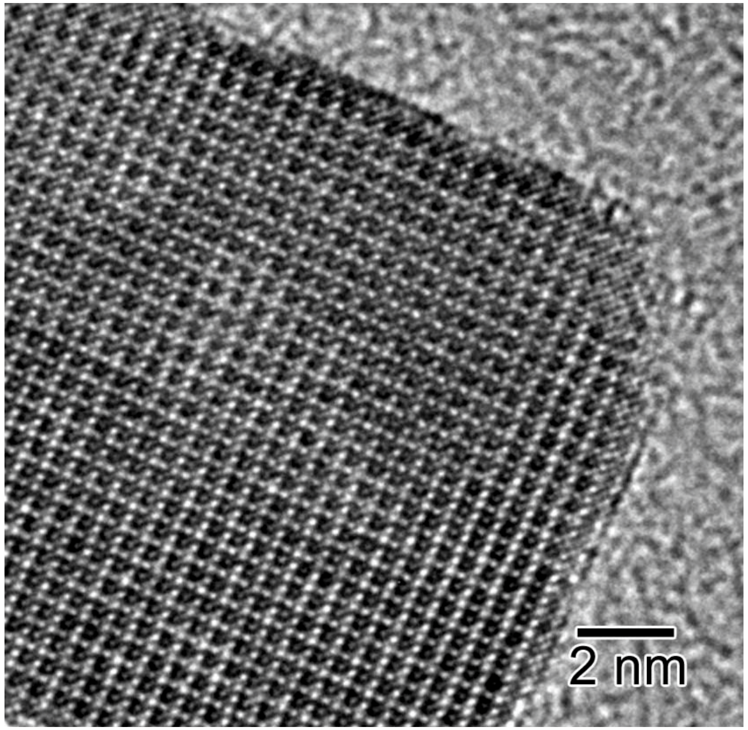
TMAH conc. 2.0, 2.5 M･･･○

TMAH conc. 1.5 M･･･✕ NaOH system･･･✕

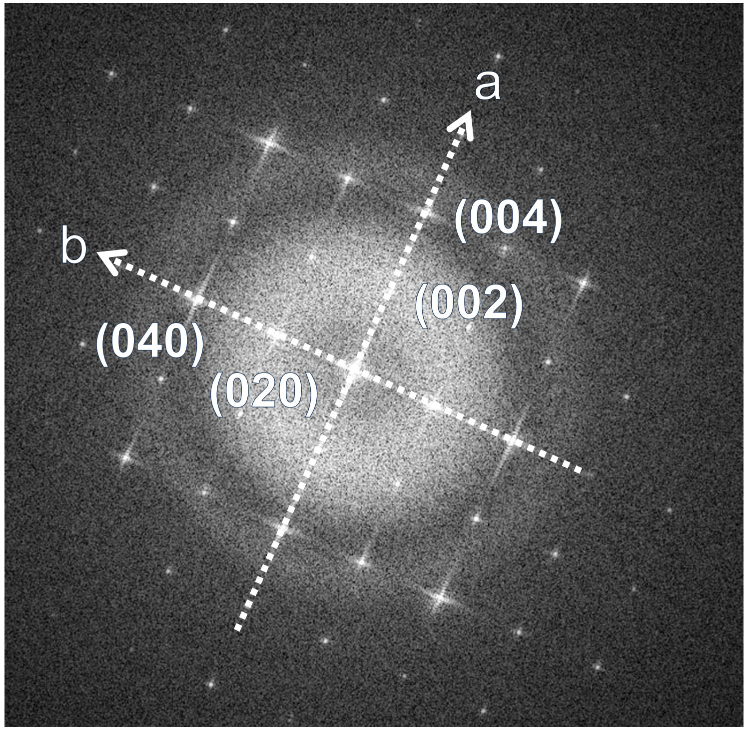
Initial gel formation is a prerequisite for monodisperse particle formation.

High resolution transmission electron microscope

HR-TEM image



FT image

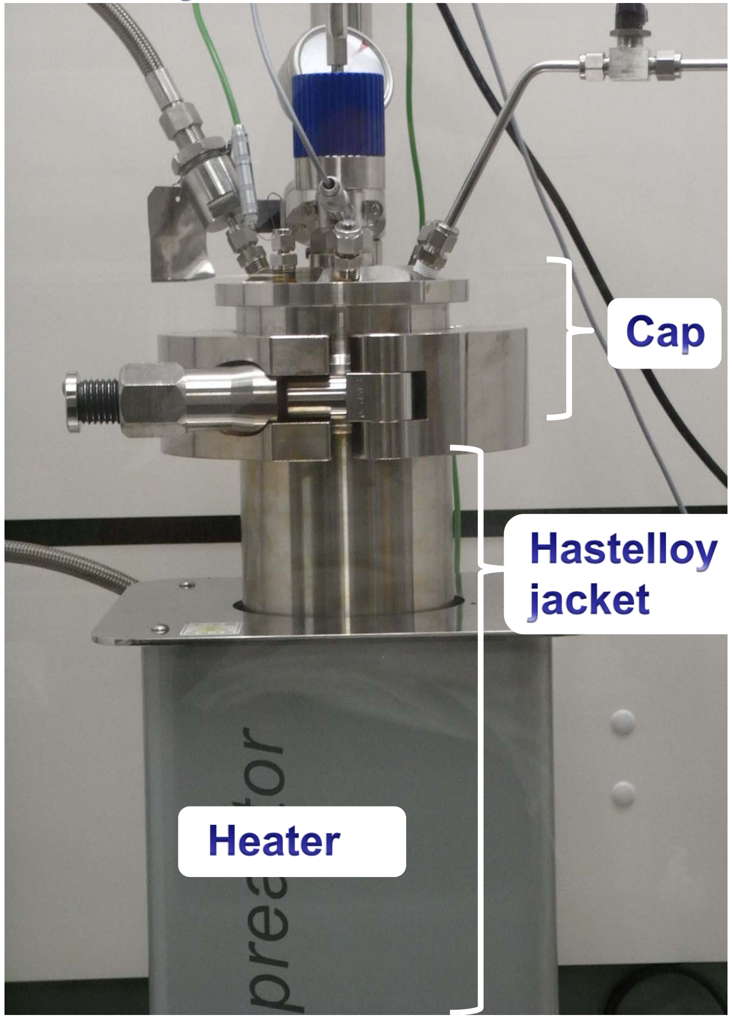


- HR-TEM image ⇨ Grain boundaries not observed ⇨ **Single crystal**
- FT image ⇨ ***Growing along the a, b, and c axes***
  Streak ⇨ **tin doping or oxygen defect**

Single-crystal ITO nanoparticles surrounded by {200} facet

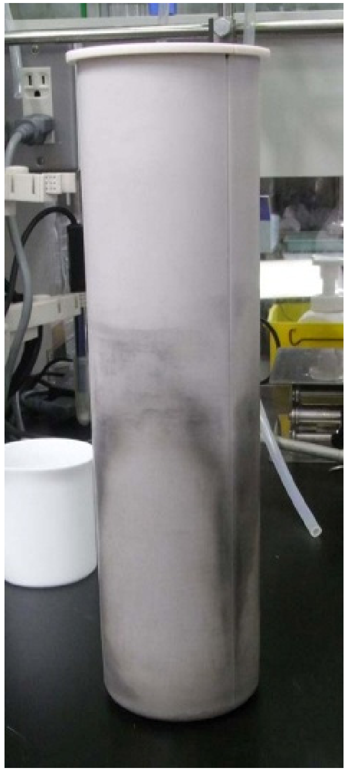
Large-scale synthesis of transparent conductive nanoparticles using a large-scale reactor

Mass synthesizer



Temp. ~250 °C

Pressure resistance : 100 bar



Teflon inner cylinder (2000 mL) >>

Normal reactor capacity (23 mL)

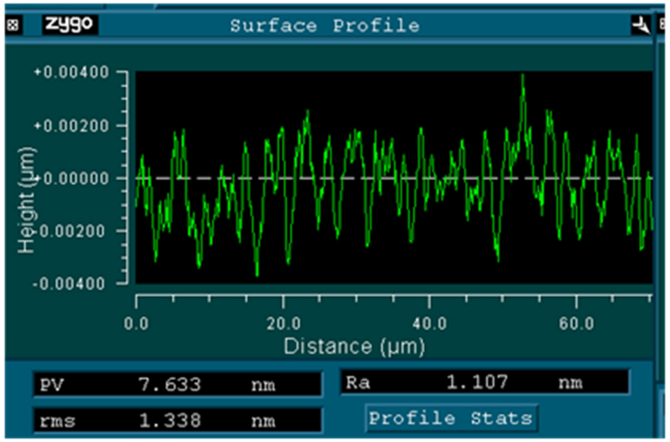
Amount synthesized : ~30 g ~0.3 g

- **100x scale of the lab**
  ➡ Synthesis of ink-evaluable ITO nanoparticles

National project, METI & NEDO: Rare metal substitute material development project

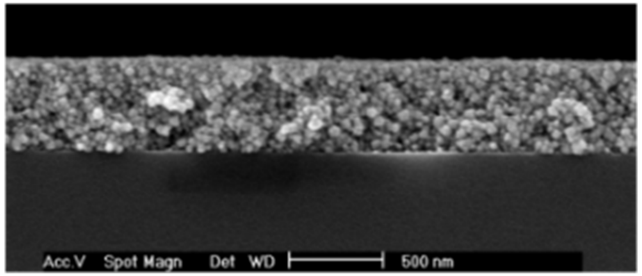
ITO nanoparticles to ink

ITO nano-ink

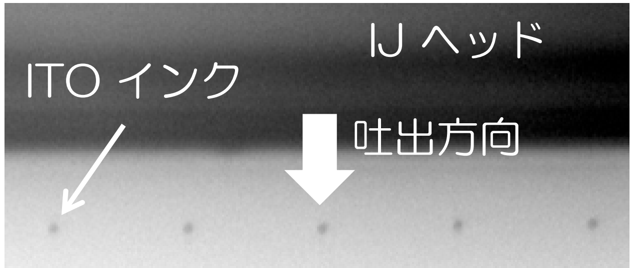


Ra: 1.1 nm

Ra measurement result of ITO coated film by laser interferometer



Cross-sectional photograph of ITO ink coating film



Ink jet ejection of ITO ink

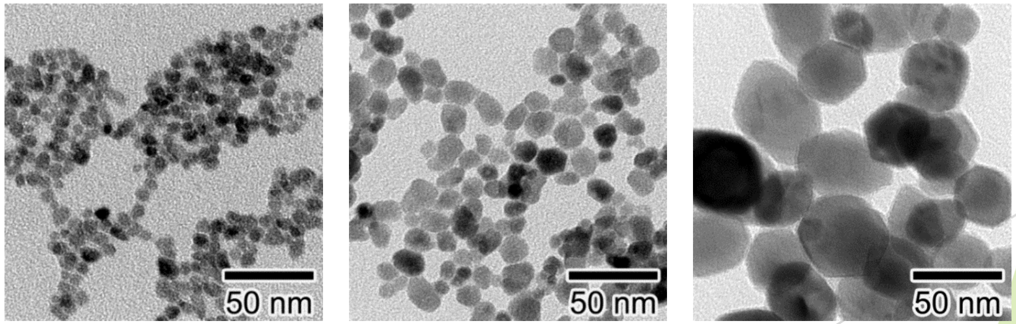
ITO nano ink for inkjet application

- Uniform coating with a film thickness of 100 nm or less
- More than 90% transmittance
- Haze 1% or less
- Resistance value ca 10^{-2} Ω cm achieved

ITO substitute nano ink

ITO alternative materials are also research targets

- AZO = Aluminum doped Zinc Oxide
- GZO = Gallium doped Zinc Oxide
- ATO = Antimony doped titanium oxide



3/9　化学工業日報　4面

透明電極用ITOナノインキ

抵抗値を1ケタ低減

インジウム使用量10％減　20年めど実用化

東北大学など開発

東北大学、アルバック、三井金属、DOWAエレクトロニクスのグループは、従来より1ケタ以上低い抵抗値を示すインジウム・スズ酸化物（ITO）ナノインキを開発した。インクジェット法により低抵抗のITO塗布膜を実現。ターゲット材を用いる成膜方法と比べてインジウム使用量を10％低減することに成功した。透明性も96％以上を達成している。同グループは液晶パネルやタッチパネル、色素増感型太陽電池の電極として、2020年をめどに実用化を目指す。

同グループでは、原料となるインジウムやスズなどの粒径や結晶形状をコントロール、最適化することで低抵抗、高い結晶性を持った新規のITOナノ粒子の作成に成功。さらに、溶媒中で高い分散性を持たせることにより、低抵抗のITOナノインキを実現した。焼成温度も200度C程度と従来より低温化し、抵抗値は10のマイナス3乗～4乗オームセンチメートル、透明性も96％以上を達成した。

インジウムは、世界生産量がスクラップの再生も含めて1000トンにも満たないレアメタル。一方、ITO透明電極は大型液晶パネル、スマートフォンなどの透明電極として使用量が増えており、希少金属であるインジウムの使用量削減に対する研究開発が進められている。

ナノインキによる電極形成は、ターゲット材によるスパッタリング法に比べて使用効率が高く、製造時のロスも減らせることからインジウム使用量削減への期待が高い。しかし実用化には低抵抗値化、高い透過率、焼成温度の低減などが課題となっていた。

同グループでは、組成を変えてインジウムを50％削減するターゲット材の開発や、金属膜との複合化によって膜厚を半減する手法の開発も進めており、用途や使用方法によって最適な手法を選択できるよう検討を進めていく。

Transparent conductive nanoink

- Remains transparent and conductive when bent or folded
- A soft display is realized!
- When you don't need it, you can roll it up and put it away!
- It can also be applied to future solar cells!