2012/11/06

The 7th Japanese-German International Workshop on Mathematical Fluid Dynamics

Optimization of flow state for the control of the reduction-oxidation reaction

Masahiro Kunimoto
Department of Applied Chemistry
Waseda University

Collaborative work with Prof. Dr. Dieter Bothe (TU Darmstadt)

Outline

1. Self-introduction – Applied physical chemistry

   - Electrochemistry and its applications

   - Fluid dynamics and Electrochemistry

2. Motivation for main topic – Nanoparticles

   - What is nanoparticles ?

   - Objective of this research

3. Strategy for process optimization

   - Fundamental concept

   - Strategies for process optimization

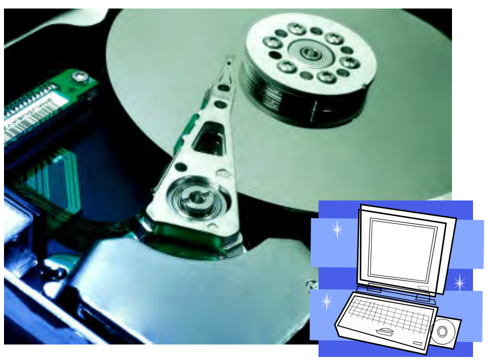
Introduction of Applied Physical Chemistry lab.

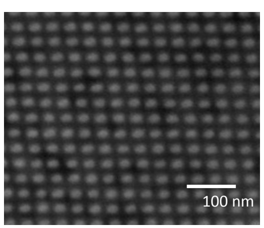
Our research topic

- Development of new devices using Electrochemistry
- Elucidation of phenomena in Electrochemistry

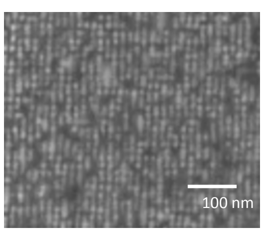
Device Development

Recording media



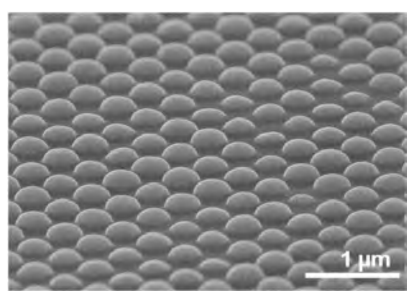


Diameter: 20 nm
Pitch: 35 nm



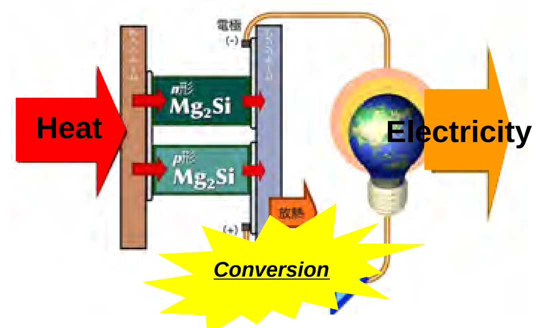
Diameter: 8 nm
Pitch: 18 nm

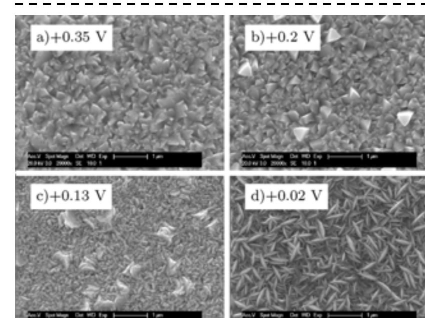
Solar cells



Si nano-Pillar array

Thermoelectric conversion





Electro-deposited Bi_xTe_y

＊H. P. Nguyen et al, Electrochimica Acta 68, 9-12 (2012).

Introduction of Applied Physical Chemistry lab.

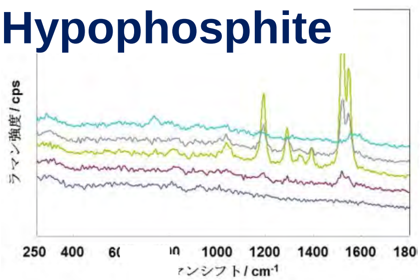
Our research topic

- Development of new devices using Electrochemistry
- Elucidation of phenomena in Electrochemistry

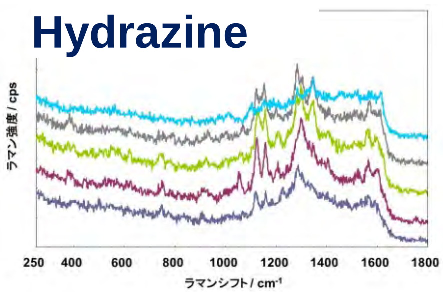
Phenomena Understanding

Spectroscopic analysis

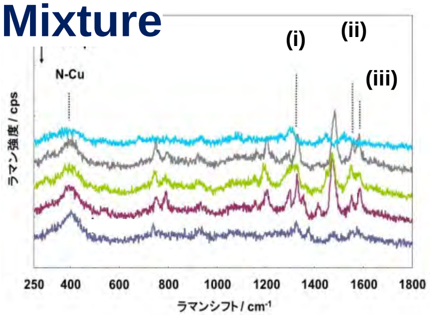
Hypophosphite

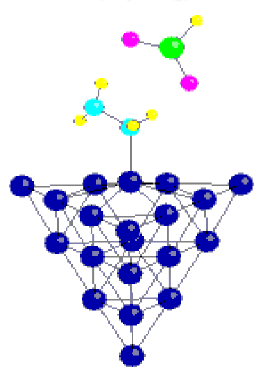


Hydrazine

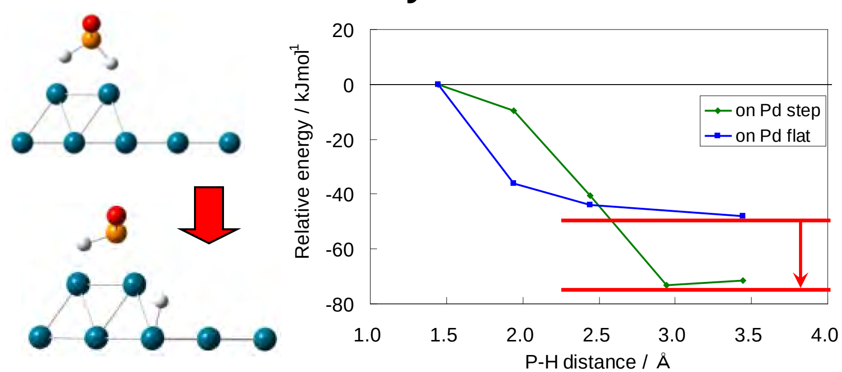


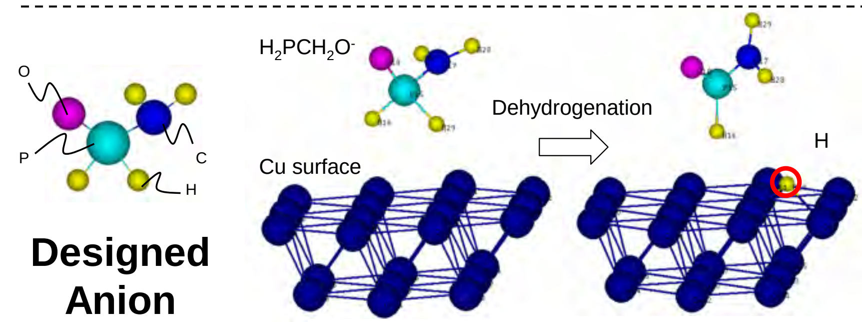
Mixture





Theoretical analysis





Reaction barrier = +18.77 kJ/mol

Electrochemistry

Subject of Reduction/Oxidation (Redox) reaction occurring at (Solid-Liquid) Interface

『Redox reaction』

→ External power source controls the reaction behavior

『Reaction at Interface』

→ State of interface should be well understood

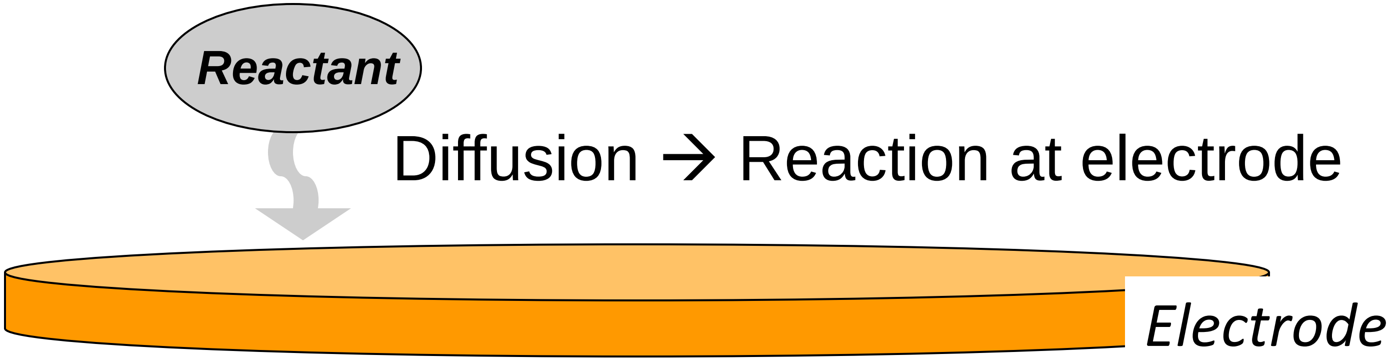
→ Both reaction at the interface and transport toward the interface should be well considered

↓

Fluid Dynamics enormously contribute to Electrochemistry

How to use Fluid Dynamics in Electrochemistry ?

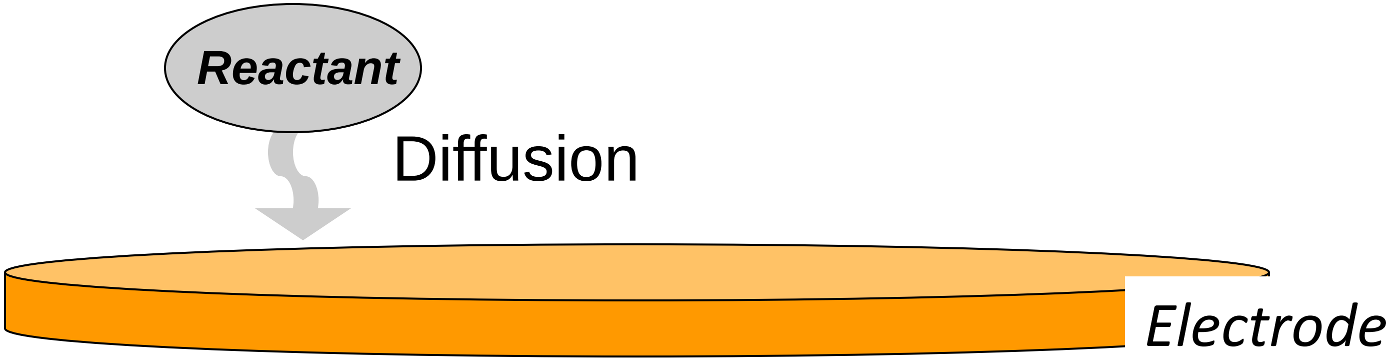
Fluid Dynamics provide the method to control
transport behavior of reactants in electrochemistry



Diffusion behavior of reactant determines
the rate of electrochemical phenomena

How to use Fluid Dynamics in Electrochemistry ?

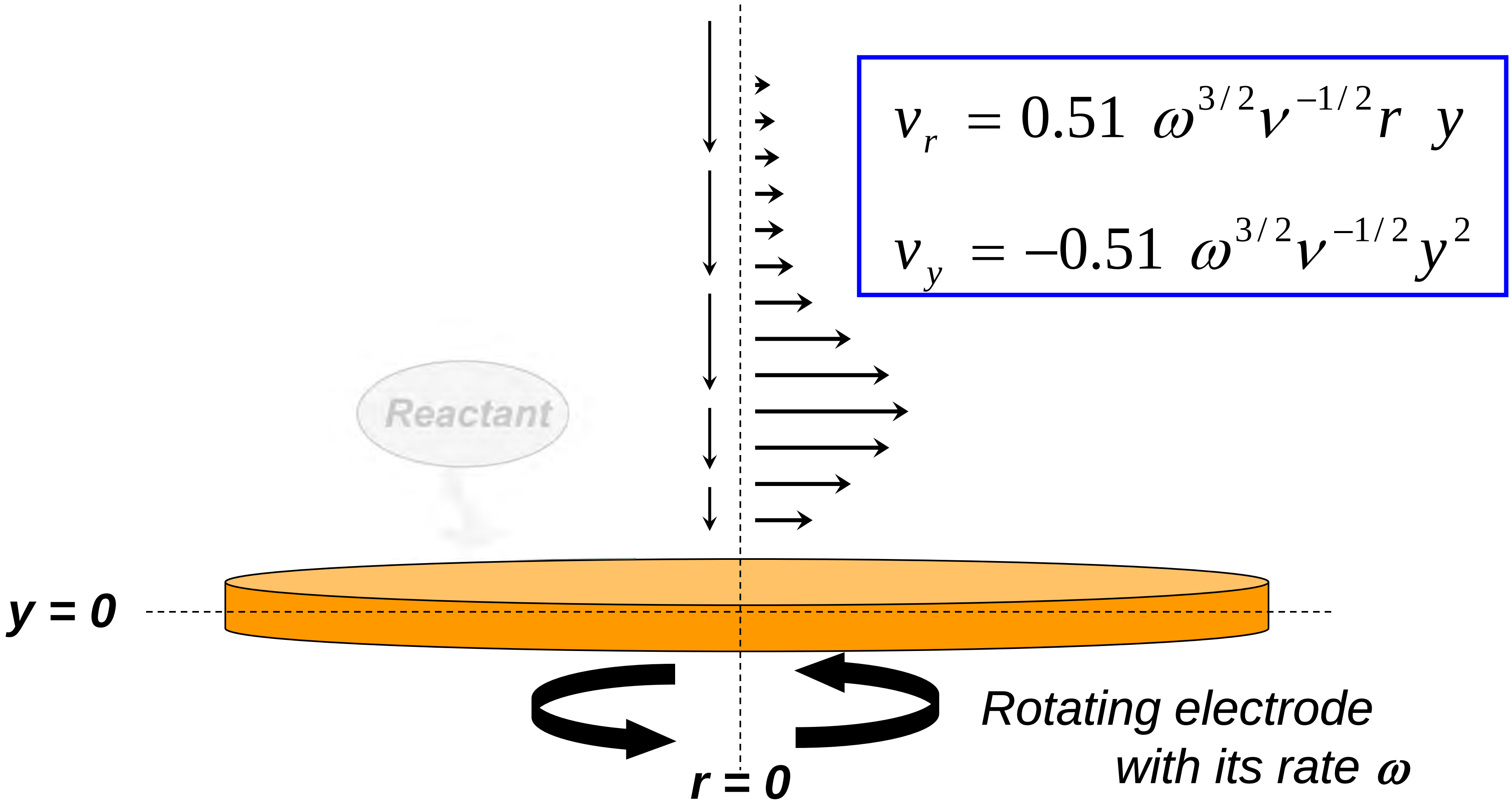
Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



How to control the diffusion behavior ??

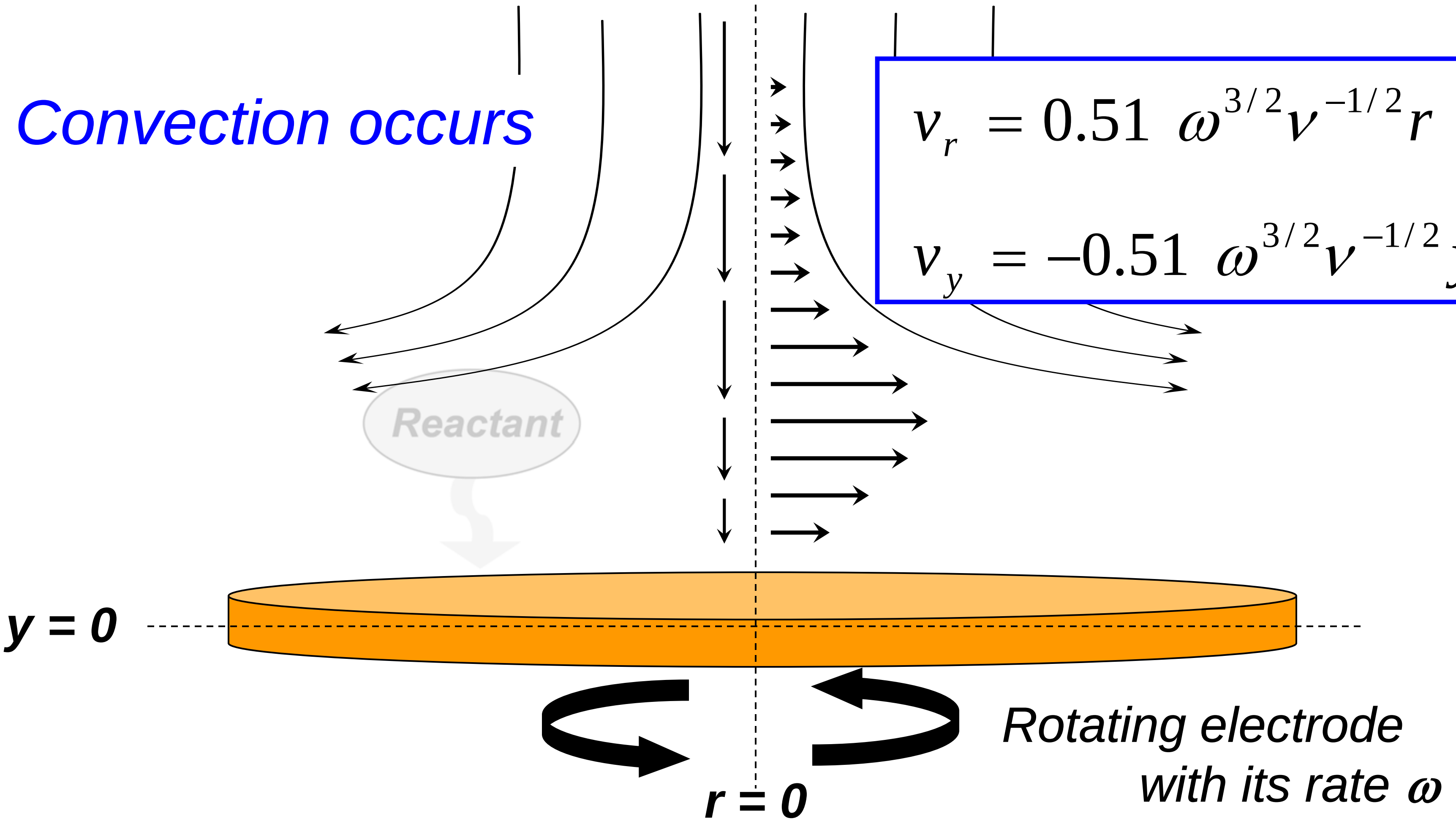
How to use Fluid Dynamics in Electrochemistry ?

Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



How to use Fluid Dynamics in Electrochemistry ?

Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



$$v_r = 0.51\ \omega^{3/2} \nu^{-1/2} r\ y$$

$$v_y = -0.51\ \omega^{3/2} \nu^{-1/2} y^2$$

How to use Fluid Dynamics in Electrochemistry ?

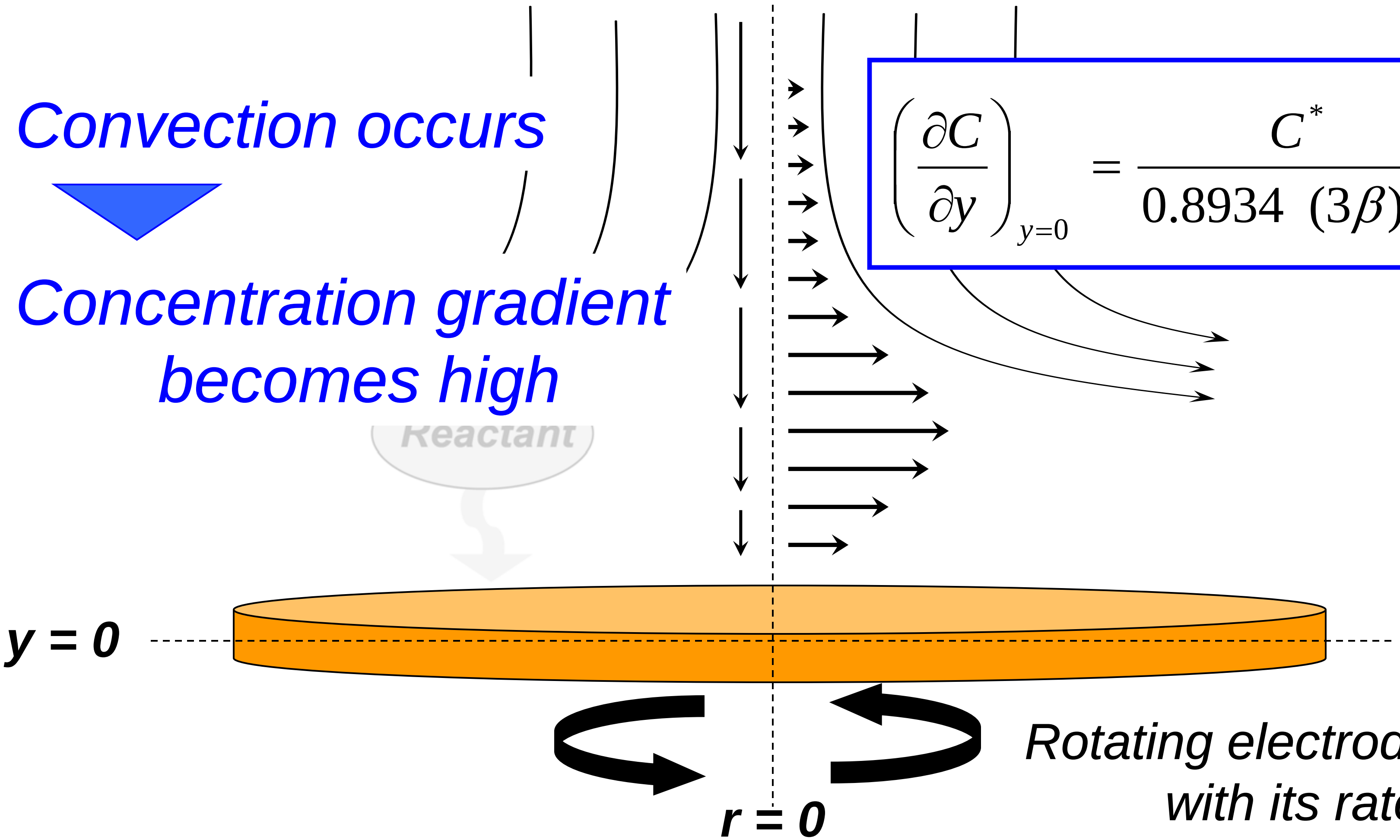
Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry

Convection occurs

▼

Concentration gradient becomes high

$$\left(\frac{\partial C}{\partial y}\right)_{y=0} = \frac{C^{*}}{0.8934\ (3\beta)^{1/3}}\ \underline{\underline{\omega^{1/2}}}$$



Rotating electrode with its rate ω

How to use Fluid Dynamics in Electrochemistry ?

Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry

Convection occurs

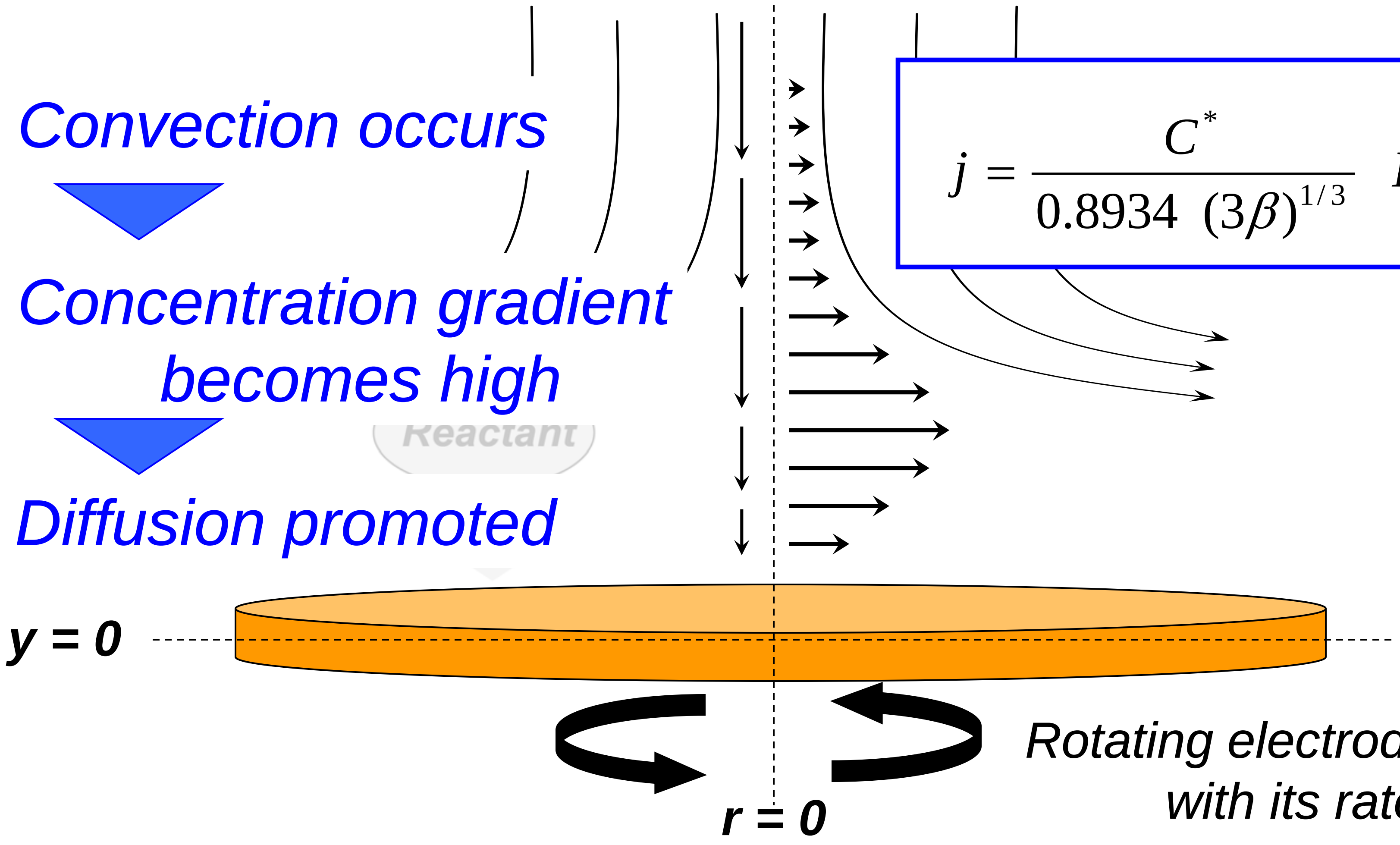
▼

Concentration gradient becomes high

▼

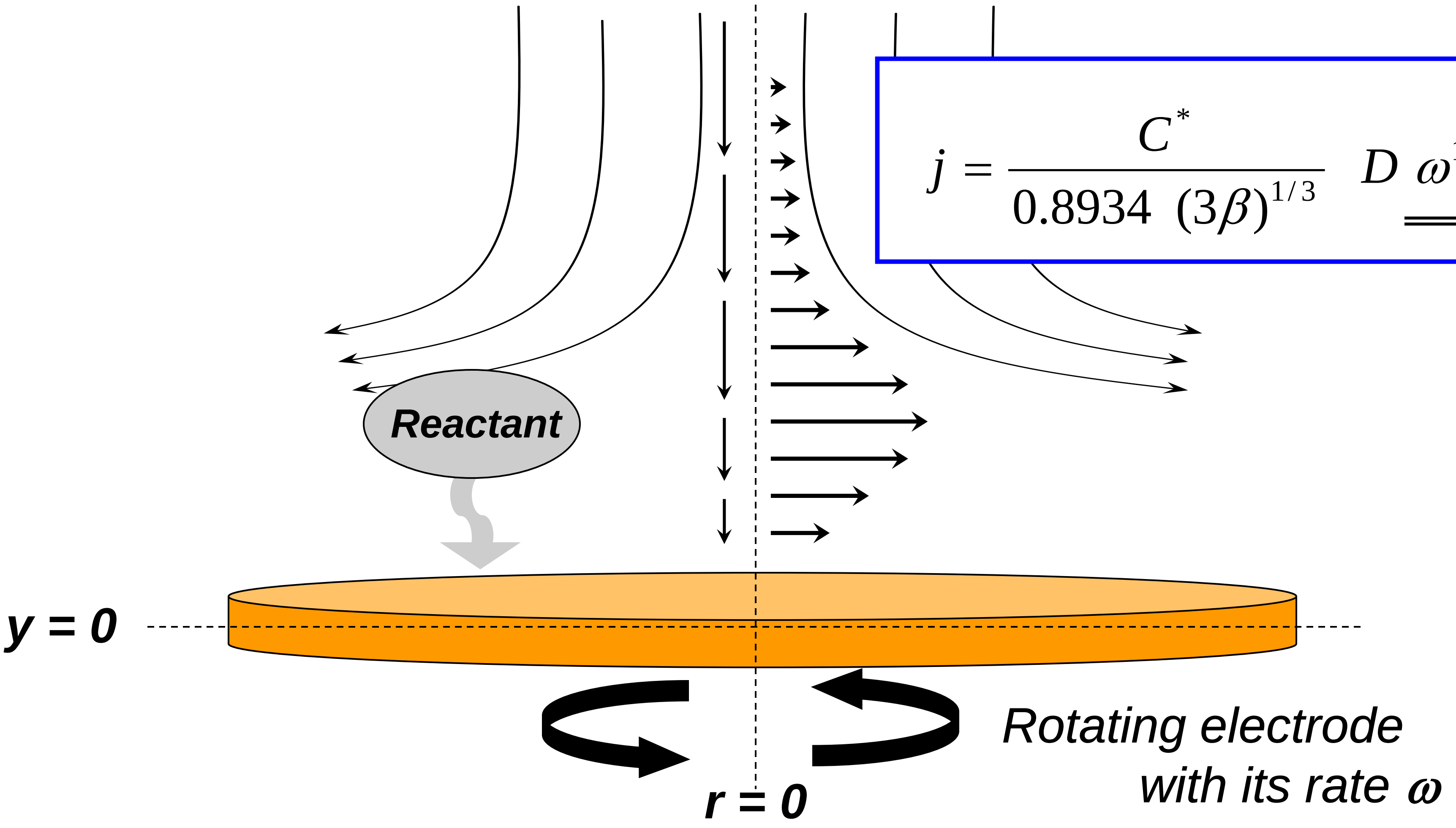
Diffusion promoted

$$j = \frac{C^*}{0.8934\ (3\beta)^{1/3}}\ D\ \underline{\underline{\omega^{1/2}}}$$



How to use Fluid Dynamics in Electrochemistry ?

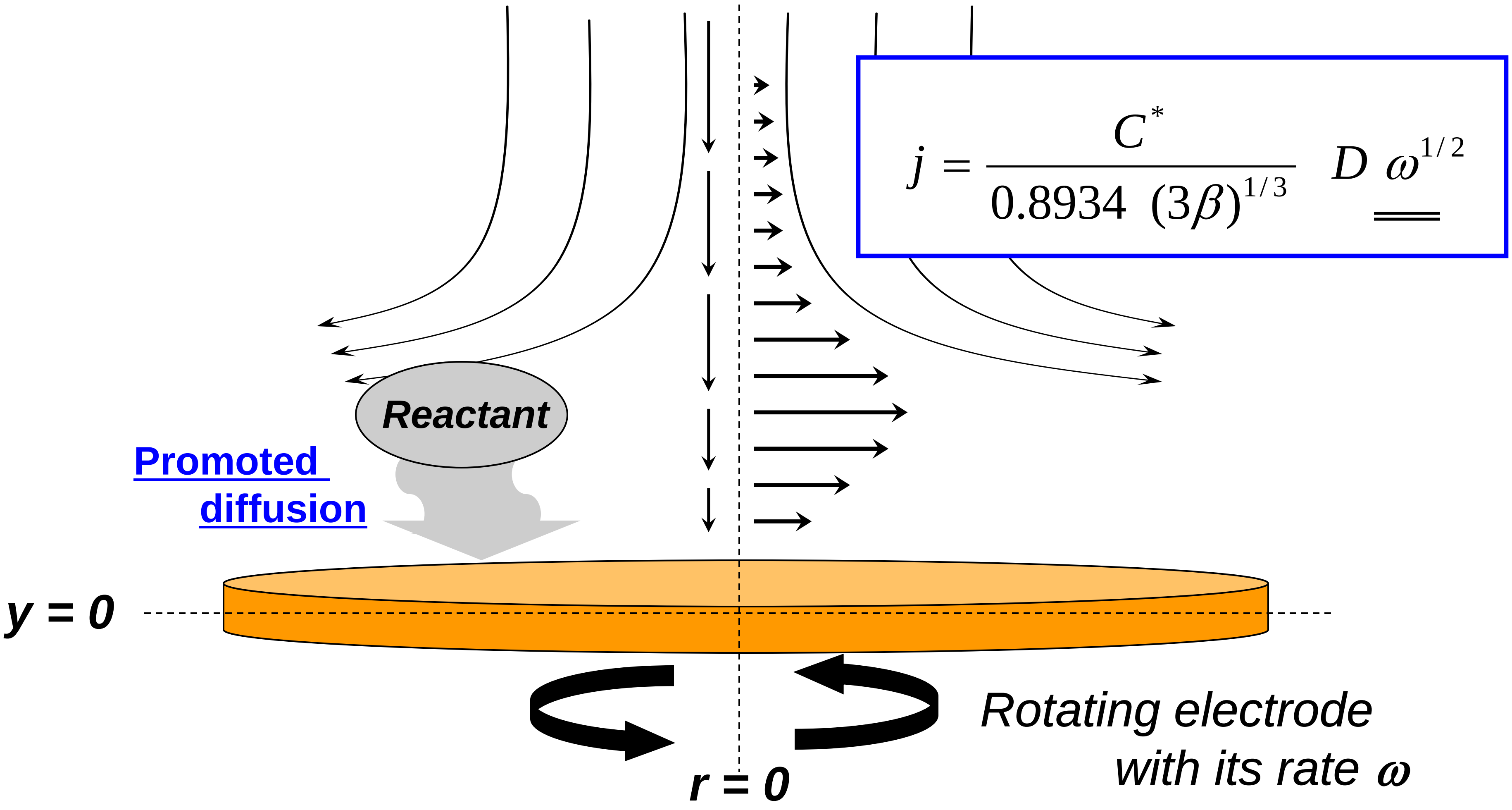
Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



$$j = \frac{C^*}{0.8934\ (3\beta)^{1/3}}\ \underline{\underline{D\ \omega^{1/2}}}$$

How to use Fluid Dynamics in Electrochemistry ?

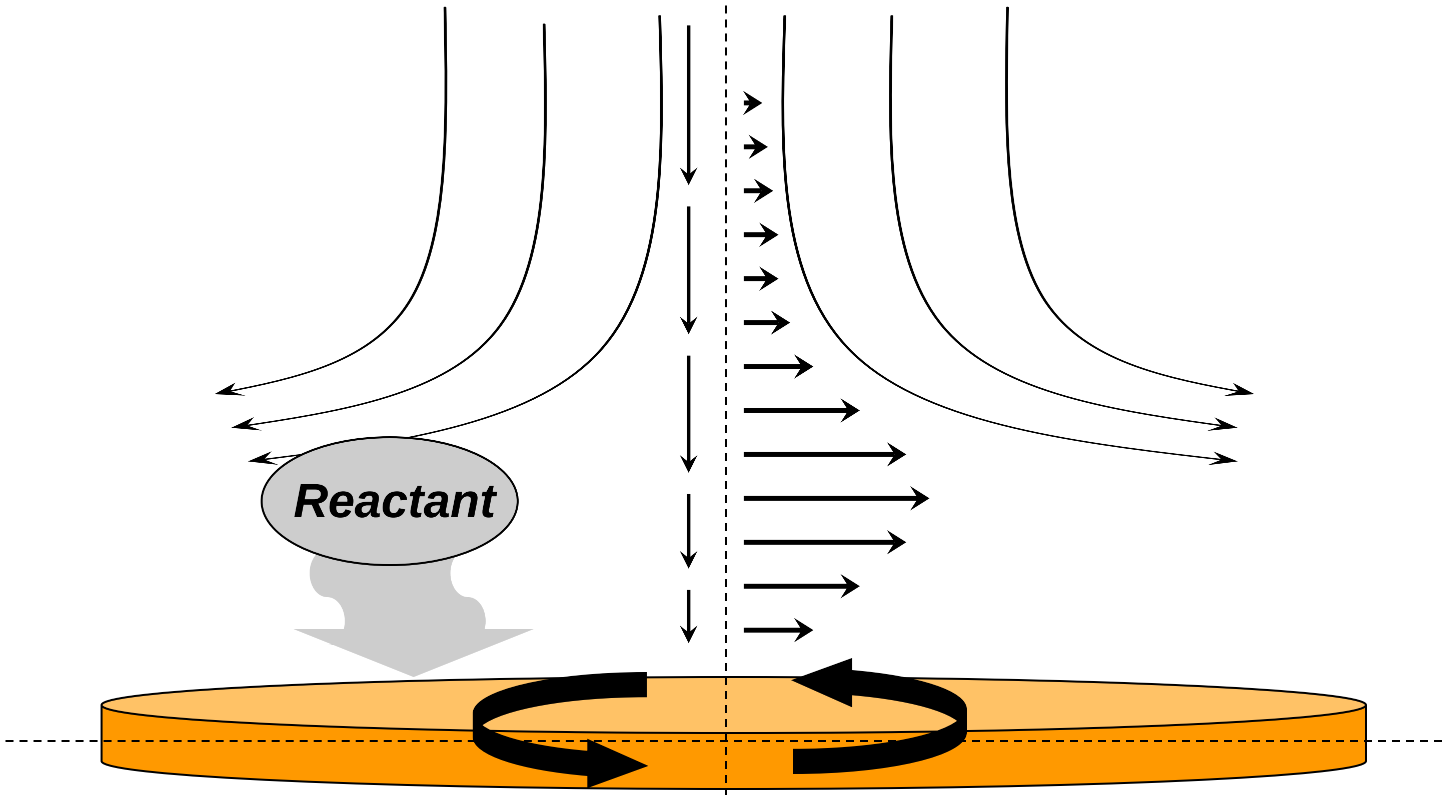
Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



$$j = \frac{C^{*}}{0.8934\ (3\beta)^{1/3}}\ \underline{\underline{D\ \omega^{1/2}}}$$

How to use Fluid Dynamics in Electrochemistry ?

Fluid Dynamics provide the method to control transport behavior of reactants in electrochemistry



Fluid Dynamic solution controls the rate of electrochemical reaction

T. von Karman, *Z. Angew. Math. Mech.,* **1**, 233 (1921).
W. G. Cochran, *Proc. Cambridge Philos. Soc.,* **30**, 364 (1934).,
V. G. Levich, “Physicochemical Hydrodynamics”, Prentice-Hall, Englewood Cliffs, NJ (1962).

Electrochemistry

Electrochemistry

Subject of Reduction/Oxidation (Redox) reaction occurring at (Solid-Liquid) Interface

Fluid Dynamics enormously contribute to Electrochemistry

Using Fluid Dynamics efficiently

↓

Building finer electrochemical processes

Outline

1. Self-introduction – Applied physical chemistry
   - Electrochemistry and its applications
   - Fluid dynamics and Electrochemistry

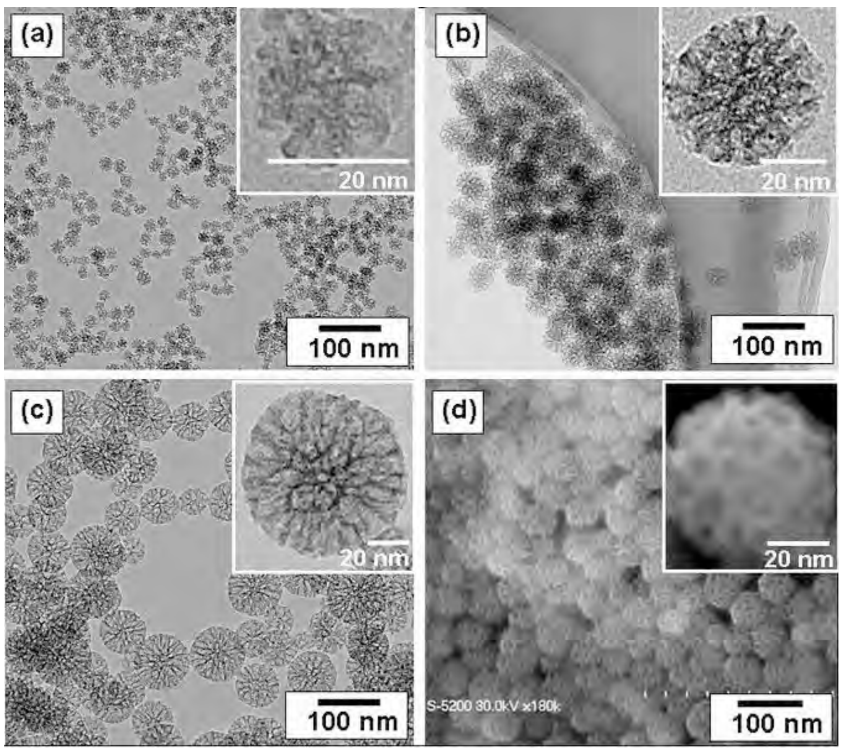
2. Motivation for main topic – Nanoparticles
   - What is nanoparticles ?
   - Objective of this research

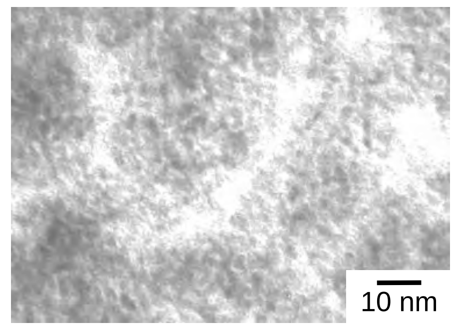
3. Strategy for process optimization
   - Fundamental concept
   - Strategies for process optimization

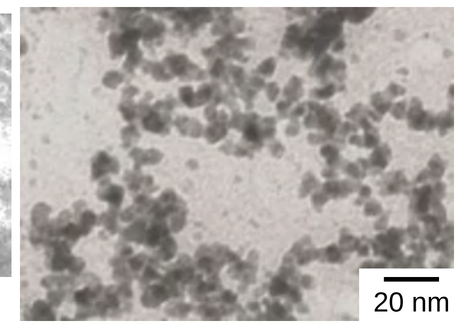
Nanoparticle

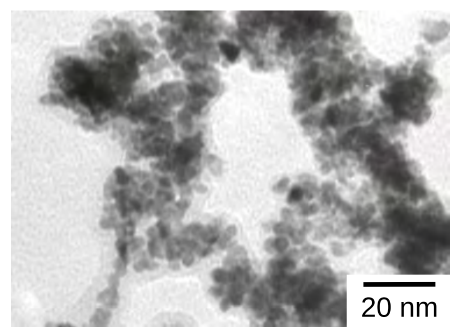
Nanoparticle ･･･ Nano-size structure with diameter 1 – 10, 100 nm, which shows totally different characteristics from bulk structure

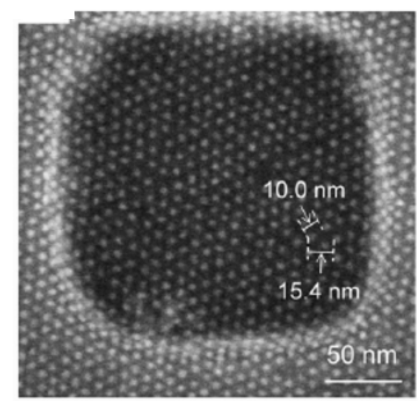
Application ･･･ Electronic devices, Medical systems, Cosmetics, *etc.*











Which factor should be controlled ??

Ⅰ. Size (diameter) and its distribution

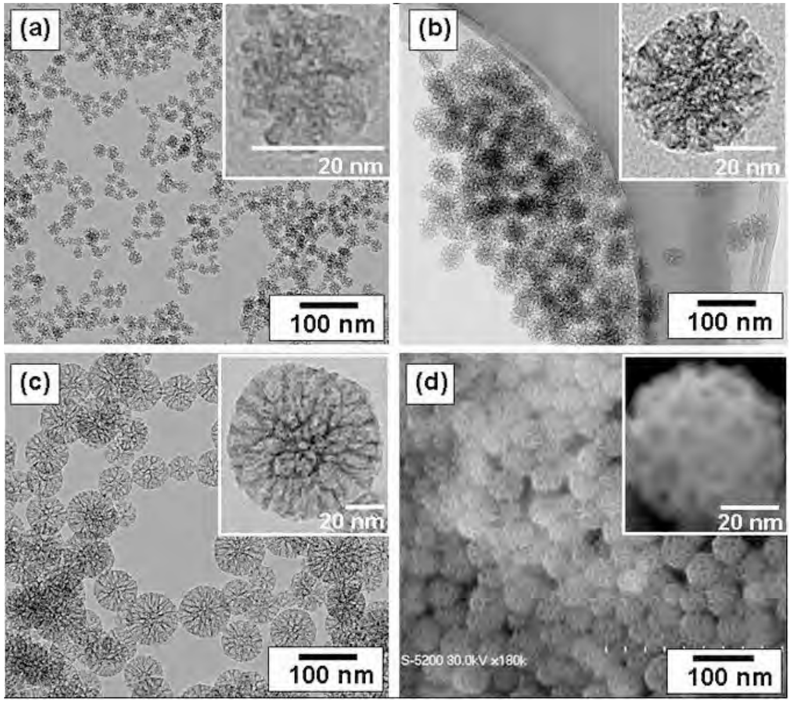
→ Minimizing the distribution of size

Ⅱ. Crystallinity

→ Customizing crystallinity

Ⅲ. Composition

→ Customizing composition



How to control these factors ??

Ⅰ. Size (diameter) and its distribution

→ **Providing simultaneous nucleation and nuclear growth with same speed**

Ⅱ. Crystallinity

→ **Providing stable and calm nuclear growth**

Ⅲ. Composition

→ **Optimizing reactant composition**

How to control these factors ??

Ⅰ. Size (diameter) and its distribution

→ **Providing simultaneous nucleation and nuclear growth with same speed**

Ⅱ. Crystallinity

→ **Providing stable and calm nuclear growth**

Focused !!

Ⅲ. Composition

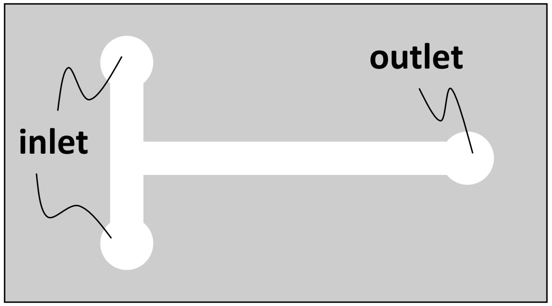
→ **Optimizing reactant composition**

Overview of the research topic

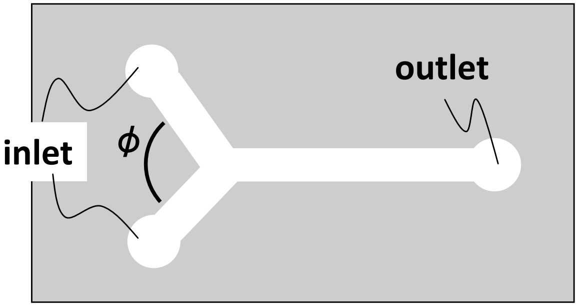
Directionalities

- Using micro-reactor (2 inlets/ 1 outlet)

T-shaped



Y-shaped



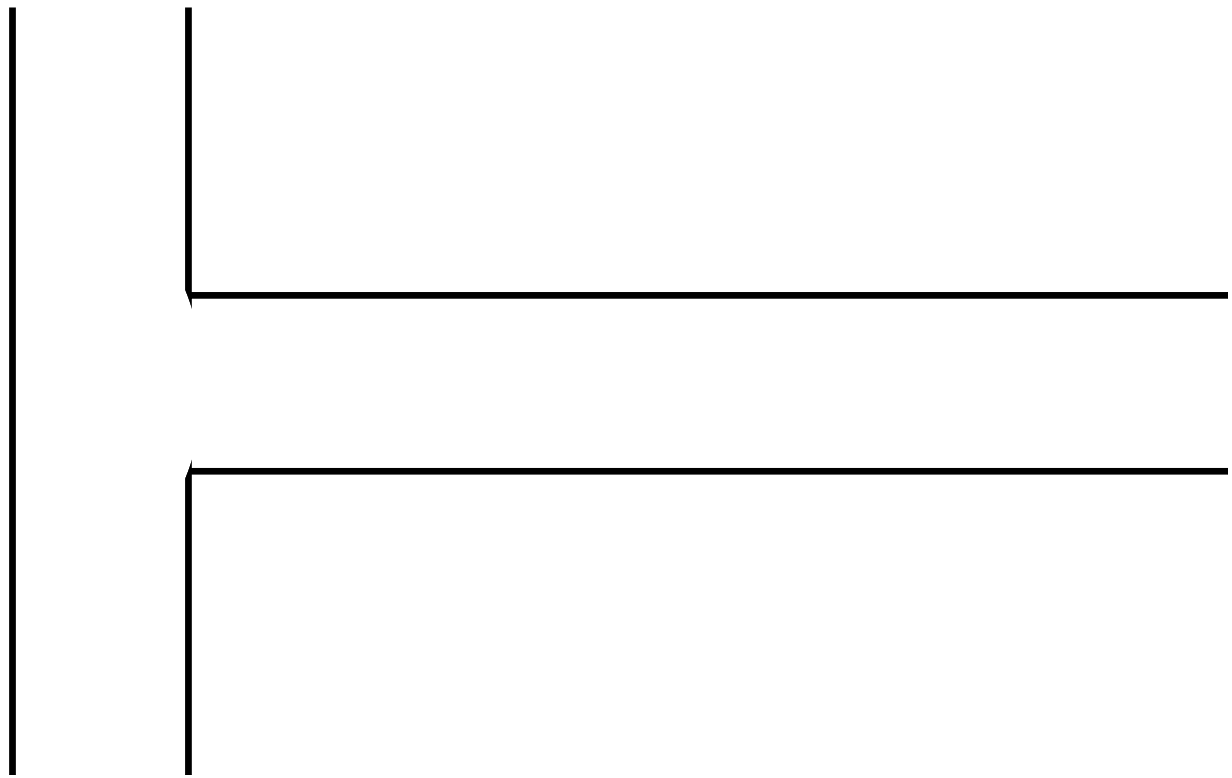
- Using optimized flow and reaction in the reactor

Target

- Co (Cobalt) nanoparticles for magnetic recording media

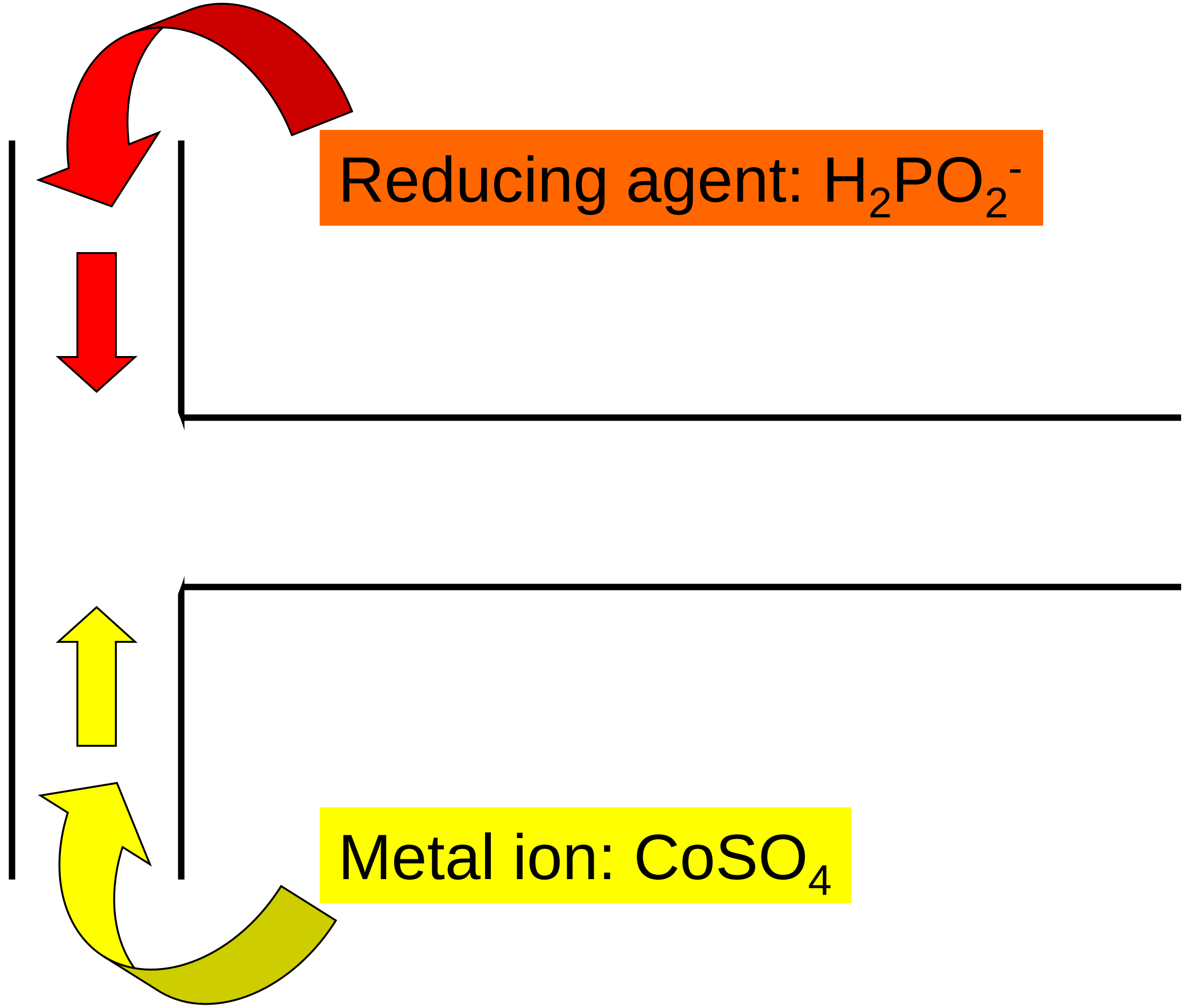
Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor



Fundamental concept of the process

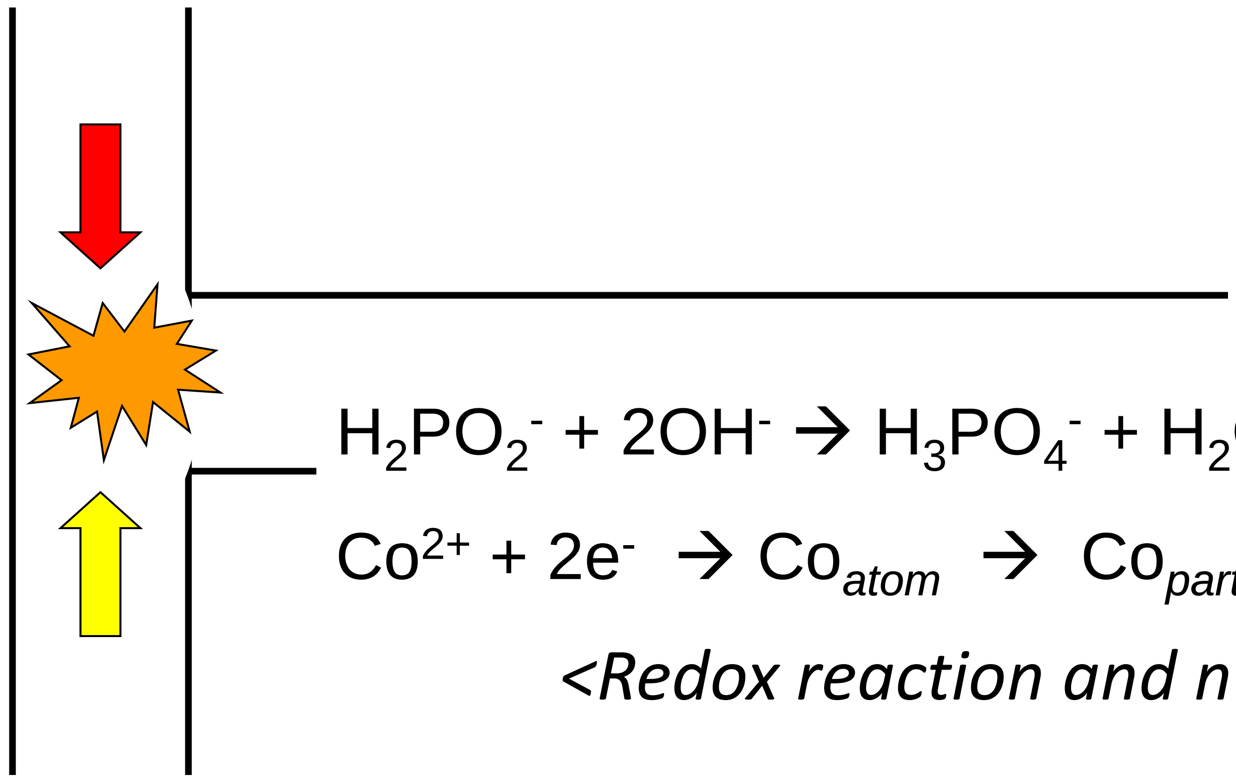
Creating particle by Redox reaction in T-shaped reactor



Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor

Reducing agent: $H_2PO_2^-$



$$H_2PO_2^- + 2OH^- \rightarrow H_3PO_4^- + H_2O + 2e^-$$

$$Co^{2+} + 2e^- \rightarrow Co_{atom} \rightarrow Co_{particle}$$

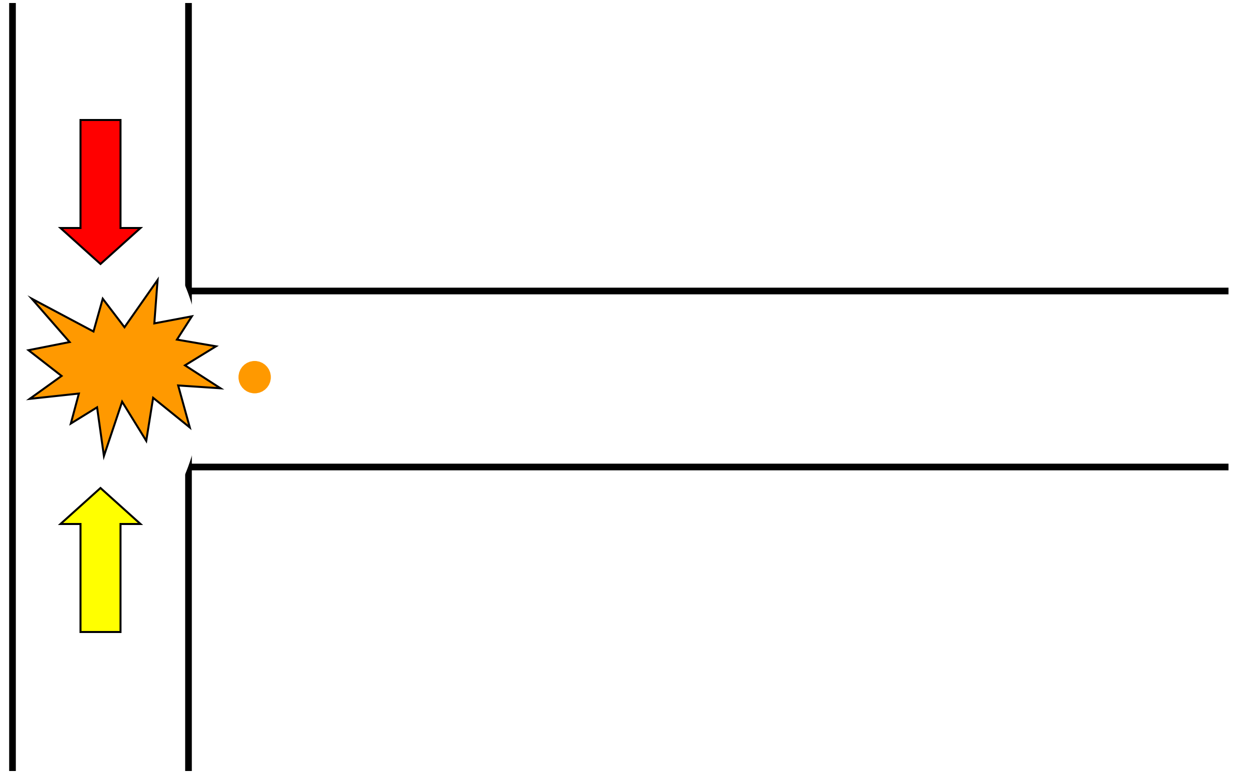
<Redox reaction and nucleation>

Metal ion: $CoSO_4$

Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor

Reducing agent: $H_2PO_2^-$

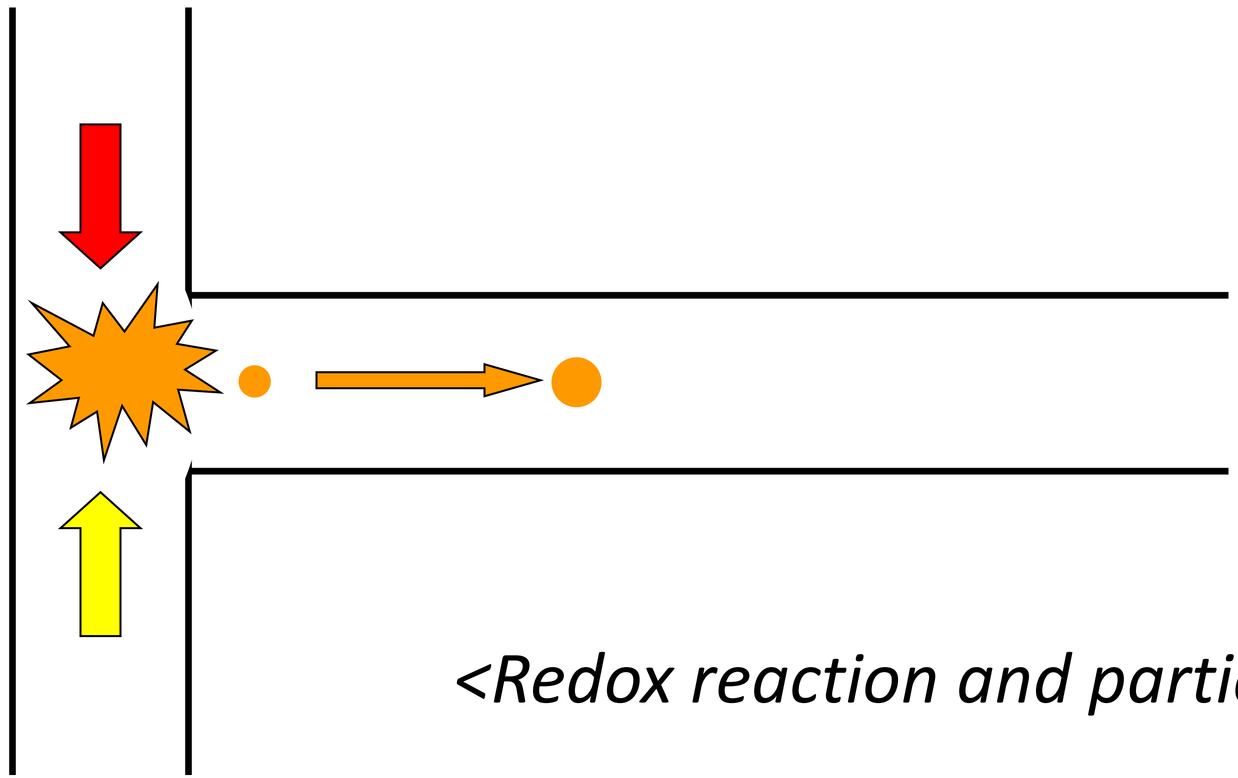


Metal ion: $CoSO_4$

Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor

Reducing agent: $H_2PO_2^-$



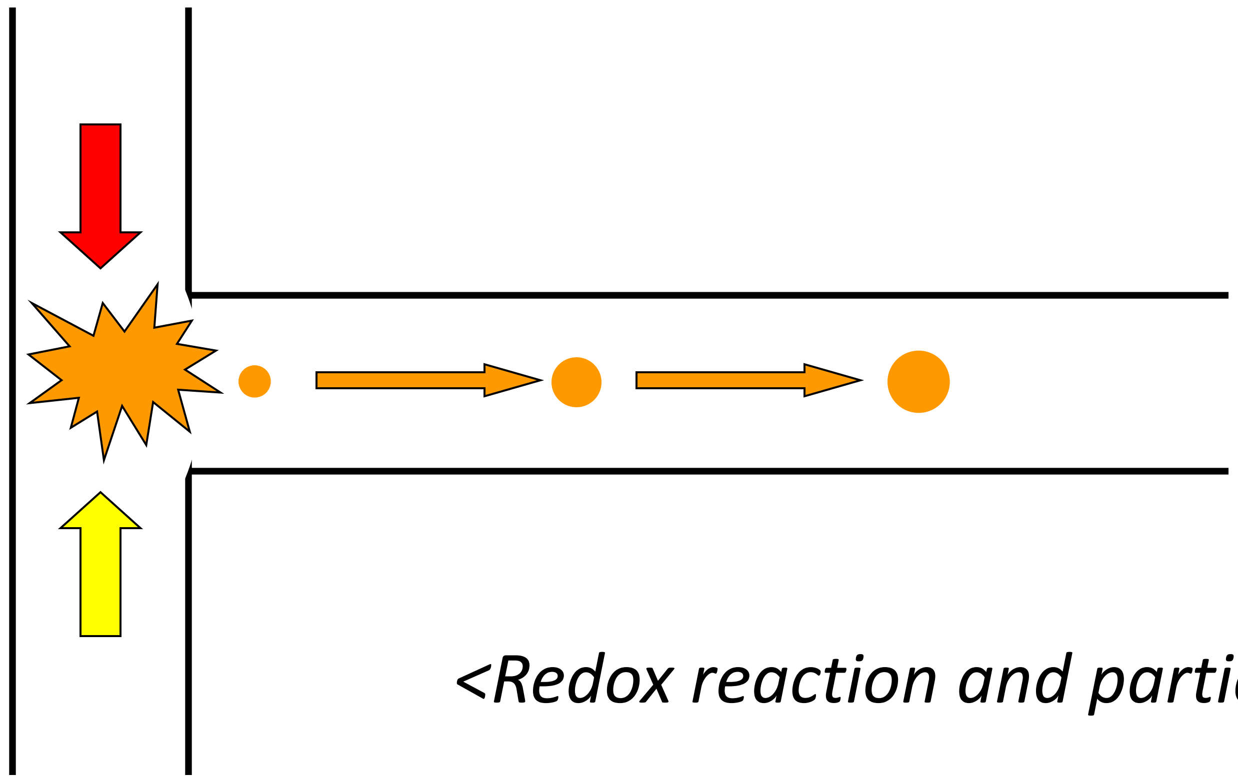
<Redox reaction and particle growth>

Metal ion: $CoSO_4$

Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor

Reducing agent: $H_2PO_2^-$



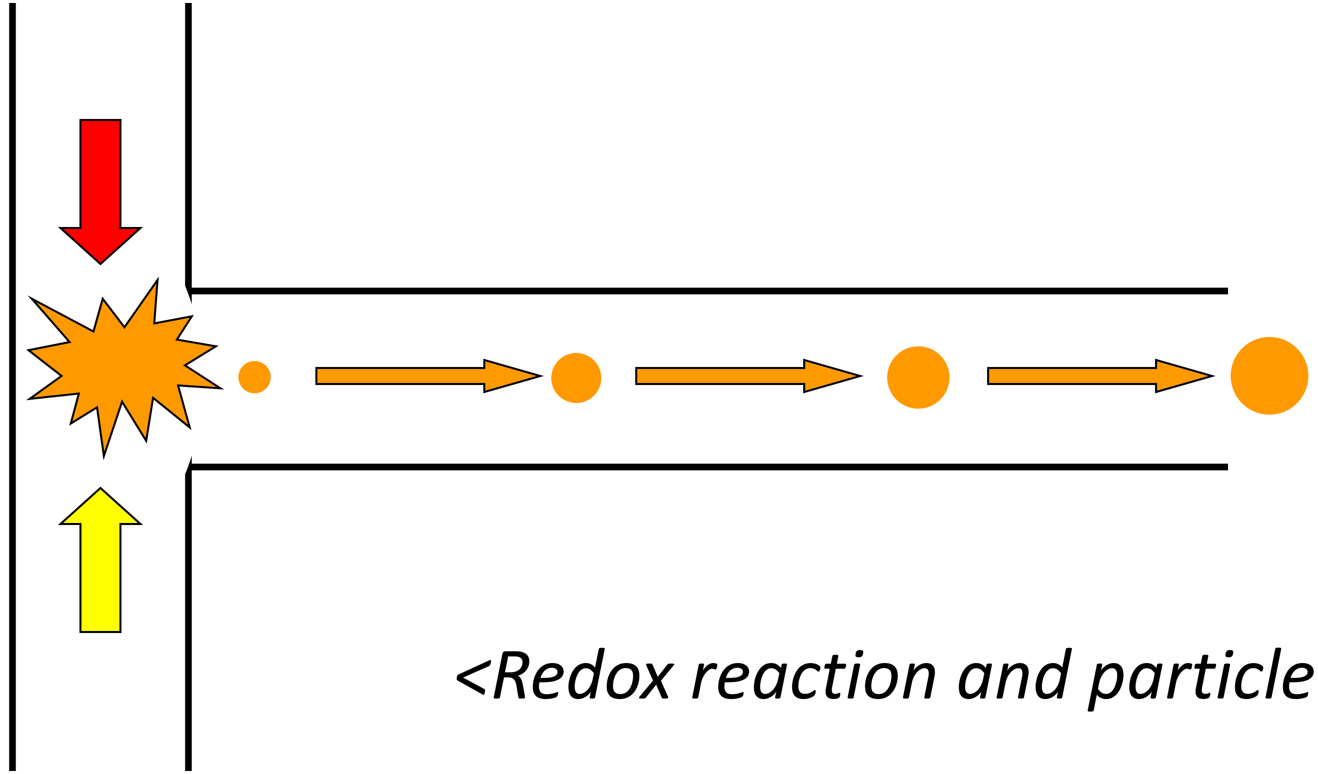
<Redox reaction and particle growth>

Metal ion: $CoSO_4$

Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor

Reducing agent: $H_2PO_2^-$

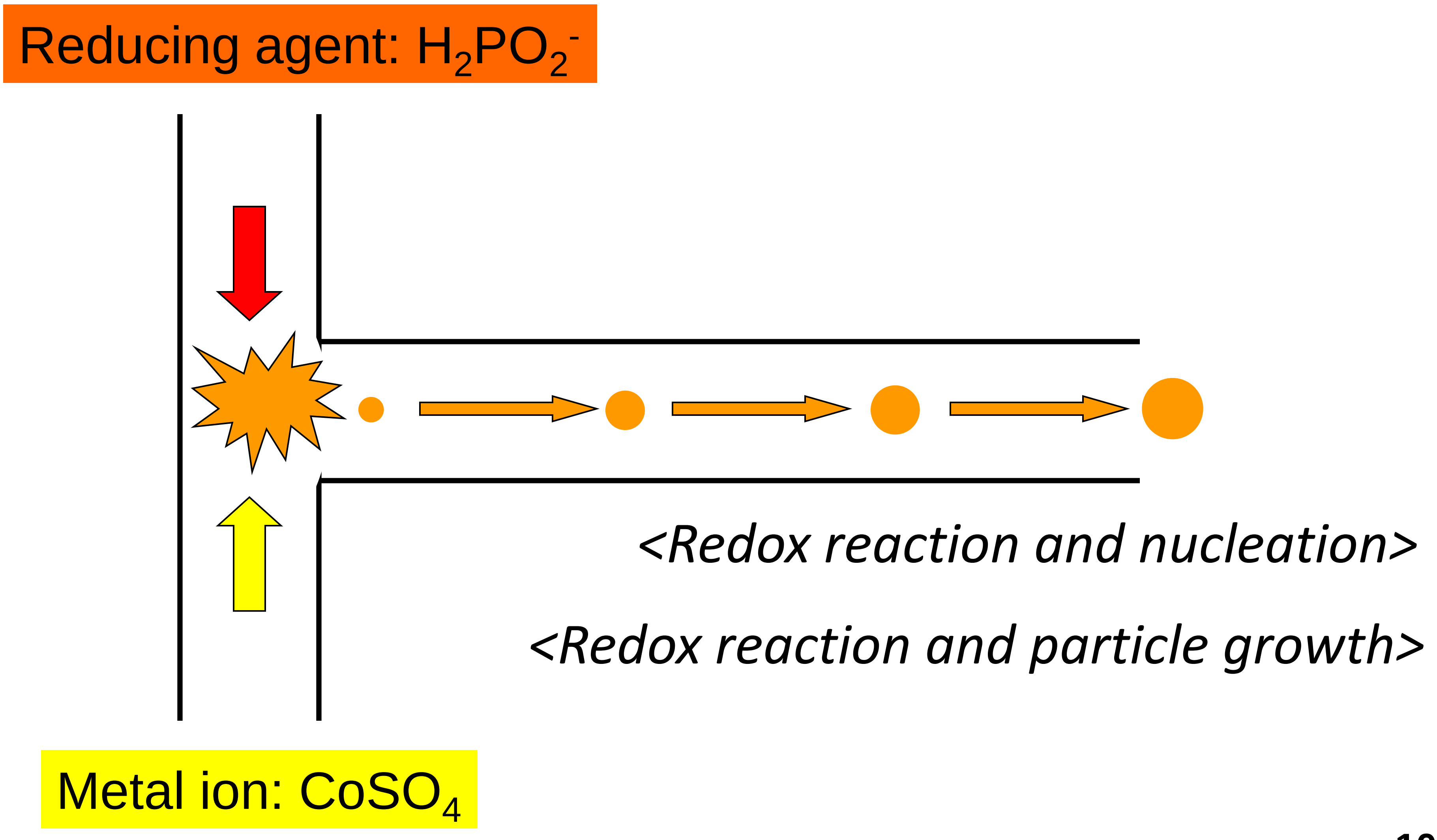


<Redox reaction and particle growth>

Metal ion: $CoSO_4$

Fundamental concept of the process

Creating particle by Redox reaction in T-shaped reactor



Fundamental concept of the process

Factors we trying to control and the way to control

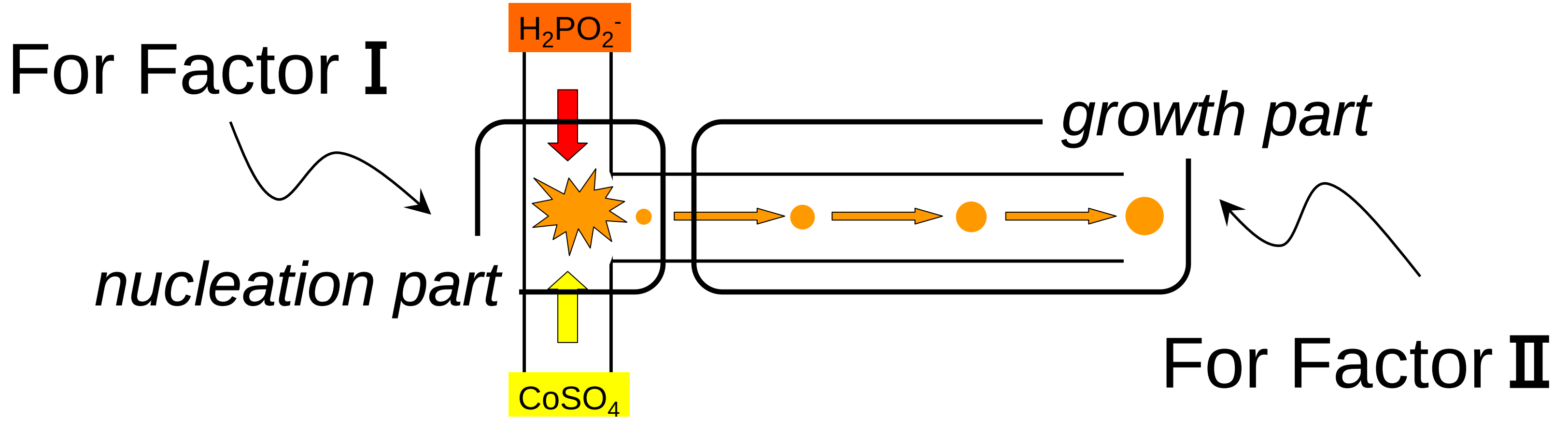
Ⅰ. Size (diameter) and its distribution

→ **Providing simultaneous nucleation and nuclear growth with same speed**

Ⅱ. Crystallinity

→ **Providing stable and calm nuclear growth**

Parts we should design



Outline

1. Self-introduction – Applied physical chemistry

   - Electrochemistry and its applications

   - Fluid dynamics and Electrochemistry

2. Motivation for main topic – Nanoparticles

   - What is nanoparticles ?

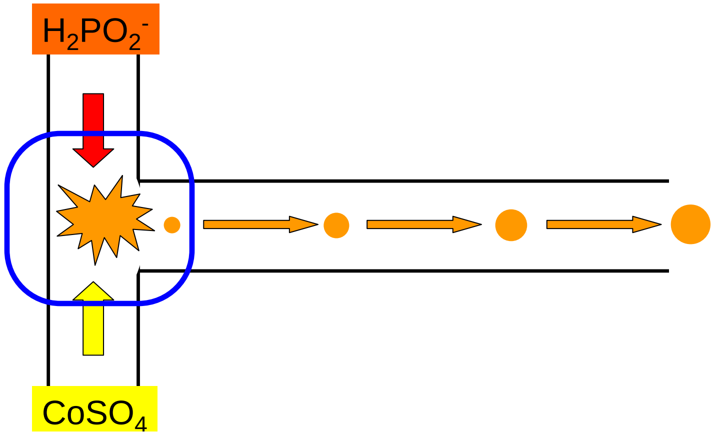
   - Objective of this research

3. Strategy for process optimization

   - Fundamental concept

   - Strategies for process optimization

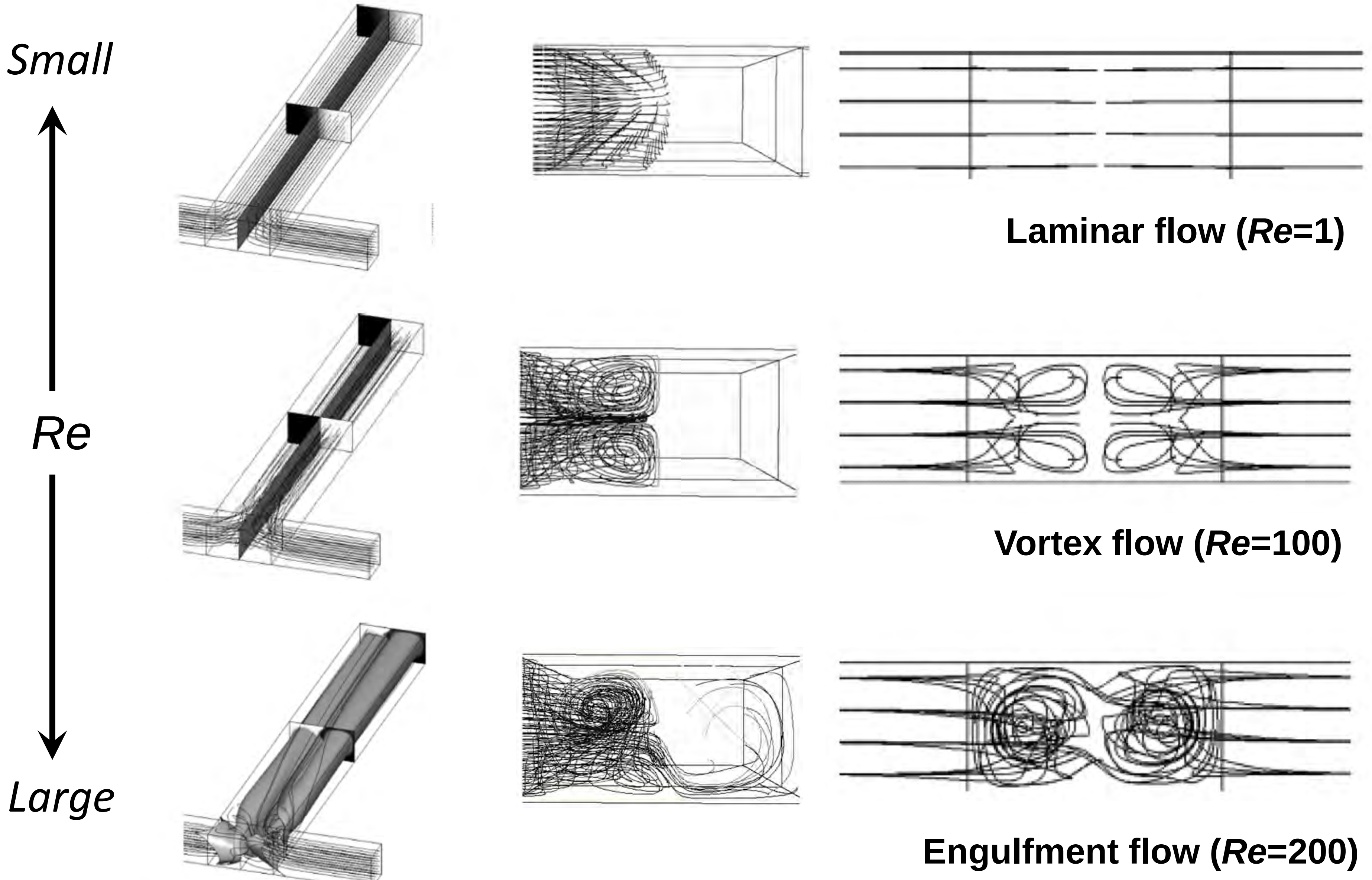
Strategy No. 1



How to bring together
two solutions ?

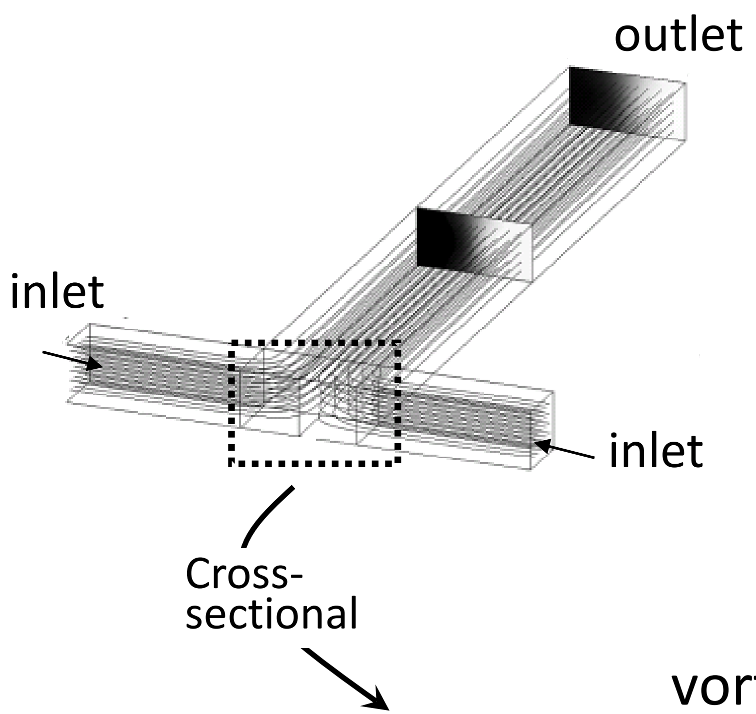
Inject solutions with moderate *Re*,
generating "vortex" around contact part

A few flow types at the junction part



D. Bothe et al., *Chem. Eng. Sci.,* **66**, 6424 (2011).
S. Dreher et al., *Heat Trans. Eng.,* **30**, 91 (2009).,

Merit of “vortex flow”

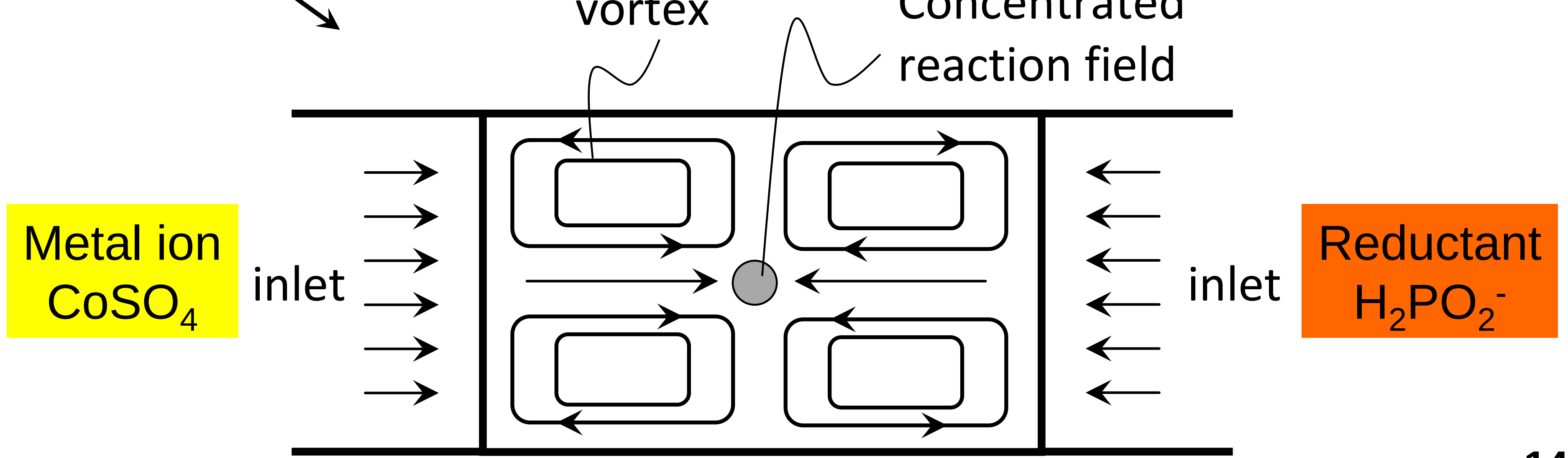


Moderate *Re*,

generating “vortex flow”

⬇

Reaction field is concentrated into the center of channel



Merit of “vortex flow”

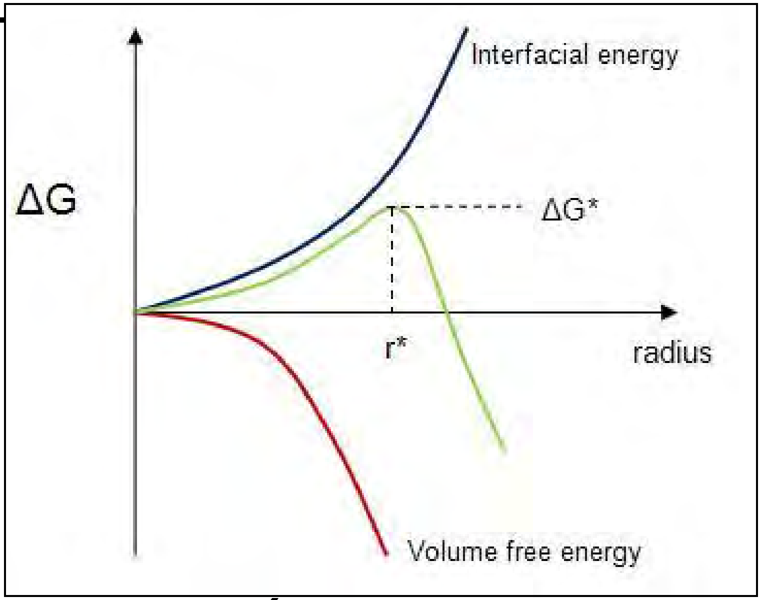
Nucleation

<1> *Redox reaction*

$$H_2PO_2^- + 2OH^- + Co^{2+}$$
$$\rightarrow H_3PO_4^- + H_2O + Co_{atom}$$

<2> *Aggregation*

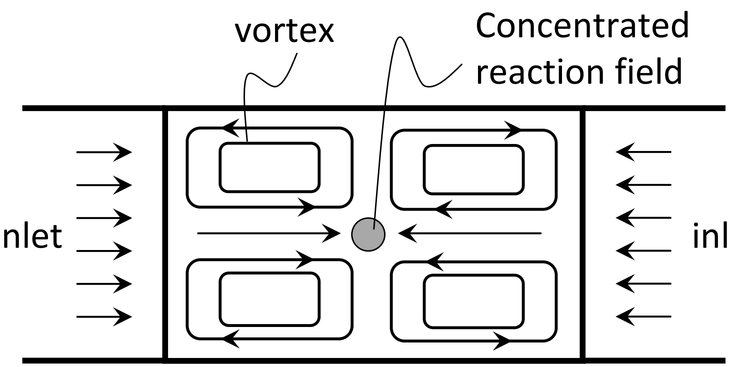
$$n\ Co_{atom} \rightarrow Co_{particle}$$



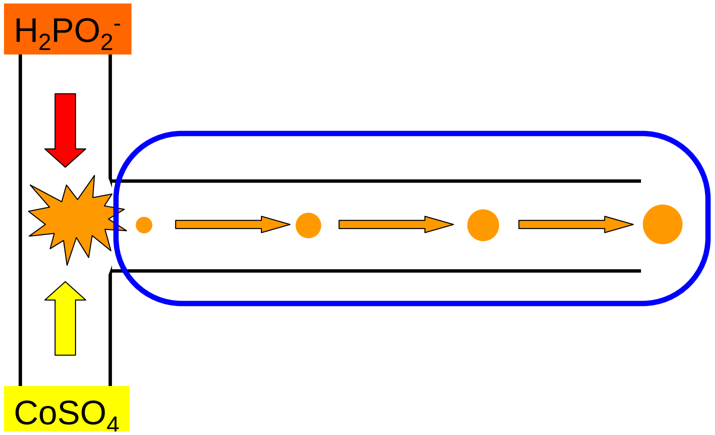
Reaction field for *Redox reaction* is concentrated

↓

Efficient and simultaneous nucleation is realized



Strategy No. 2

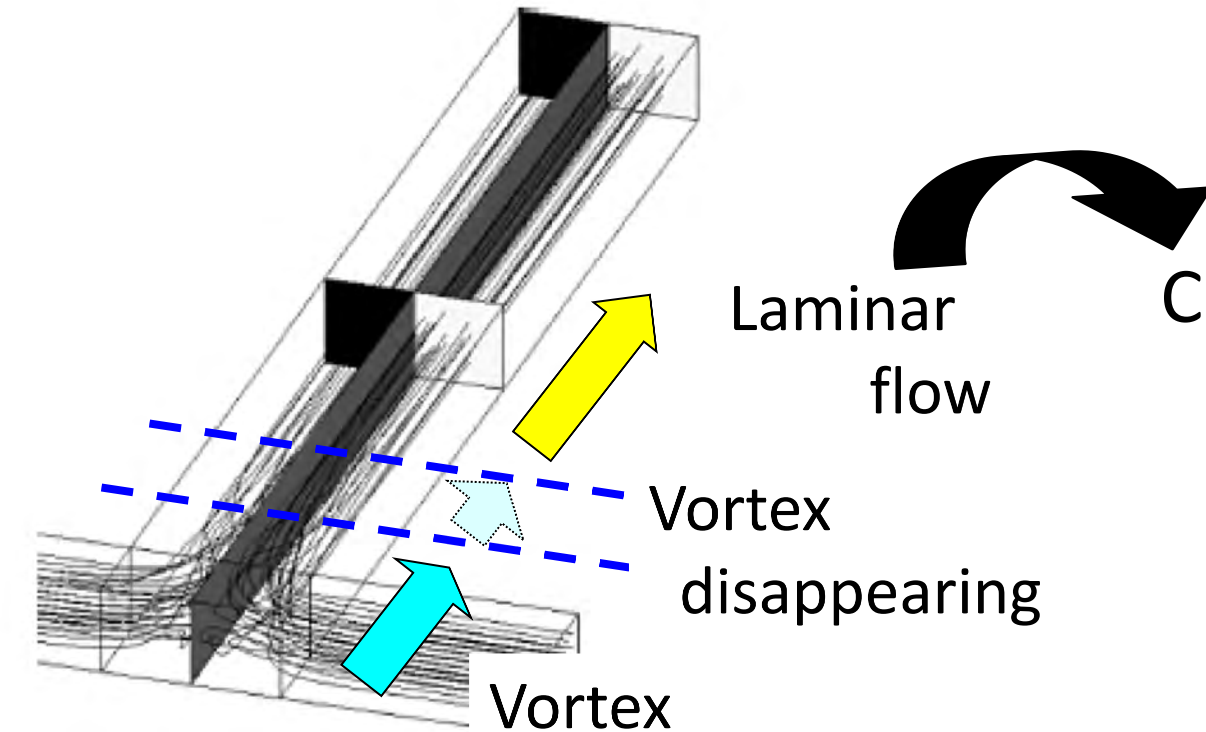


How to provide stable and calm growth ?

Inject solutions with adequate *Re and surface modification for the channel wall,* generating "symmetric laminar" flow

Merit of moderate *Re*

Flow transition of vortex flow in reactor



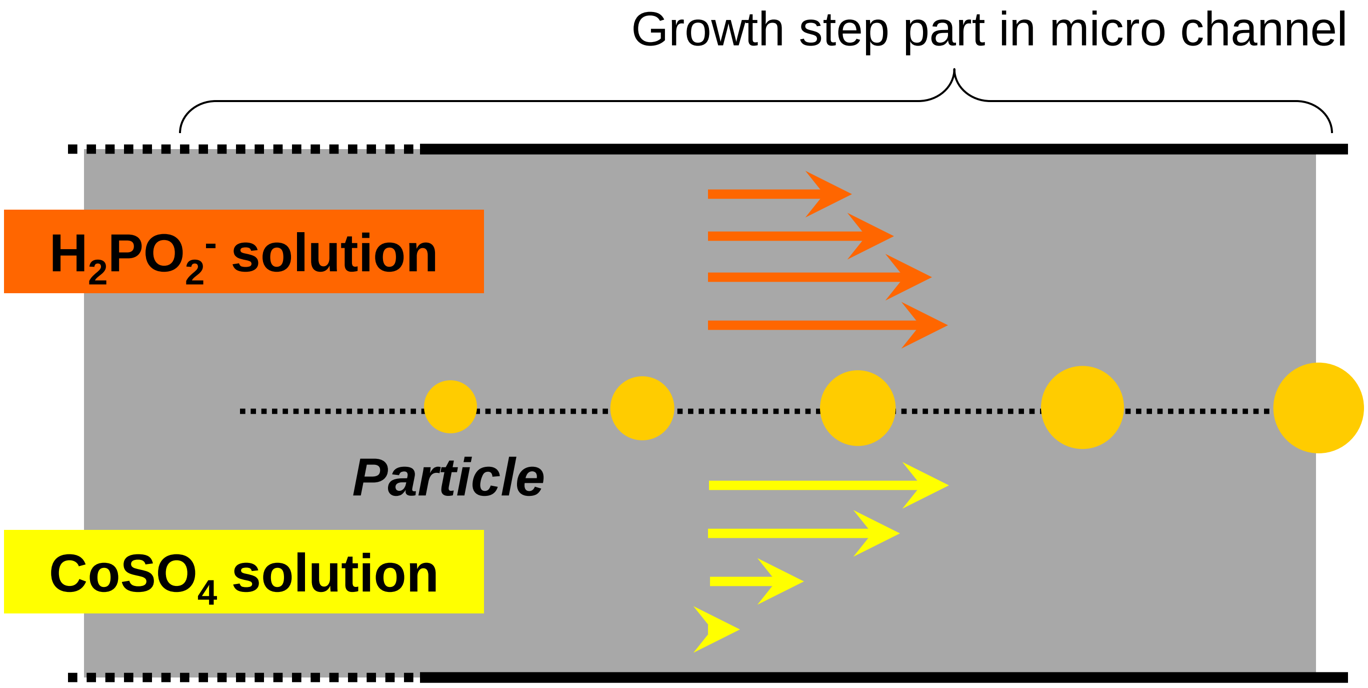
Capable to provide stable and calm particle growth

Vortex flow system is helpful for both nucleation and growth

But…

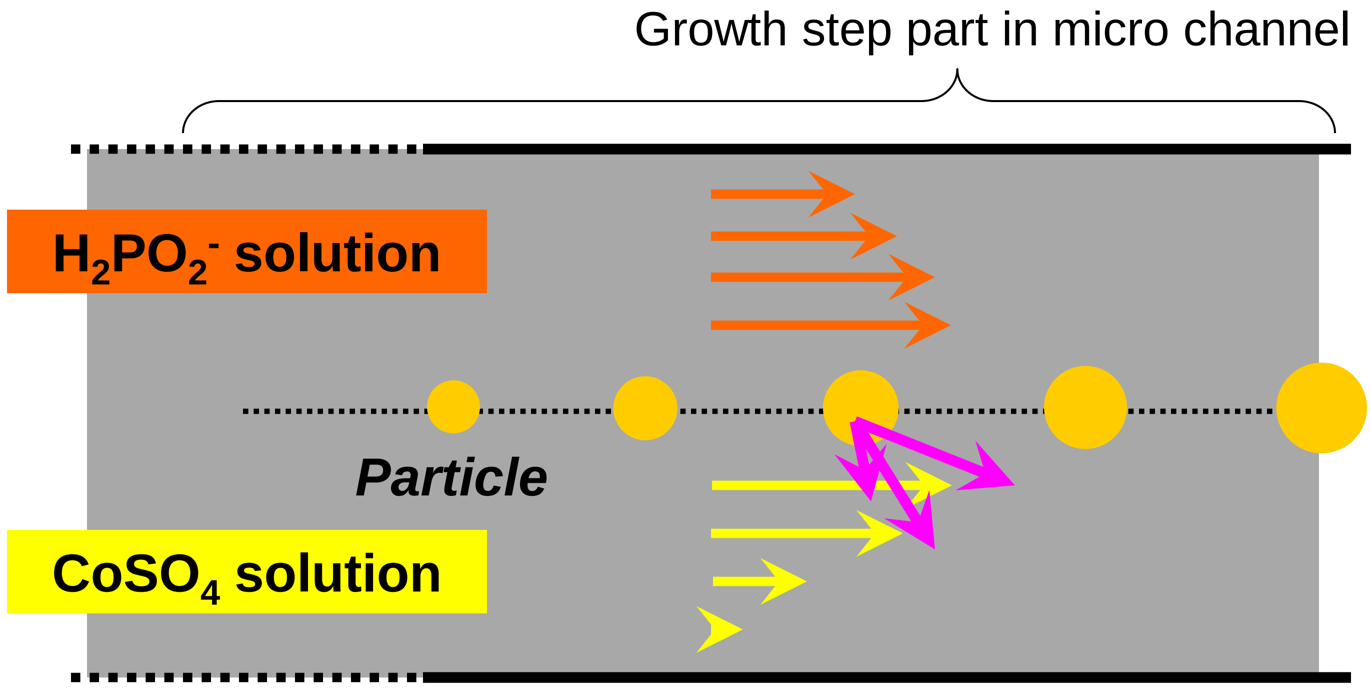
Vortex flow system can really provide stable field ??

Asymmetric laminar flow



Vortex flow system can really provide stable field ??

Asymmetric laminar flow



Additional force (vertical to the wall)

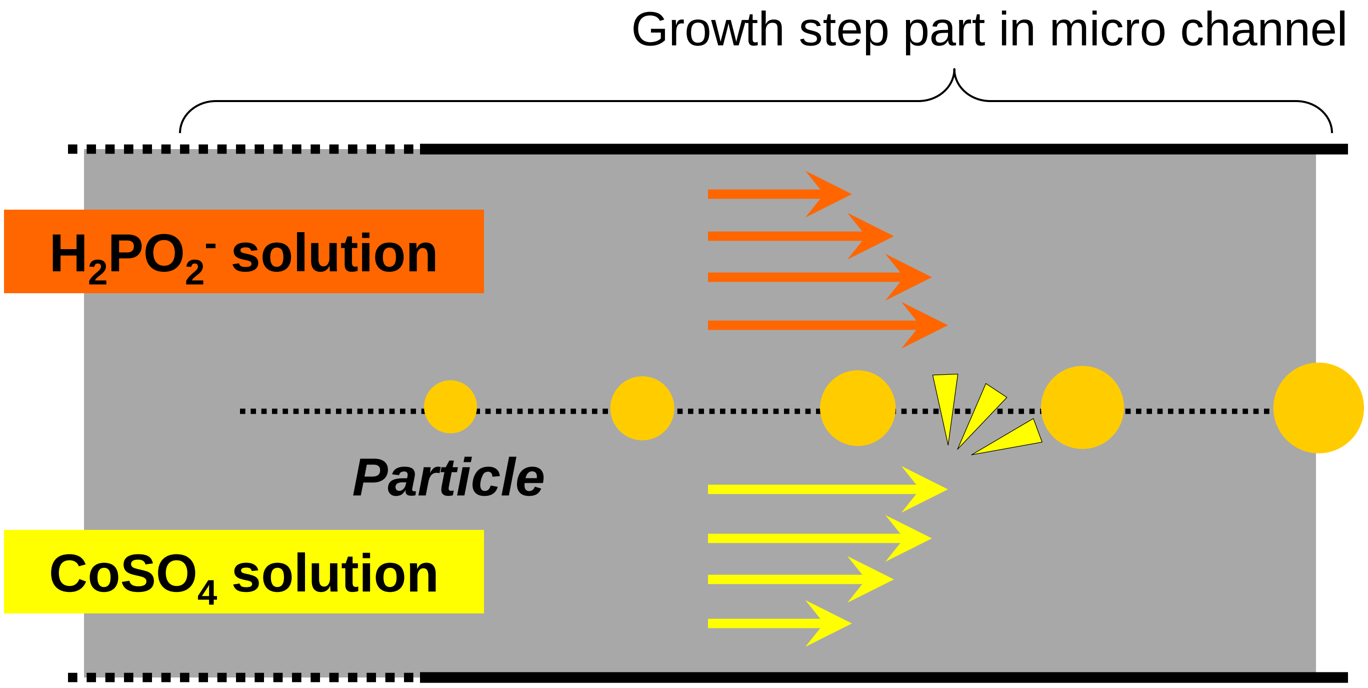
disturbing particle trajectory works for growing particle

Not stable

S. Fukuoka et al., *土木学会論文報告集*, **295**, 31 (1980).

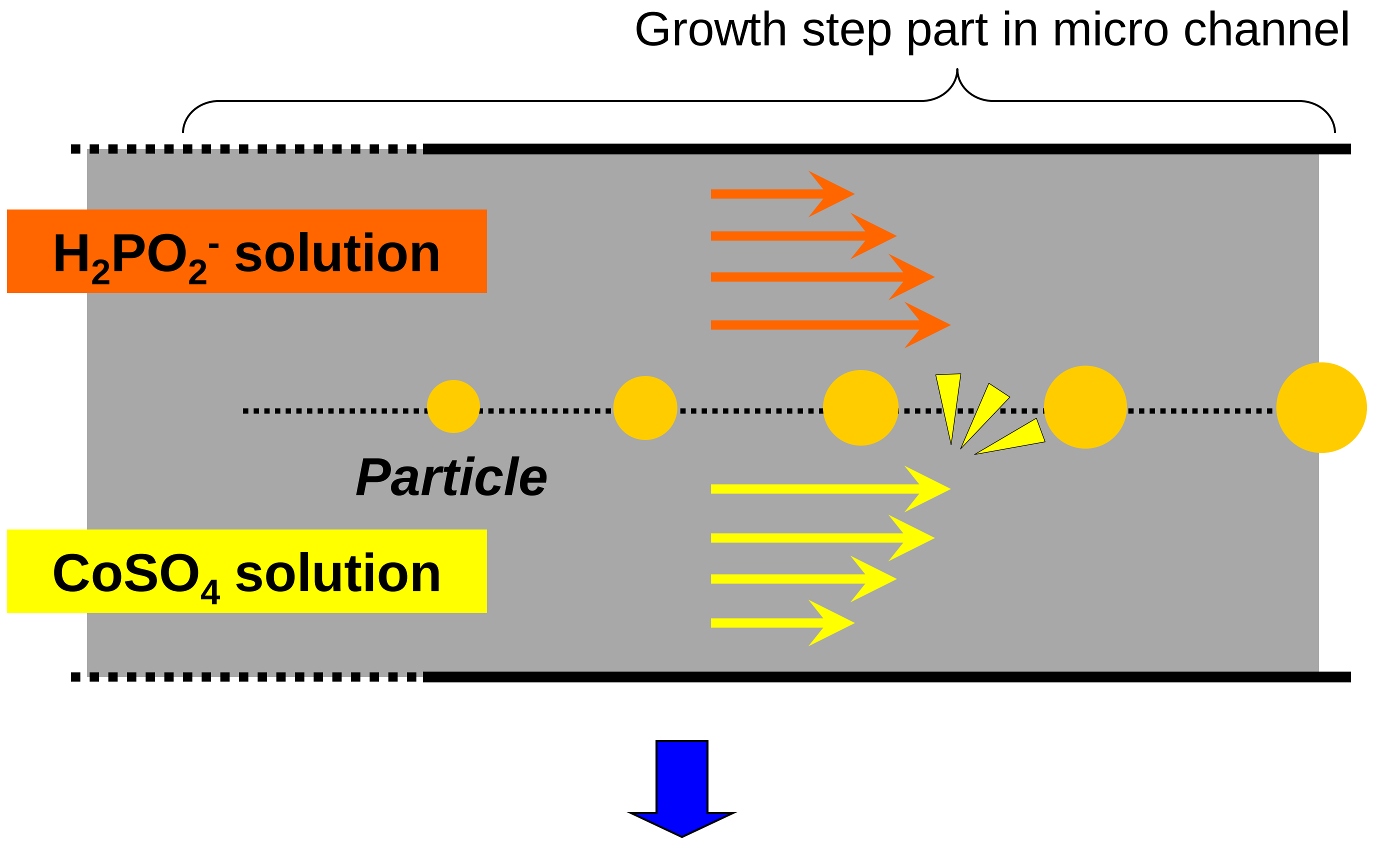
Vortex flow system can really provide stable field ??

Symmetric laminar flow



Vortex flow system can really provide stable field ??

Symmetric laminar flow

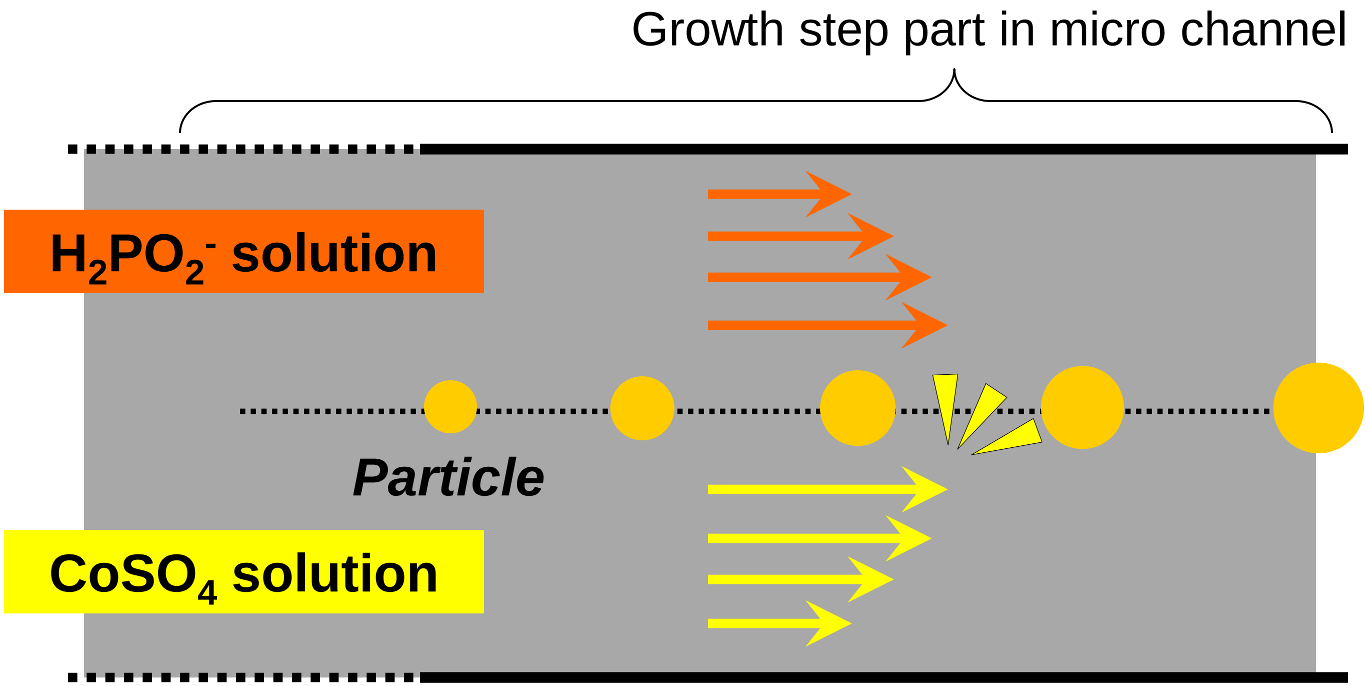


Growing field becomes stable

Adequate *Re* of solution and surface modification needed

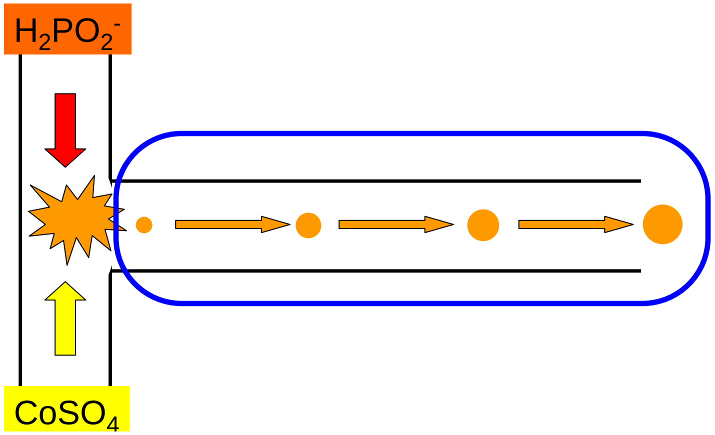
Vortex flow system can really provide stable field ??

Symmetric laminar flow



Details about the particle movement
should be analyzed by Euler/Lagrange equation

Strategy No. 3



How to deal with additional nucleation in the growth step ?

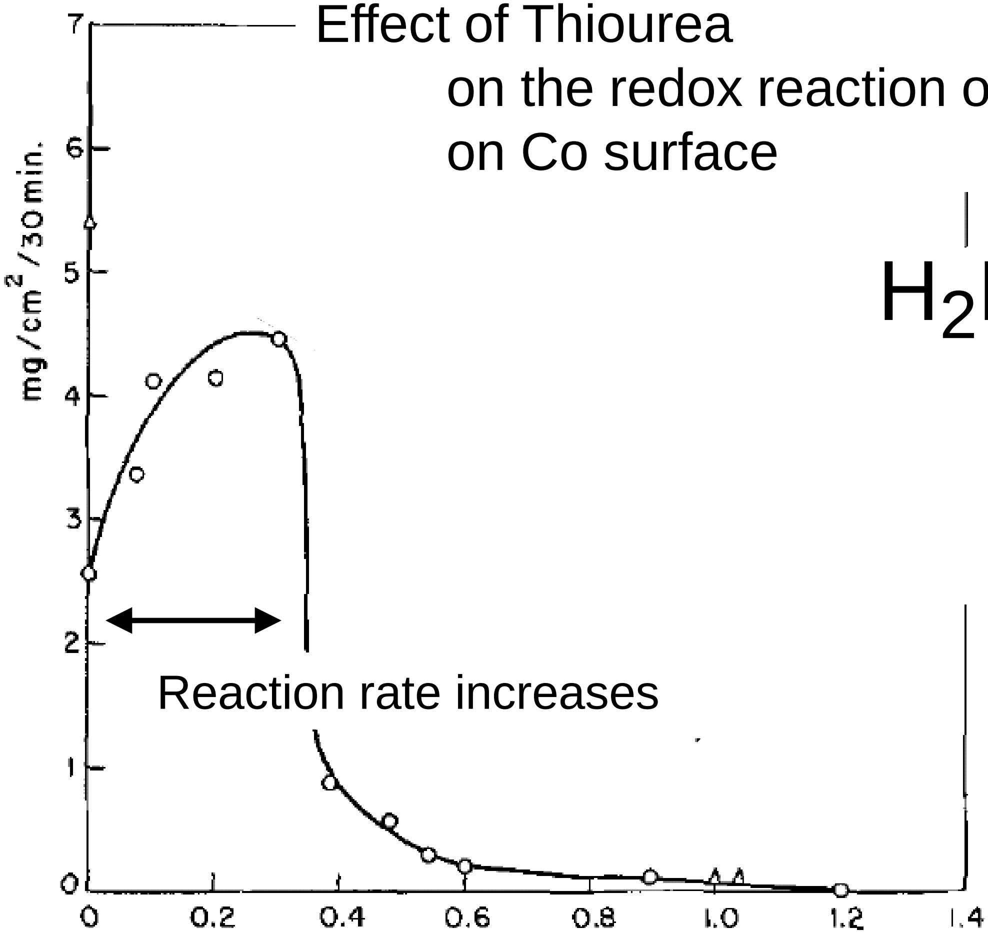
Adding "sulfuric additives", promoting surface reaction of reductant

Effect of sulfuric additive

Effect of Thiourea

on the redox reaction of $H_2PO_2^-$ and Co^{2+}

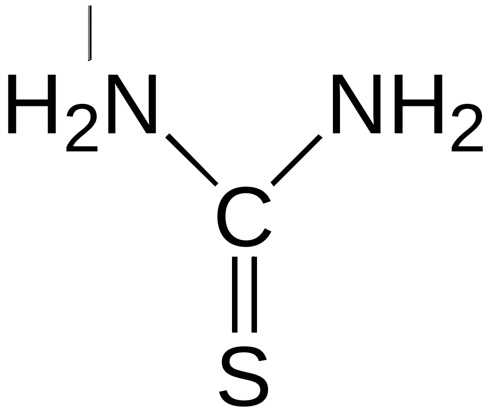
on Co surface



Redox reaction rate on the metal surface

Reaction rate increases

Added amount of additive (thiourea mg/L)

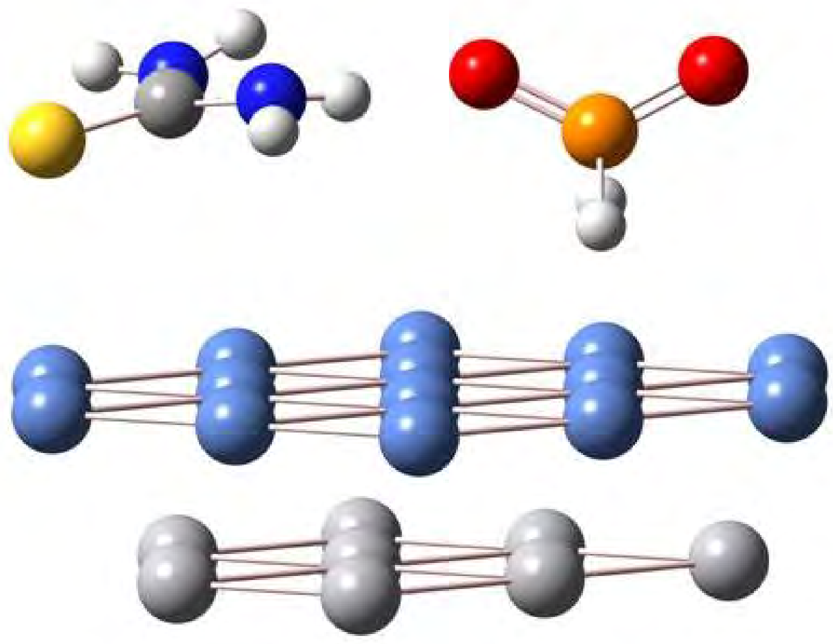


Thiourea

A little amount of Thiourea promote redox reaction on **metal surface**

J. Kivel et al., *J. Electrochem. Soc.*, **112**, 1201 (1965).,

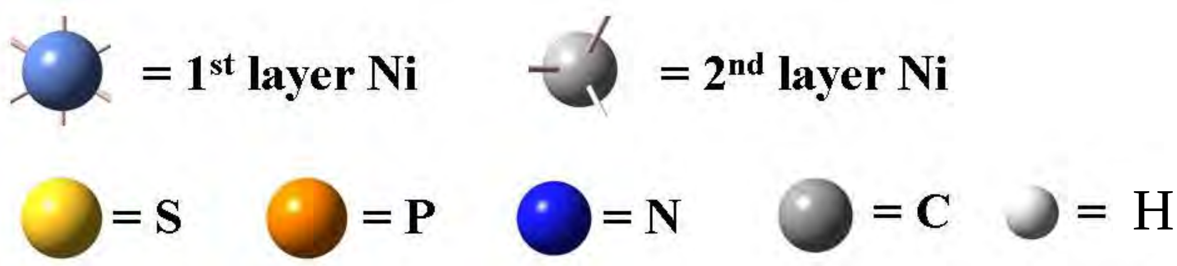
Theoretical understanding of additive effect



Analysis of the effect of additives on metal (Ni) surface, using Quantum Chemistry (QM) simulation technique

$$\hat{H}\Psi = E\Psi$$

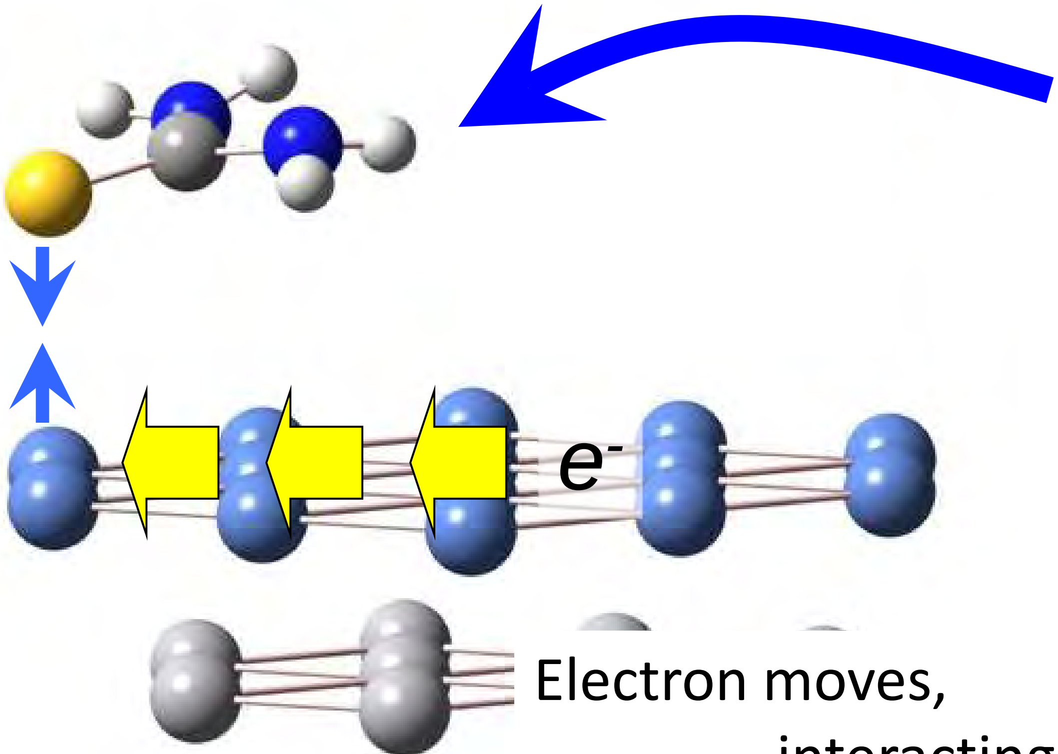
Solving Schrödinger eq. for electrons of the system

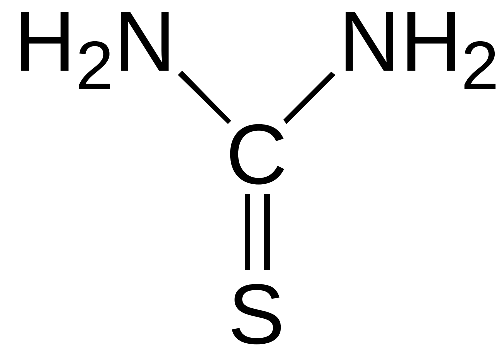


Theoretical understanding of additive effect

Accelerating mechanism of thiourea

Thiourea adsorbs on metal surface



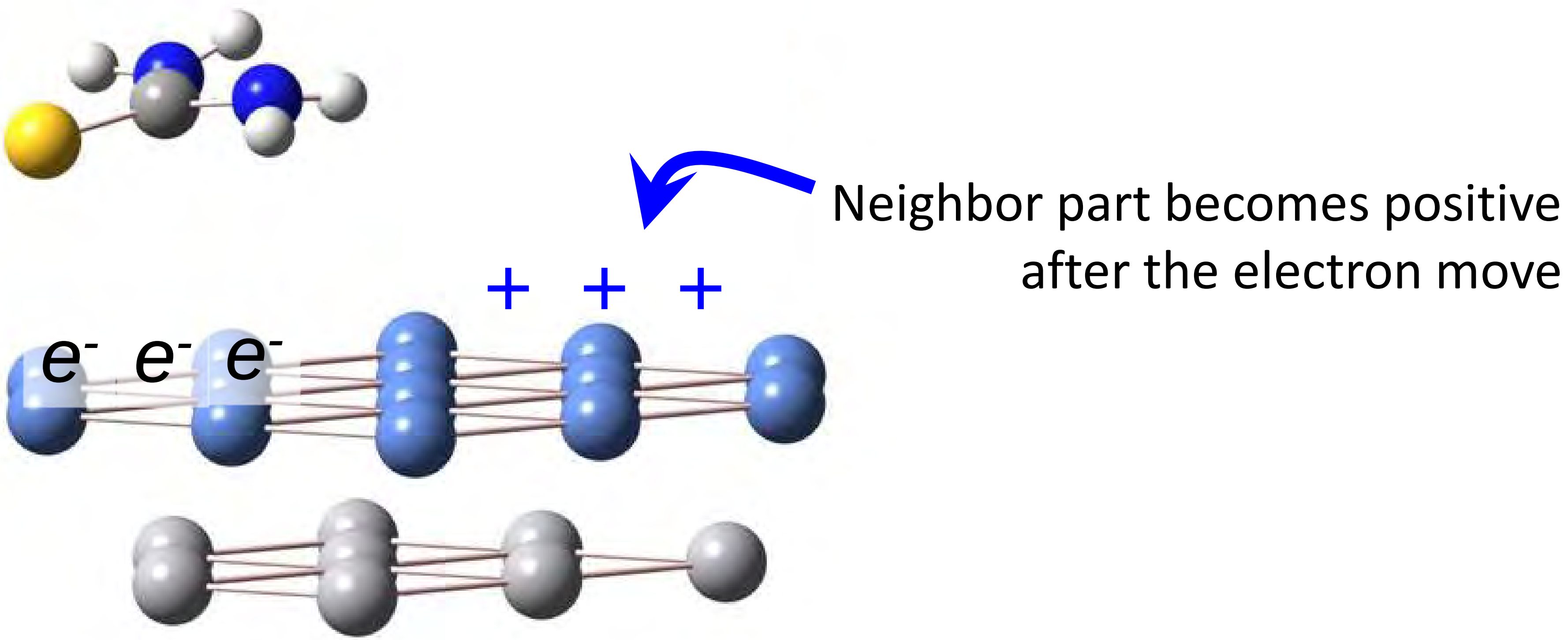


Thiourea
(sulfuric additive)

Electron moves,
interacting with S atom of thiourea

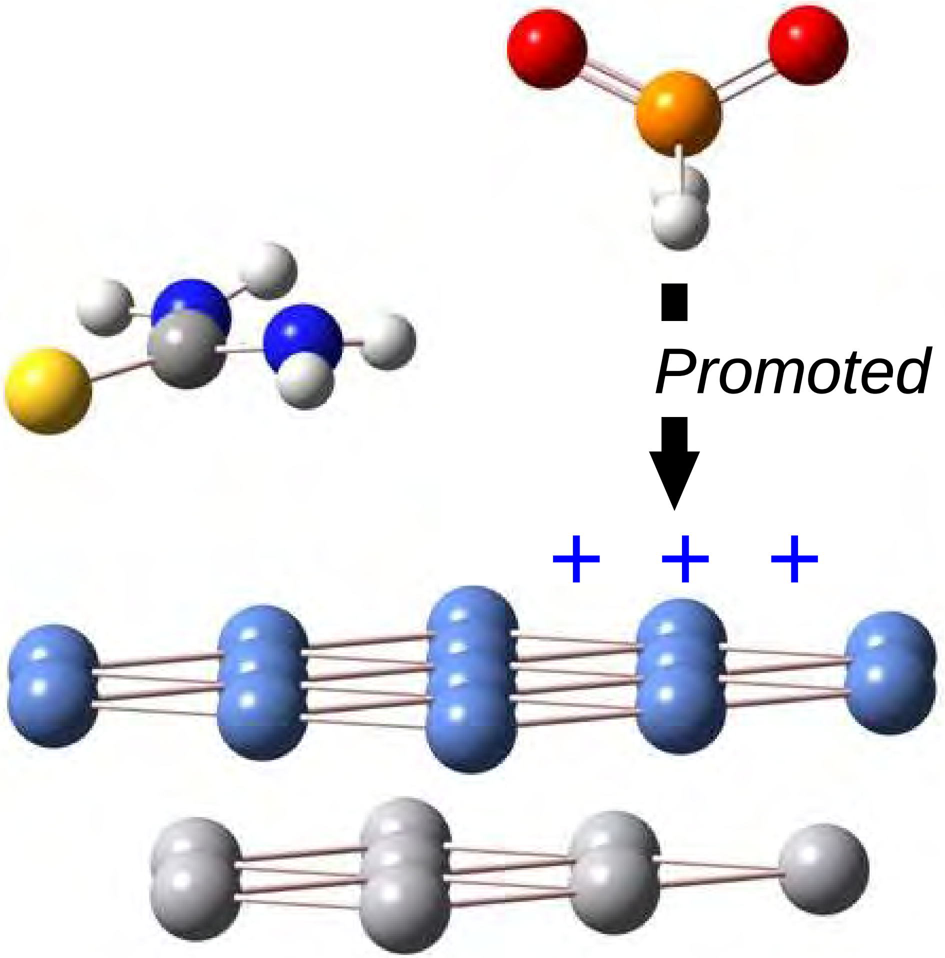
Theoretical understanding of additive effect

Accelerating mechanism of thiourea



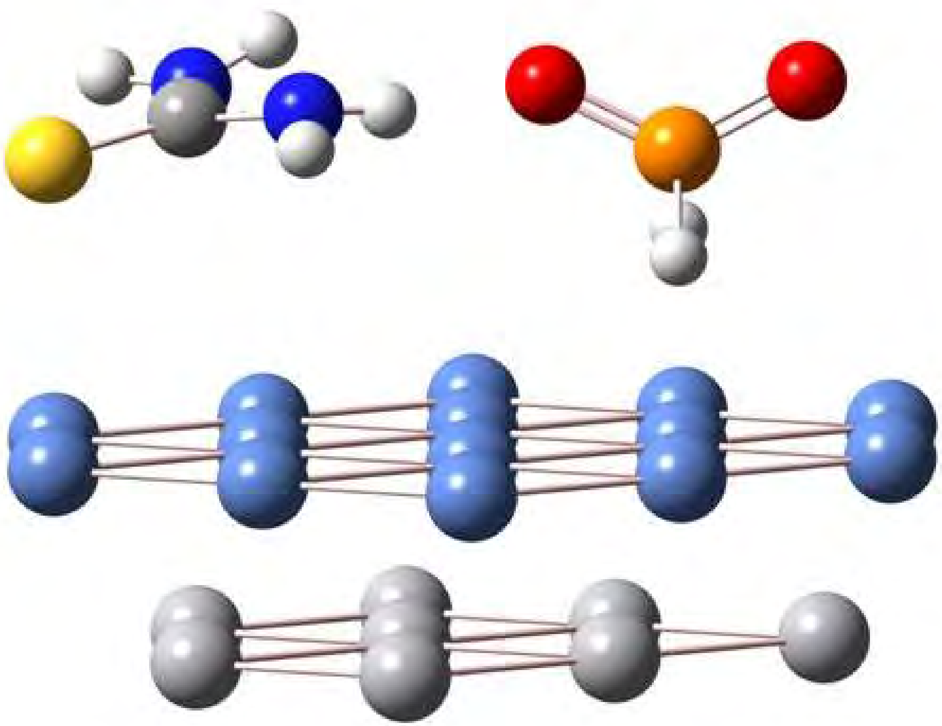
Theoretical understanding of additive effect

Accelerating mechanism of thiourea



Adsorption of anion reductant, $H_2PO_2^-$, is enhanced by additive

Theoretical understanding of additive effect



Reaction of $H_2PO_2^-$

$H_2PO_2^- + 2OH^- \rightarrow$

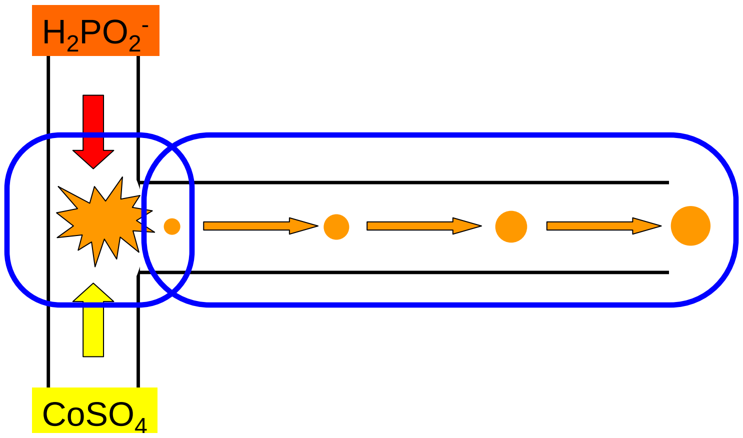
$H_3PO_4^- + H_2O + 2e^-$

is promoted by additive

On Metal >> In Solution

Suppress new nucleation
in the growth step part

Strategy No. 4



How to analyze
the flow state and
the reaction behavior ?

Using
"CFD simulation" and "QM simulation"

Quantum Mechanics (QM) simulation

Capability of QM simulation

QM

$$\hat{H}\Psi = E\Psi$$

Solving Schrödinger eq.

- **Potential energy**
- **Vibration behavior**
- **Polarization** **etc….**

of one chemical system

+ Statistic Thermodynamics

$$S = k \ln W$$

- **Entropy**
- **Enthalpy**
- **Gibbs' Free Energy**

+ Activated Complex Theory

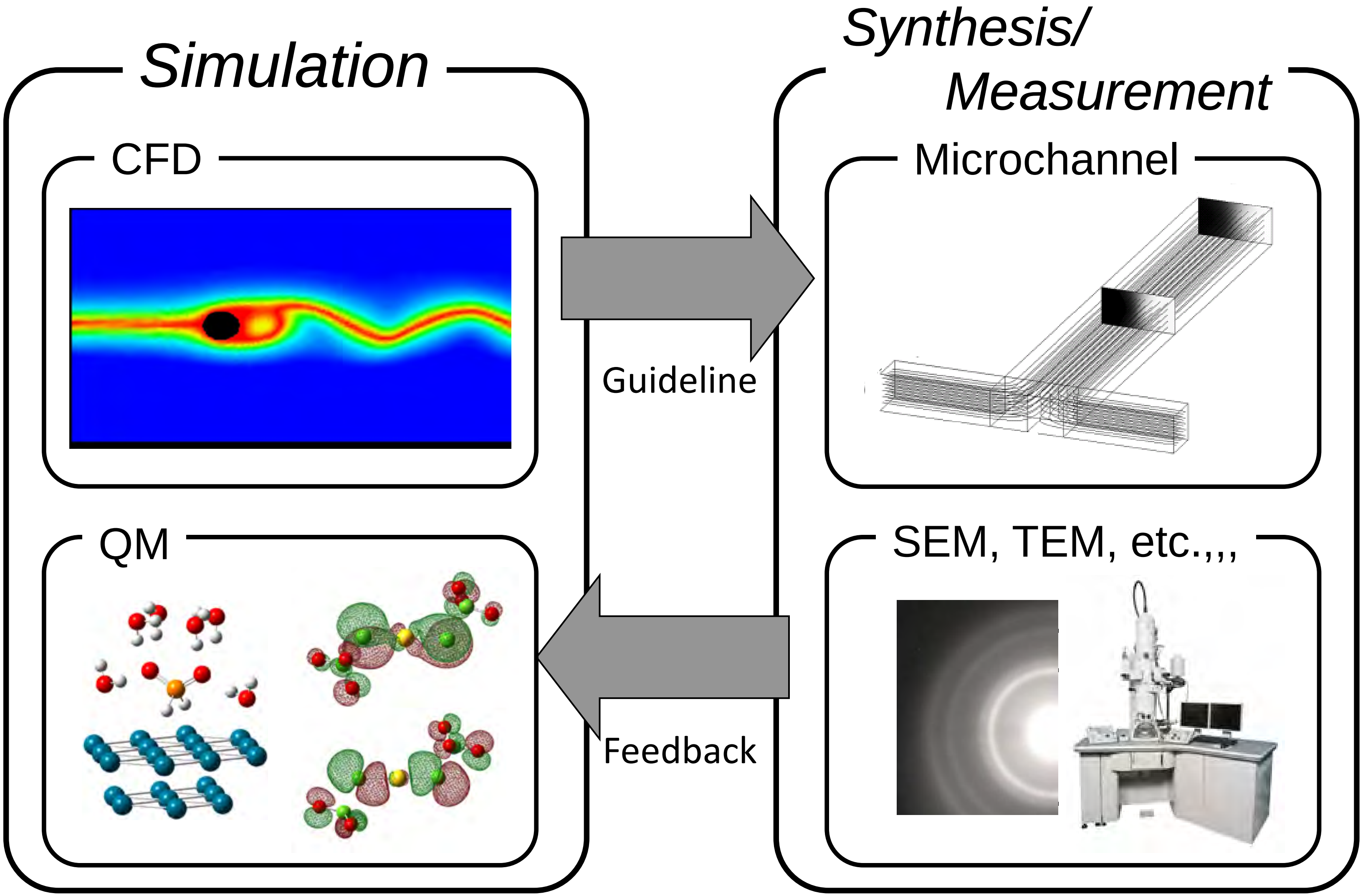
$$K = B \exp(-\Delta G_a / RT)$$

- **Rate constant of reaction**

Capable to evaluate reactivity, reaction rate, physical stability

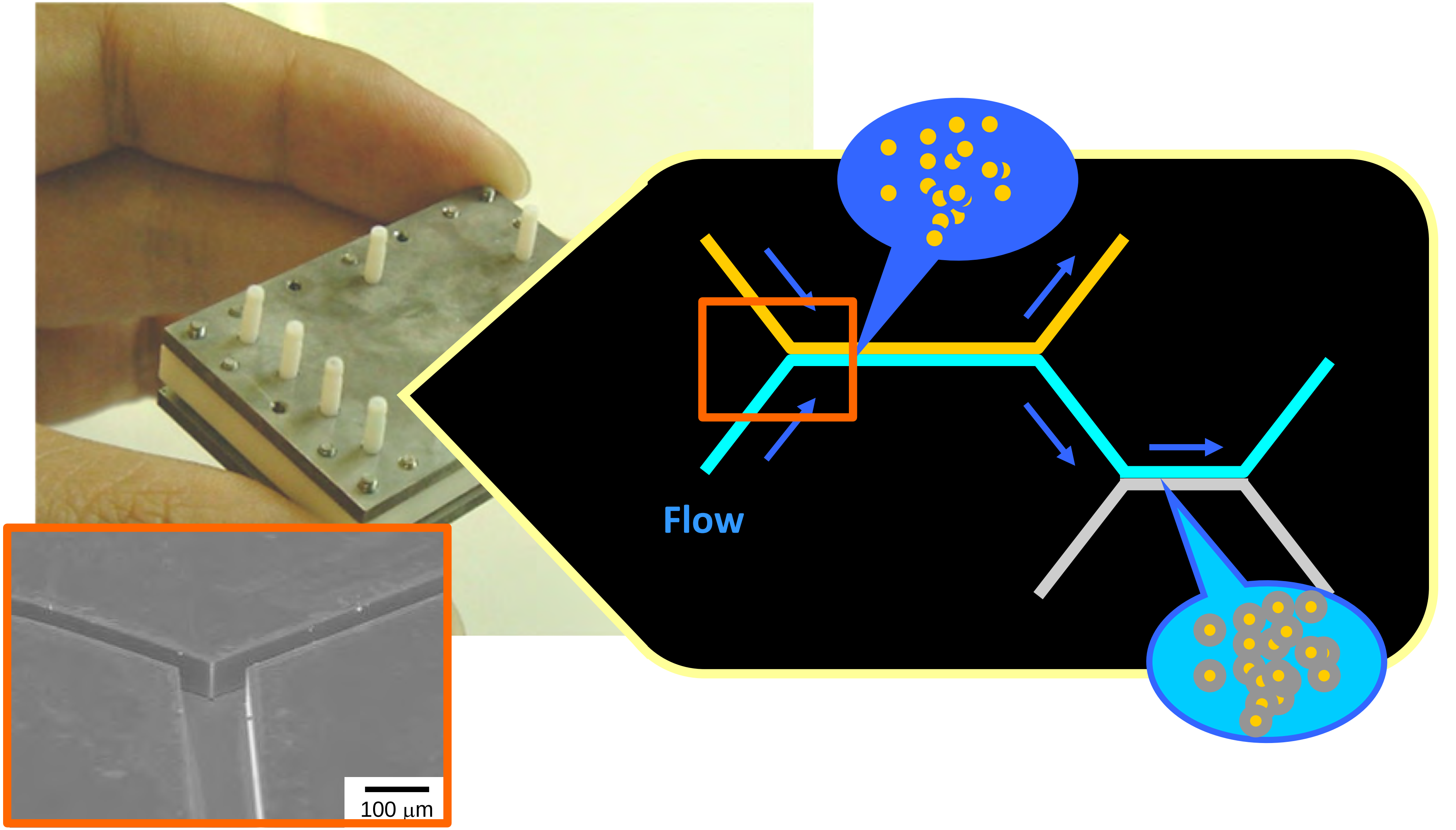
Concept of methodology

Analysis system of the research



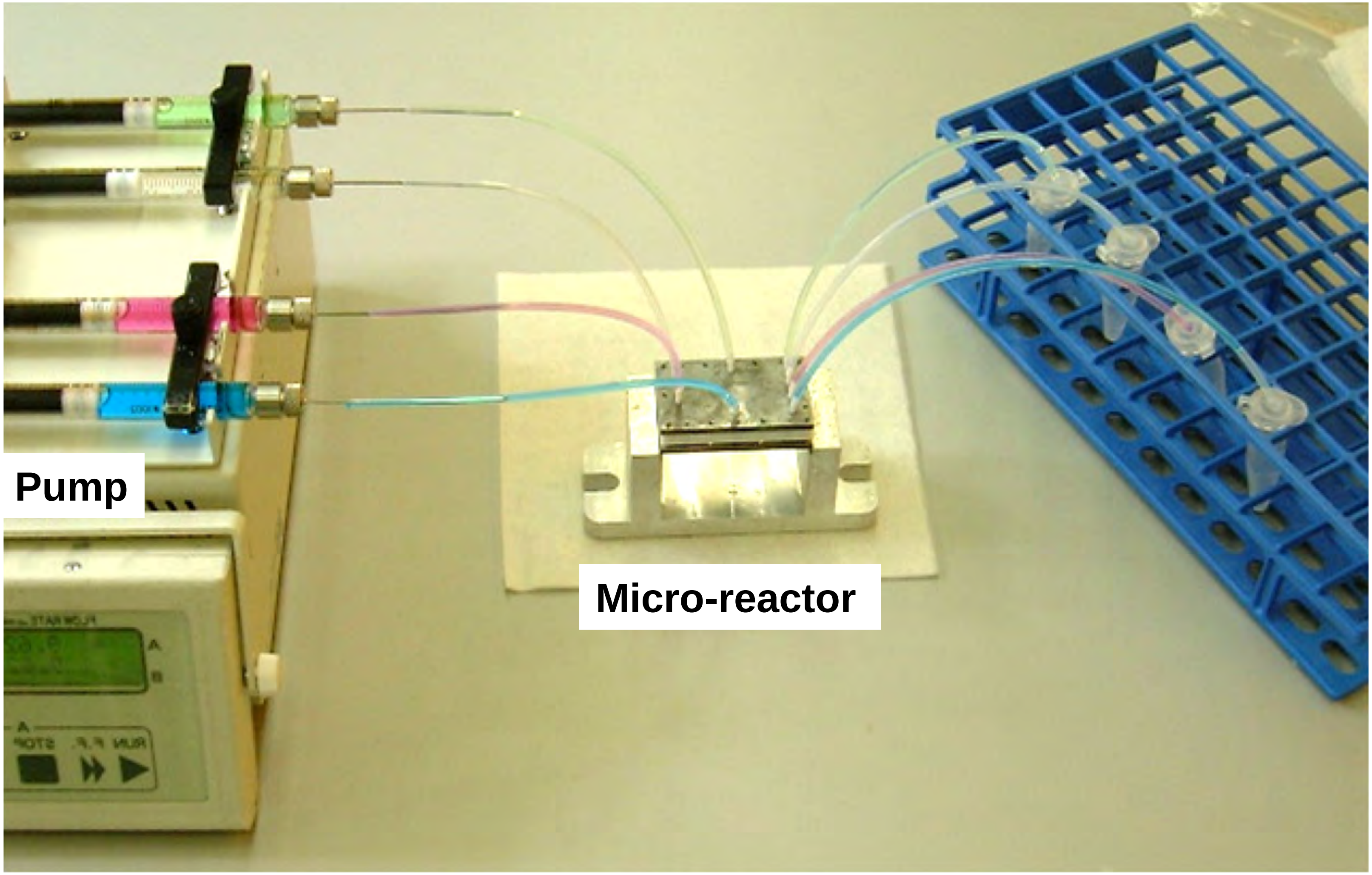
Actual process

Nanoparticle synthesis using Y-shaped reactor



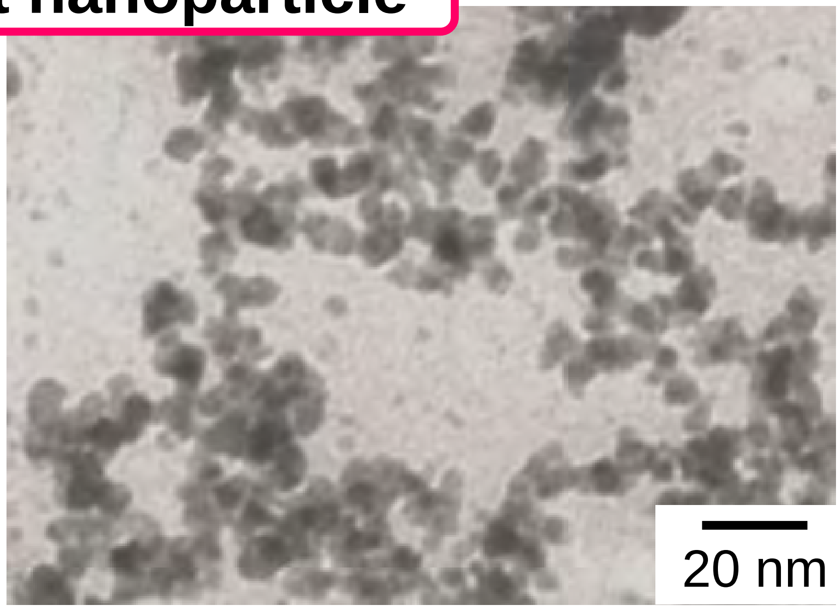
Nanoparticle synthesis using Y-shaped reactor

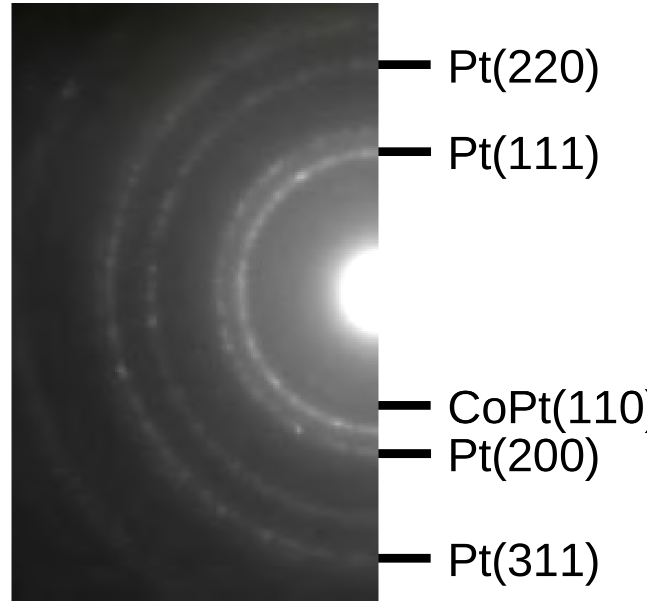
■ Description of micro-reactor system



Tentative results

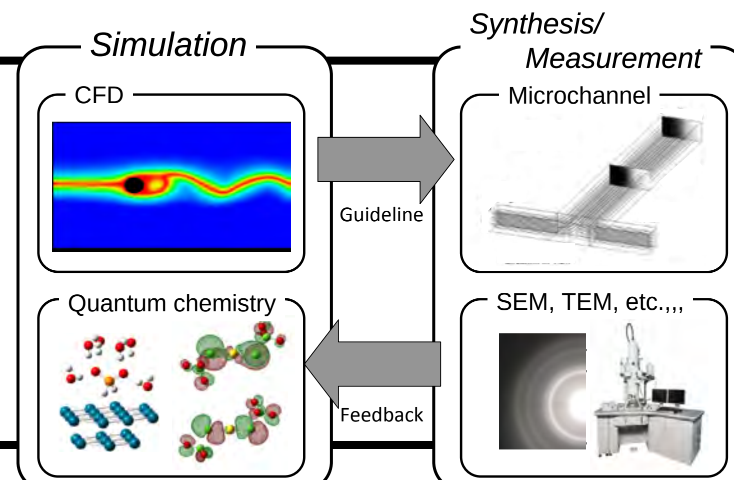
CoPt nanoparticle





Aggregation of particles and size distribution are observed

More precise control using strategies shown in this presentation is needed



Summary

Objective

Control of ⎧ Size and its distribution ⎫ of Nanoparticles
⎩ Crystallinity ⎭

Methodology

Redox reaction in T or Y-shaped micro-reactor

Strategies

Simulations $\rightleftarrows$ Synthesis/Measurement

↓

Moderate *Re*, Modified surface, Designed additive

↓

(i) Vortex flow (at junction part)
(ii) Symmetric Laminar flow (at channel part)
(iii) Promoted Redox reaction on the particle surface

Acknowledgement

This presentation is composed, based on the discussion with Prof. Dr. Dieter Bothe (TU Darmstadt)

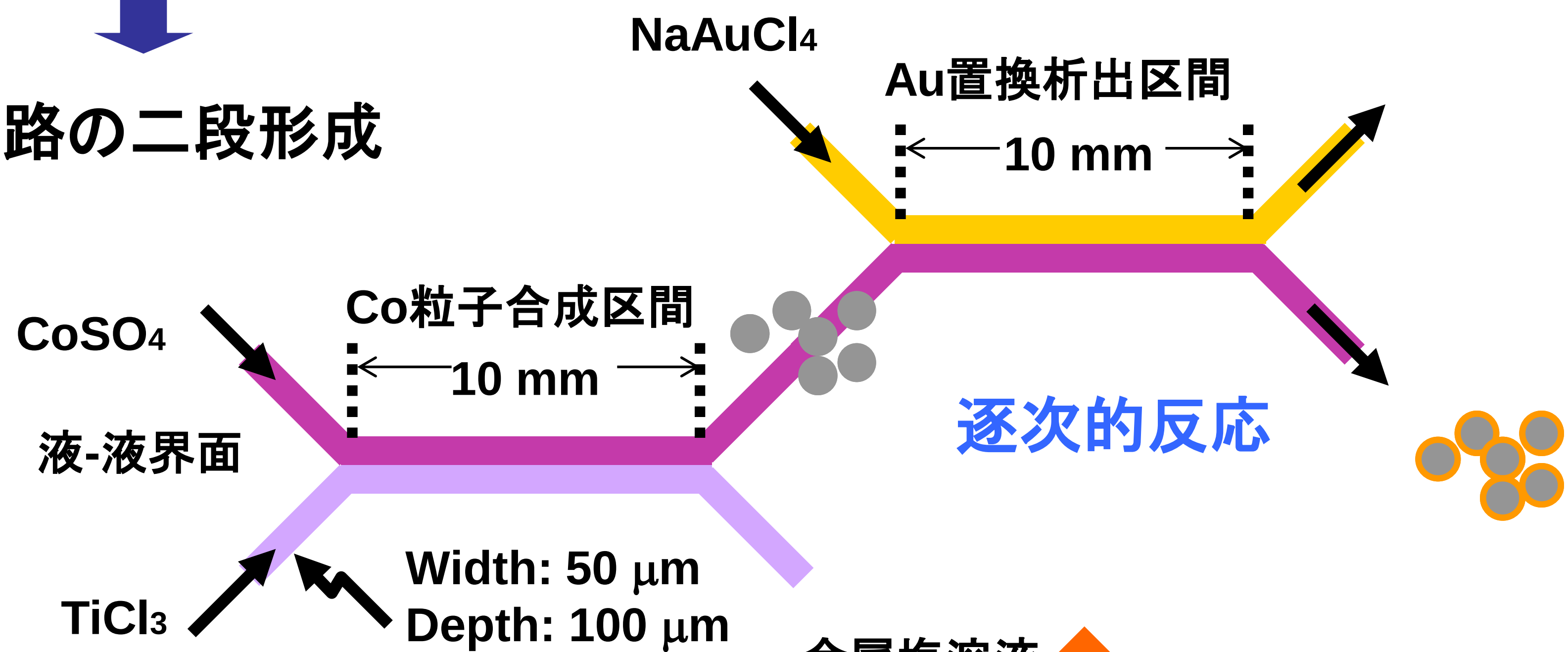
The presenter appreciate the enormous contribution by Prof. Dr. Shibata, Prof. Dr. Bothe and IRTG program

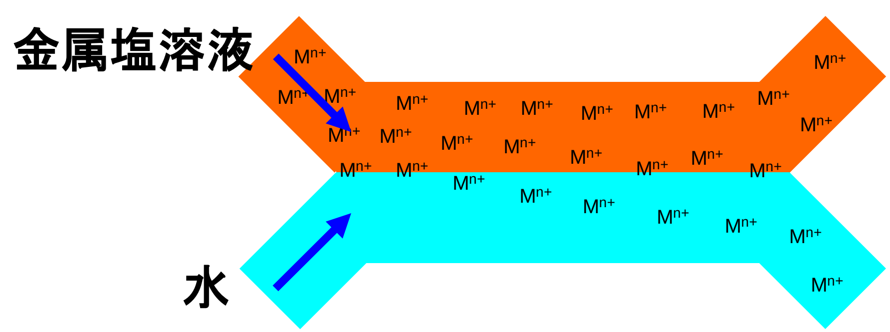
マイクロ流路を用いたナノ粒子合成ー実験方法

コアシェル構造金属ナノ粒子の合成

微小流路内へ二液を同時に導入した際に形成される液-液界面を用いて反応を試みた.

流路の二段形成





マイクロ流路系のモデル化ー基礎式

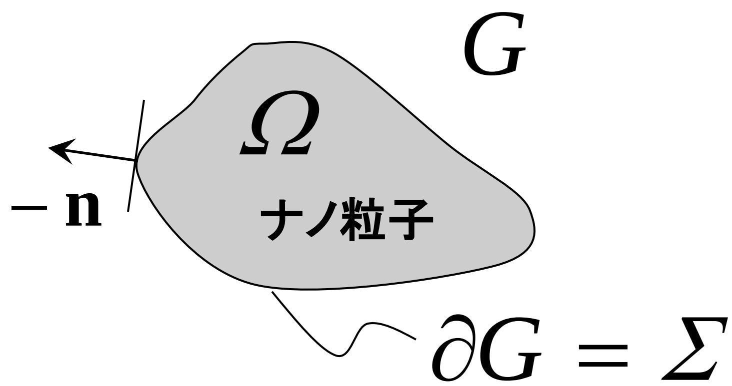
$$\partial_t \theta_i - \nabla \cdot (D_i^{surf} \nabla_\Sigma \theta_i^{mol,\Sigma}) = \mathbf{j}_i^{mol} \cdot \mathbf{n} + R_i^\Sigma$$

$$\mathbf{j}_i^{mol} \cdot \mathbf{n} = r_i^{ad,\Sigma} - r_i^{de,\Sigma}$$

$$\mathbf{j}_i^{mol} = \mathbf{u} \cdot c_i - D_i \nabla c_i$$

$$R_i^\Sigma = r_i^{gen,\Sigma} - r_i^{count,\Sigma}$$

$$r^\Sigma = k \prod_k \theta_k^{n_k}$$



$\mathbf{j}^{mol}$：モル流速　R：正味の反応速度　r^{gen}：生成反応速度　r^{count}：逆反応速度

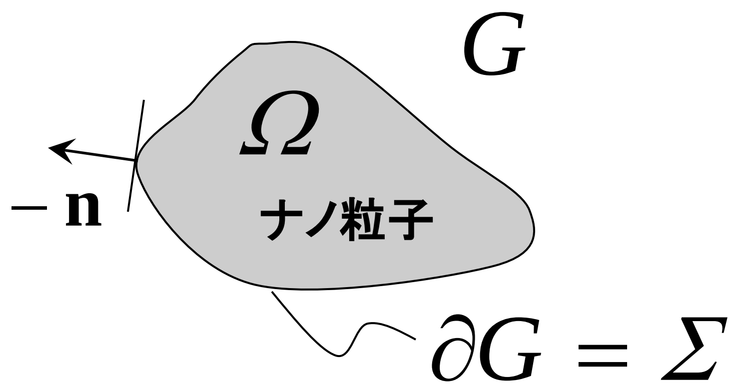
r^{ad}：吸着速度　r^{de}：脱離速度　θ：表面被覆率（面濃度）　D_i^{surf}：表面拡散係数

マイクロ流路系のモデル化ー基礎式

$$\partial_t \theta_i - \nabla \cdot (D_i^{surf} \nabla_\Sigma \theta_i^{mol,\Sigma}) = \mathbf{j}_i^{mol} \cdot \mathbf{n} + R_i^\Sigma$$

$\partial_t \theta_i \rightarrow 0$

$$\mathbf{j}_i^{mol} \cdot \mathbf{n} = r_i^{ad,\Sigma} - r_i^{de,\Sigma}$$



$$\mathbf{j}_i^{mol} = \mathbf{u} \cdot c_i - D_i \nabla c_i$$

$$R_i^\Sigma = r_i^{gen,\Sigma} - r_i^{count,\Sigma}$$

$$r^\Sigma = k \prod_k \theta_k^{n_k}$$

仮定 その3）

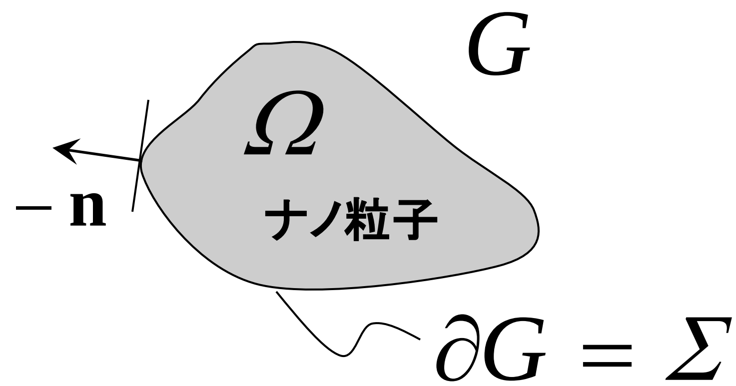
<u>ナノ粒子上の吸着子の被覆率は</u>

<u>定常状態にあると近似することができる</u>

マイクロ流路系のモデル化ー基礎式

$$\underbrace{\partial_t \theta_i}_{0} - \underbrace{\nabla \cdot (D_i^{surf} \nabla_{\Sigma} \theta_i^{mol,\Sigma})}_{0} = \dot{\mathbf{j}}_i^{mol} \cdot \mathbf{n} + R_i^{\Sigma}$$

$$\dot{\mathbf{j}}_i^{mol} \cdot \mathbf{n} = r_i^{ad,\Sigma} - r_i^{de,\Sigma}$$



$$\dot{\mathbf{j}}_i^{mol} = \mathbf{u} \cdot c_i - D_i \nabla c_i$$

$$R_i^{\Sigma} = r_i^{gen,\Sigma} - r_i^{count,\Sigma}$$

$$r^{\Sigma} = k \prod_k \theta_k^{n_k}$$

仮定 その4）

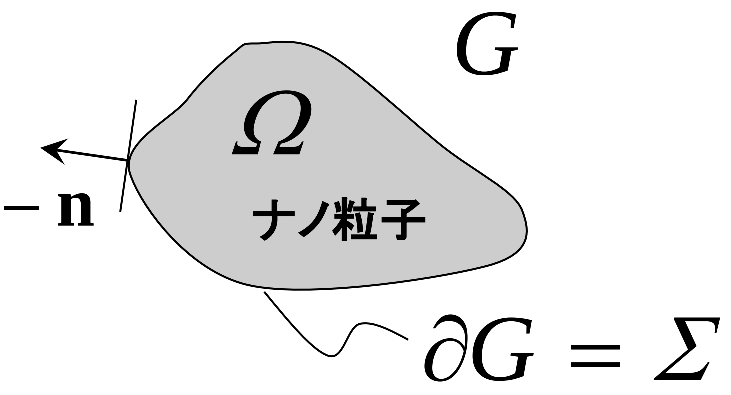
ナノ粒子上の吸着子の表面拡散は
他の事象と比較して遅く無視してよい

マイクロ流路系のモデル化ー基礎式

$$\partial_t \theta_i - \nabla \cdot (D_i^{surf} \nabla_\Sigma \theta_i^{mol,\Sigma}) = \mathbf{j}_i^{mol} \cdot \mathbf{n} + R_i^\Sigma$$

$\partial_t \theta_i \to 0$, $\nabla \cdot (D_i^{surf} \nabla_\Sigma \theta_i^{mol,\Sigma}) \to 0$

$$\mathbf{j}_i^{mol} \cdot \mathbf{n} = r_i^{ad,\Sigma} - r_i^{de,\Sigma}$$



$$\mathbf{j}_i^{mol} = \mathbf{u} \cdot c_i - D_i \nabla c_i$$

$$R_i^\Sigma = r_i^{gen,\Sigma} - r_i^{count,\Sigma}$$

$$r^\Sigma = k \prod_k \theta_k^{n_k}$$

⬇

$$\mathbf{j}_i^{mol} \cdot \mathbf{n} = -R_i^\Sigma$$

暫定的な基礎式の導出

ディスカッション内容-②核発生段階の考え方

＜これまでの大まかな考え方 [一段階式] ＞

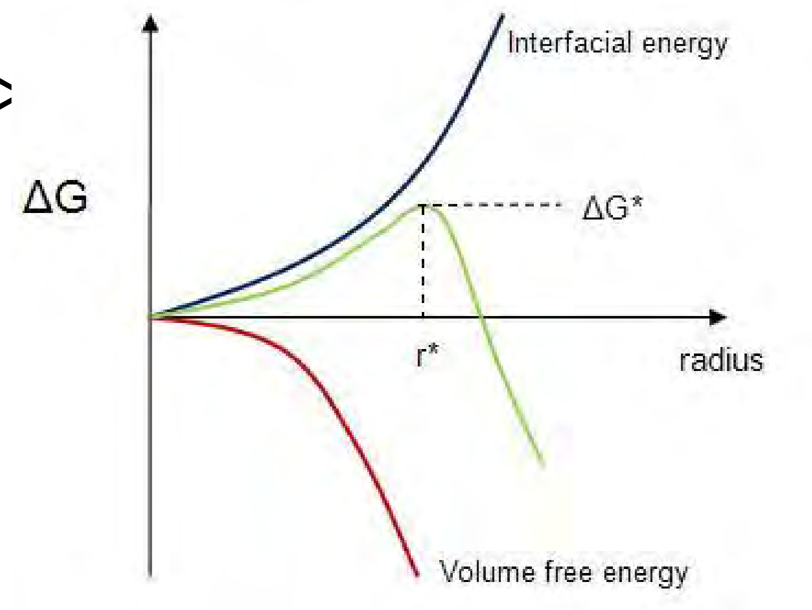
還元剤と金属イオンが反応して粒子核が発生

＜より正確な考え方 [二段階式] ＞

①還元剤と金属イオンが
反応して金属原子が生成

↓

②金属原子が局所的に
飽和して粒子核が発生



（核発生には 金属原子の
局所的発生と凝集が必要）

<u>金属原子が生成する反応が局所的に</u>

<u>同時的に起こるような反応場の設計が第一</u>

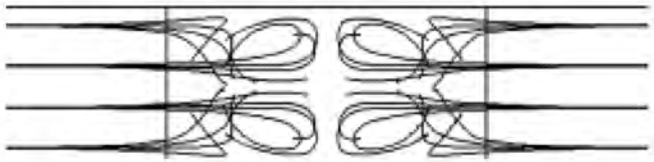
ディスカッション内容-③新しい方針

前方針の欠点：発生した核がおかれる速度場が乱雑

→ 核成長の度合いに差

→ 粒径制御への寄与 小

議論を通しての改善策：vortex flow の適用



vortex flow の利用

→ ① 反応物の接触場をchannel中心に集中

② 層流による安定した一様な核成長場の実現

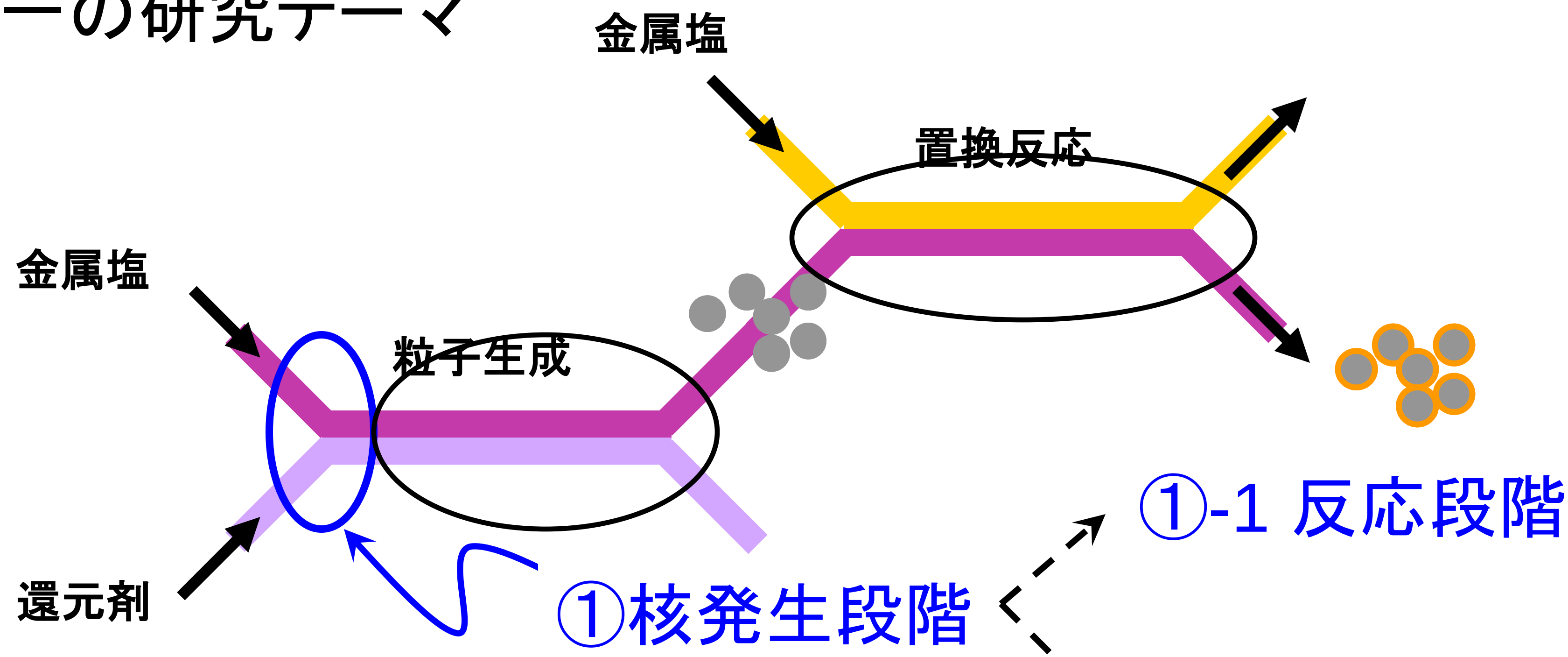
→ ① 同時的で一様な反応場の実現

② 一様な核成長場の実現

} **同時に実現**

研究の展開

第一の研究テーマ



反応段階における場の制御

→ ・vortex flow をつくるための条件の最適化

・simulation software – OpenFOAM の利用

・実験による粒径分布の計測

量子化学計算の応用

物質収支式（移流，拡散，反応）

$$\partial_t c_i + \mathbf{u} \cdot \nabla c_i = \nabla \cdot (D_i \nabla c_i) + r_i$$

i ：反応種　c ：濃度　$\mathbf{u}$ ：速度ベクトル　D ：拡散係数

r ：反応による濃度変化速度 (反応速度)

r → **量子化学計算による算出**

↓

反応流体の挙動のメカニズム解明へ

量子化学計算の他の側面

量子化学計算で他に何ができるのか？

☆ 量子化学計算で算出可能な種々のパラメータ

(1) 平衡状態における分子のエネルギー

(2) 基準振動の波数

(3) 分子の電荷分布，双極子モーメント

(4) 分子のエントロピー，エンタルピー，ギブズ自由エネルギー （(1)，(2)から）

(5) 反応の遷移状態における(1)～(4)パラメータ （(2)から）　etc.

活性錯合体理論に基づく反応速度定数　k

$$k = B \exp\left(-\frac{\Delta^{TS} G^{\circ}}{RT} \right)$$

B :（分子の運動速度，トンネル効果を考慮した補正因子等を全て含んだ因子）

$\Delta^{TS} G^{\circ}$: 始状態に対する遷移状態のギブズエネルギー　R :気体定数　T :温度

量子化学計算の他の側面

対流・拡散・反応方程式

$$\partial_t c_i + \mathbf{u} \cdot \nabla c_i = \nabla \cdot (D_i \nabla c_i) + r_i$$

i ：反応種　c ：濃度　$\mathbf{u}$ ：速度ベクトル　D_i ：拡散係数

$$r_i = k_a \prod_k c_k^{n_k} - k_b \prod_l c_l^{n_l}$$

k_a ：i 種生成反応速度定数（次数は $\sum_k n_k$ ）　k_b ：i 種生成反応速度定数（次数は $\sum_l n_l$ ）

量子化学計算によって反応項の計算に寄与

析出段階の解析

（Ⅰ） $$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C - D\Delta C$$

$$= -B^{nucl}(C/C^{sat}, t) f(t, x, r) + \int_{r_{crit}}^{\infty} B^{diss}(C, t) n(t, x, r) dr$$

（金属原子に関する species equation）

（Ⅱ） $$\frac{\partial n(t, x, r)}{\partial t} + \mathbf{v} \cdot \nabla_x n(t, x, r) + \frac{\partial}{\partial r}(n(t, x, r)\dot{R}) = b(t, x, r)$$

（粒子に関する population balance equation）

C： 金属原子濃度　B^{nucl} ： 核発生速度　B^{diss} ： 核溶解速度

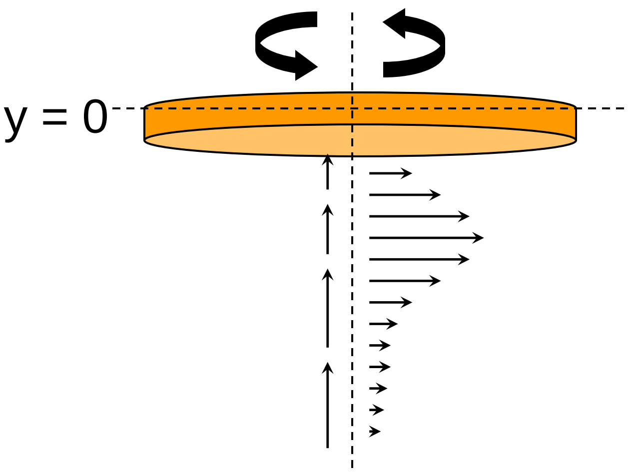
n： 粒子の密度分布関数　f ： 発生した核の密度分布関数　$\dot{R}$： 成長速度

現在のところ完全なモデル化には至っておらず

▼

今後も議論を継続

拡散層の制御例-回転電極(RDE)



ω： 電極の回転速度

ν： 動粘度

γ：$\gamma = \left(\dfrac{\omega}{\nu}\right)^{1/2} y$

$\gamma << 1$

$$v_r = r\omega \left(a\gamma - \frac{\gamma^2}{2} - \frac{1}{3} b\gamma^3 + \cdots \right)$$

$$v_y = (\omega\nu)^{1/2} \left(-a\gamma^2 + \frac{\gamma^3}{3} + \frac{1}{6} b\gamma^4 + \cdots \right)$$

$a = 0.51023 \quad b = -0.6159$

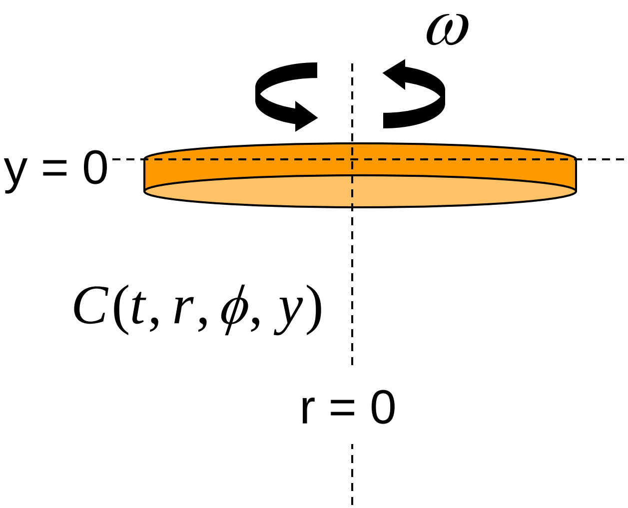
$\gamma \to 0 \quad (y \to 0)$

$$v_r = 0.51\ \omega^{3/2} \nu^{-1/2} r\ y$$

$$v_y = -0.51\ \omega^{3/2} \nu^{-1/2} y^2$$

拡散層の制御例-回転電極（RDE）

拡散層（濃度プロファイル）の計算



定常状態仮定： $\dfrac{\partial C}{\partial t} = 0$

高さ/角度方向に一様： $\dfrac{\partial C}{\partial r} = 0$ ， $\dfrac{\partial C}{\partial \phi} = 0$

$$\therefore \underbrace{\frac{\partial C}{\partial t}}_{0} = -v_r \underbrace{\left(\frac{\partial C}{\partial r}\right)}_{0} - \frac{v_\phi}{r} \underbrace{\left(\frac{\partial C}{\partial \phi}\right)}_{0} - v_y \left(\frac{\partial C}{\partial y}\right)$$

$$+ D \left[\left(\frac{\partial^2 C}{\partial y^2}\right) + \underbrace{\frac{\partial^2 C}{\partial r^2}}_{0} + \underbrace{\frac{1}{r}\frac{\partial C}{\partial r}}_{0} + \underbrace{\frac{1}{r^2}\left(\frac{\partial^2 C}{\partial \phi^2}\right)}_{0} \right]$$

$$v_r = 0.51 \ \omega^{3/2} \nu^{-1/2} r \ y$$

$$v_y = -0.51 \ \omega^{3/2} \nu^{-1/2} y^2$$

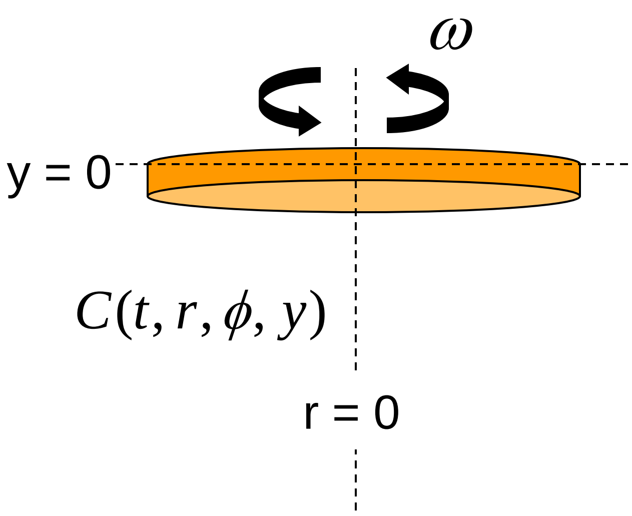
$$\therefore v_y \left(\frac{\partial C}{\partial y}\right) = D \left(\frac{\partial^2 C}{\partial y^2}\right)$$

$$\therefore \frac{\partial^2 C}{\partial y^2} = -\frac{y^2}{B} \frac{\partial C}{\partial y}$$

$$B = D \omega^{-3/2} \nu^{1/2} / 0.51$$

拡散層の制御例-回転電極（RDE）

拡散層（濃度プロファイル）の計算



$$v_r = 0.51\ \omega^{3/2} \nu^{-1/2} r\ y$$

$$v_y = -0.51\ \omega^{3/2} \nu^{-1/2} y^2$$

$$\frac{\partial^2 C}{\partial y^2} = -\frac{y^2}{B}\frac{\partial C}{\partial y}$$

↓

$$C(y) = \left(\frac{\partial C}{\partial y}\right)_{y=0} \int_0^y \exp\left(-\frac{y^3}{3B}\right) dy$$

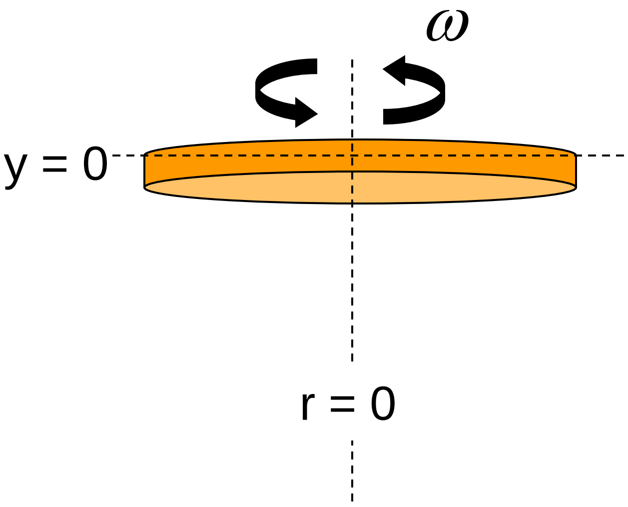
$$\lim_{y\to\infty} C(y) = C^* = \left(\frac{\partial C}{\partial y}\right)_{y=0} \int_0^\infty \exp\left(-\frac{y^3}{3B}\right) dy$$

$$= \left(\frac{\partial C}{\partial y}\right)_{y=0} 0.8934\ (3B)^{1/3}$$

$$\therefore\quad C(y) = \frac{C^*}{0.8934\ (3B)^{1/3}} \int_0^y \exp\left(-\frac{y^3}{3B}\right) dy$$

拡散層の制御例-回転電極（RDE）

拡散層（濃度プロファイル）の計算



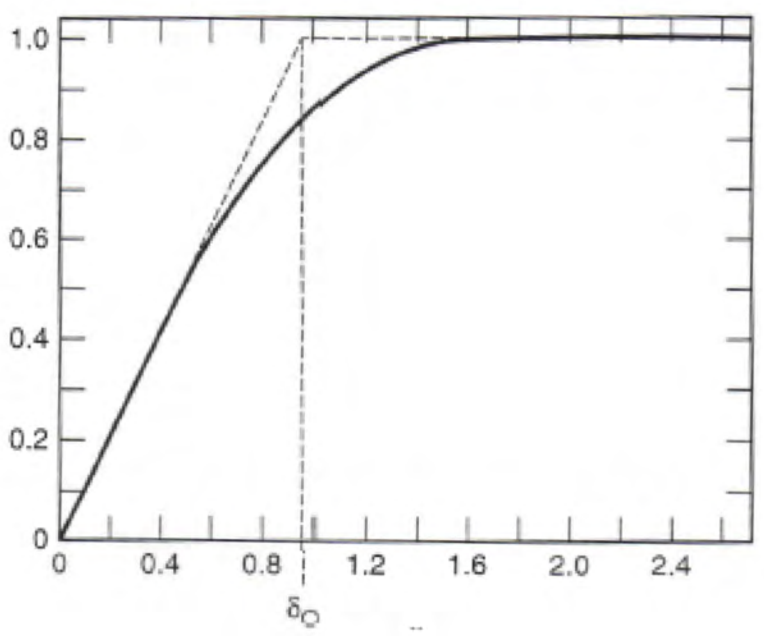
$$C(y) = \frac{C^*}{0.8934\ (3B)^{1/3}} \int_0^y \exp\left(-\frac{y^3}{3B}\right) dy$$

$$B = D\omega^{-3/2}\nu^{1/2} / 0.51$$

$$v_r = 0.51\ \omega^{3/2}\nu^{-1/2} r\ \ y$$

$$v_y = -0.51\ \omega^{3/2}\nu^{-1/2} y^2$$

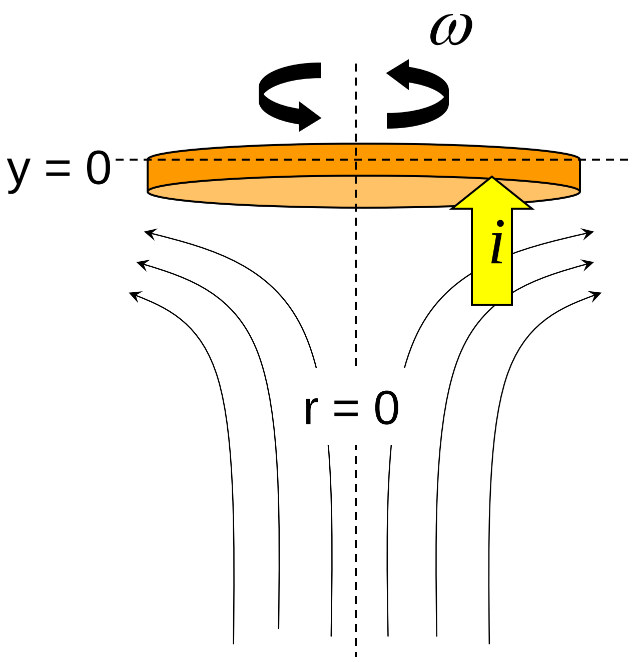
$C(y)/C^*$



拡散層/濃度プロファイルがωによって生じる流れによって制御

拡散層の制御例-回転電極(RDE)

拡散層(濃度プロファイル)の計算



$$\left(\frac{\partial C}{\partial y}\right)_{y=0} = \frac{C^*}{0.8934\ (3B)^{1/3}}$$

$$i = nFAD\left(\frac{\partial C}{\partial y}\right)_{y=0}$$

$$= \underline{0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C^*}$$

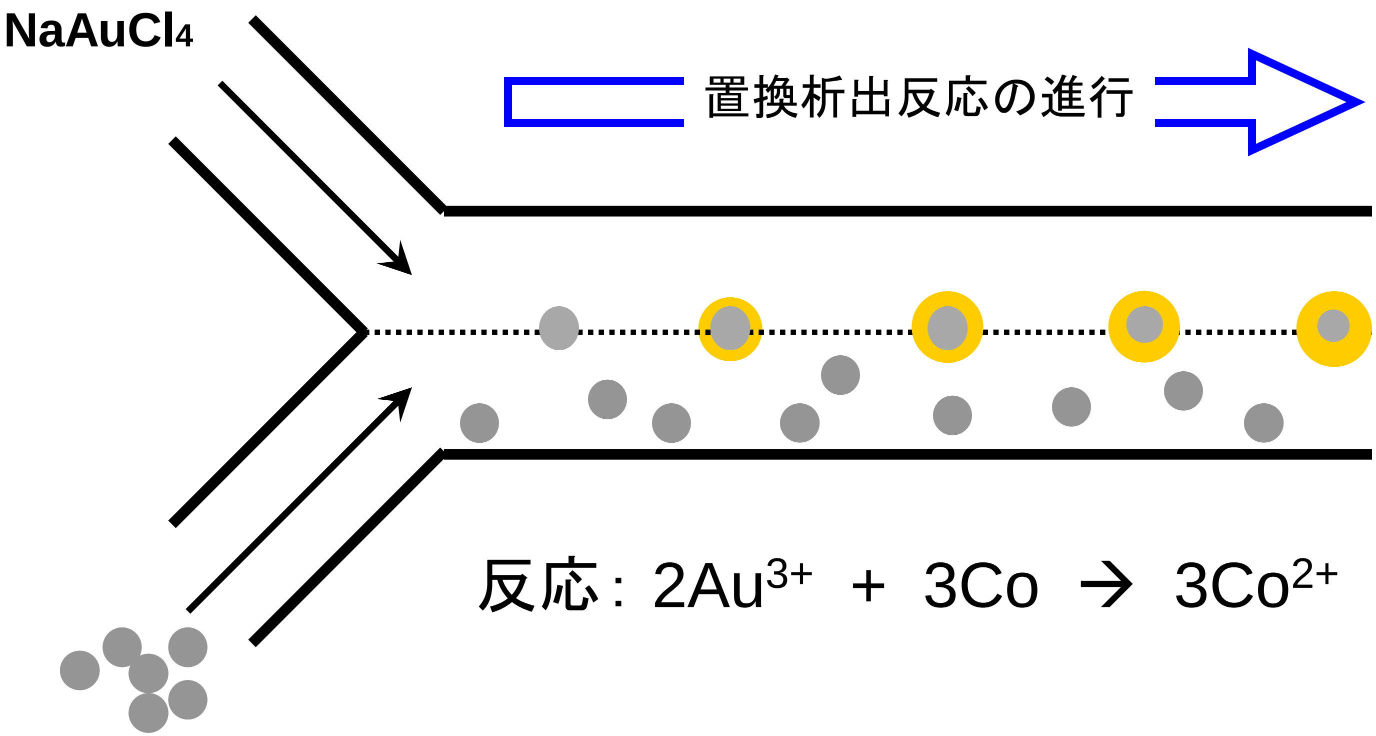
$$v_r = 0.51\ \omega^{3/2}\nu^{-1/2} r\ \ y$$

$$v_y = -0.51\ \omega^{3/2}\nu^{-1/2} y^2$$

電流値がωによって生じる流れによって制御

マイクロ流路系のモデル化ー仮定をいくつか

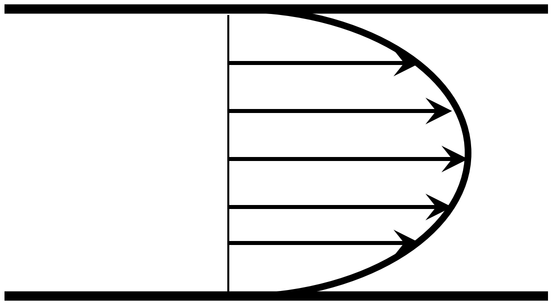
Discussion with Prof. Dr. Dieter Bothe



反応 : $2Au^{3+} + 3Co \rightarrow 3Co^{2+} + 2Au$

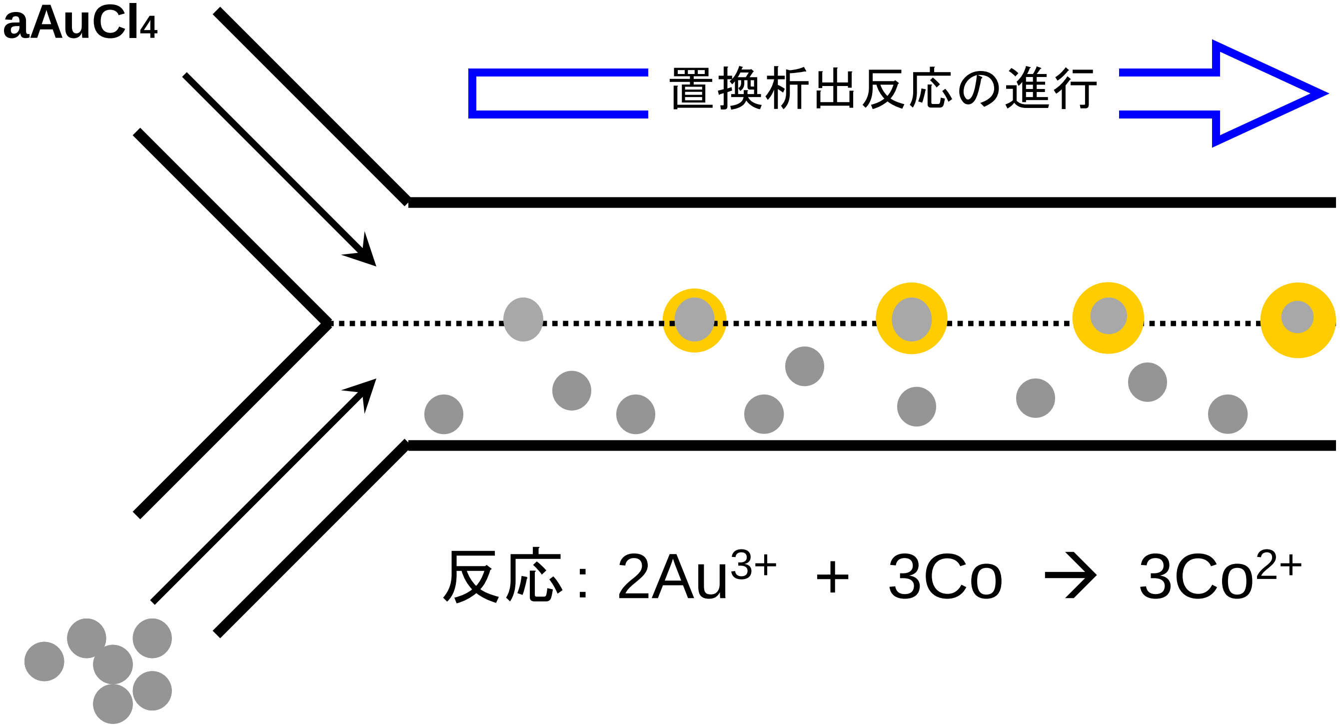
仮定 その1）

<u>流路内における</u>
<u>速度分布は放物線状である</u>



マイクロ流路系のモデル化ー仮定をいくつか

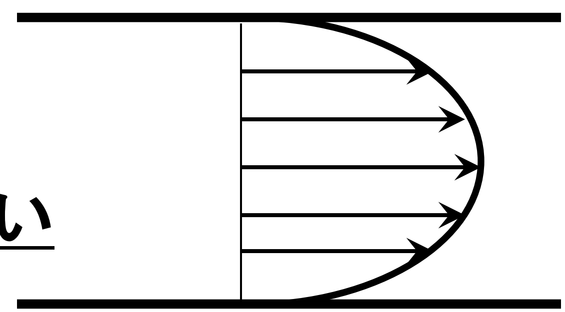
Discussion with Prof. Dr. Dieter Bothe



反応： $2Au^{3+} + 3Co \rightarrow 3Co^{2+} + 2Au$

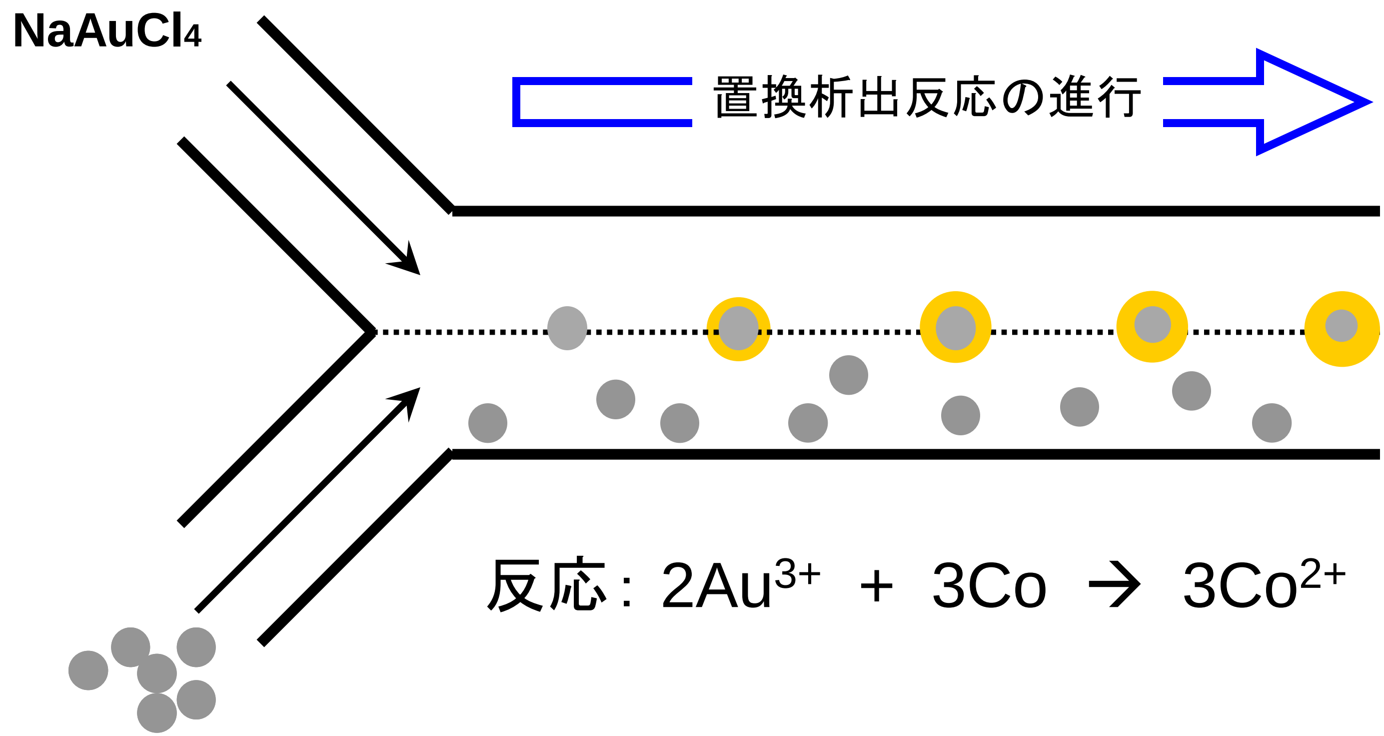
仮定 その2）

<u>流路内における</u>
<u>速度分布は粒子によって影響を受けない</u>



マイクロ流路系のモデル化ー仮定をいくつか

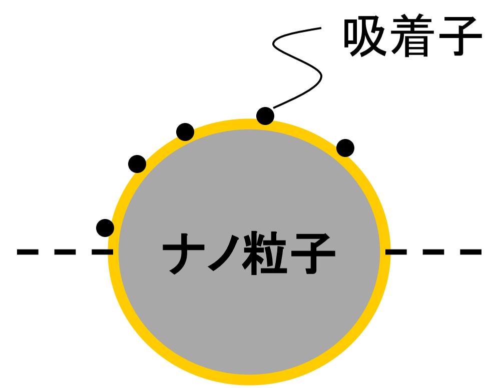
Discussion with Prof. Dr. Dieter Bothe



反応 : $2Au^{3+} + 3Co \rightarrow 3Co^{2+} + 2Au$

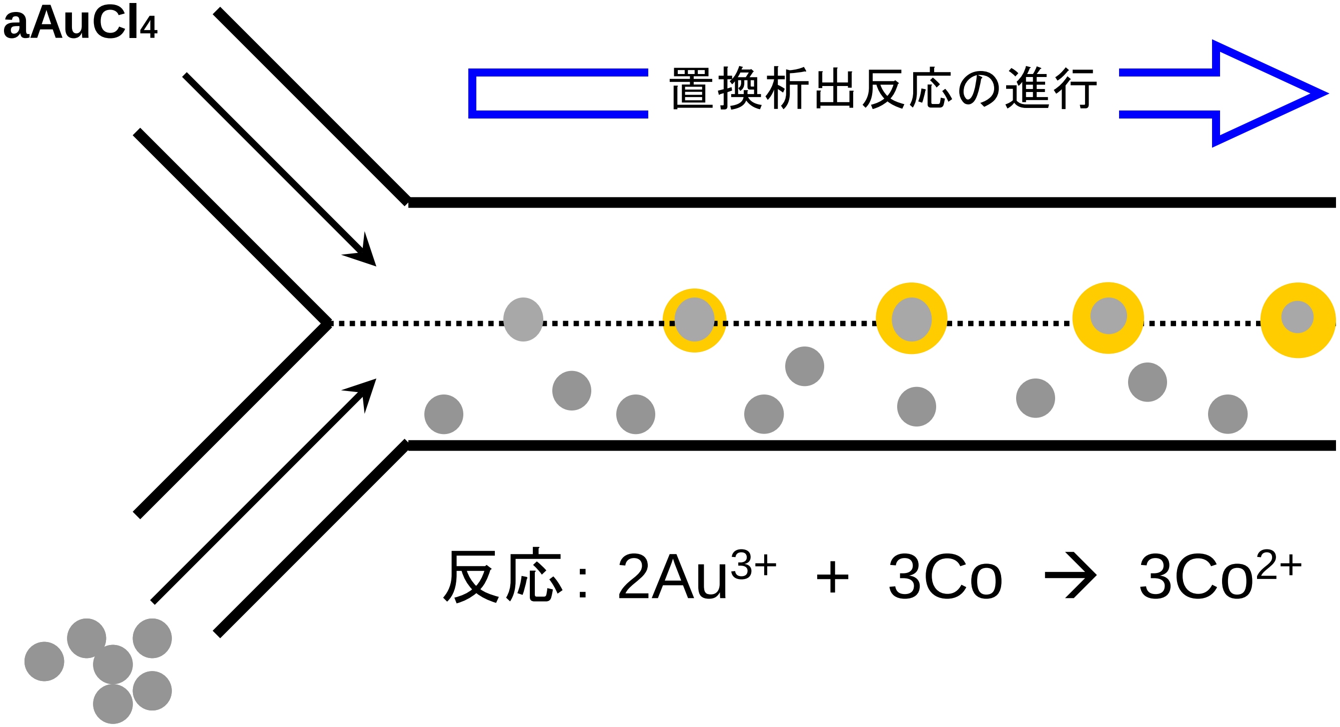
仮定 その3）

<u>ナノ粒子上の吸着子の被覆率は定常状態にあると近似することができる</u>



マイクロ流路系のモデル化ー仮定をいくつか

Discussion with Prof. Dr. Dieter Bothe



反応: $2Au^{3+} + 3Co \rightarrow 3Co^{2+} + 2Au$

仮定 その4）

<u>**ナノ粒子上の吸着子の表面拡散は**</u>
<u>**他の事象と比較して遅く無視してよい**</u>