

Nature-Guided Nanotechnology for Chemical Tectonics of Inorganic Materials

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CREST, Japan Science and Technology Agency

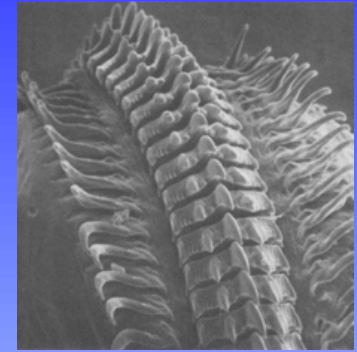
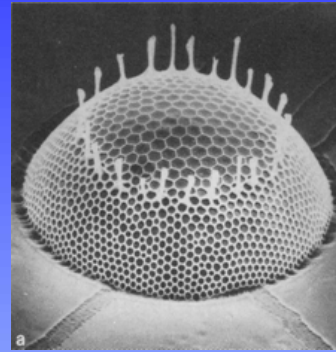
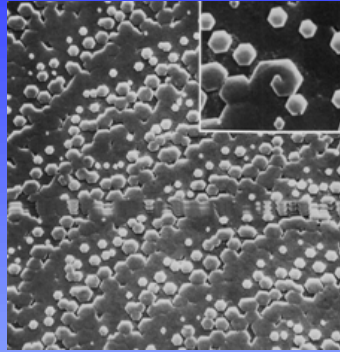
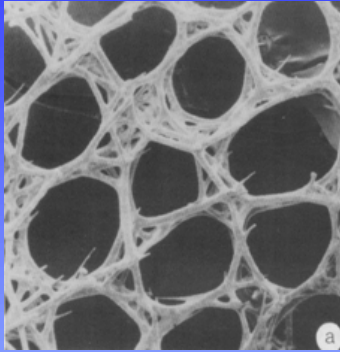
Part I : Bio-inspired Materials Tectonics

- 1. Nature's Nanotechnology for Materials Processing*
- 2. Nano/Micropatterning on SAM Templates*
- 3. Particle Assembly through Self-organization*
- 4. Catalyst/Enzyme-assisted Synthesis*
- 5. Synthesis of BaTiO₃ Nanowires in Alcohol*

Part II : Oxide Thermoelectric Materials

- 1. Thermoelectric Energy Conversion*
- 2. Oxide Superlattices*
- 3. Thin Film TE Devices*

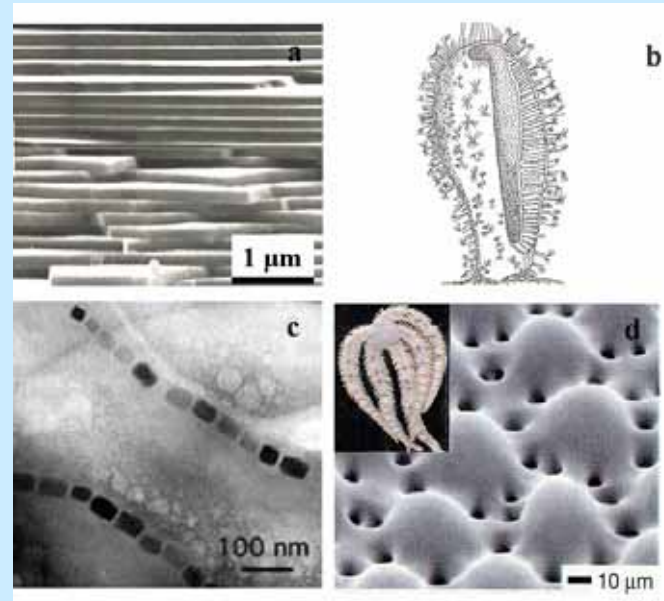
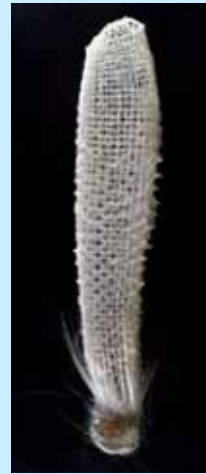
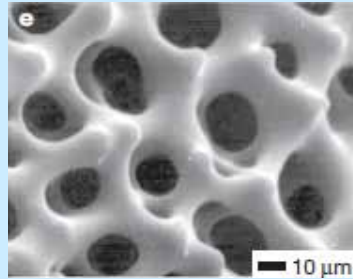
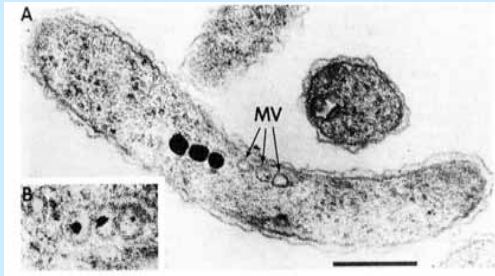
Biomimneralization



Essence of Materials Manufacture in Nature

- **Construct materials in the right place at the right time controlling their shape and size.**
- **Never waste resources, never make wastes.**
- **Consume minimum amounts of mass and energy.**
- **Keep the material life-long by metabolic self-repair**
- **Return to the nature after death.**

Biomimneralization



Building Process
建築過程

Function
機能

Biological Archetype
生物の原型

1. Plot Development
設計図

Delineated
reaction sites
反応場の設計

Supramolecular
preorganization
生体高分子の組織化

2. Foundations
土台・基礎

Site-selective
inorganic nucleation
位置選択的核生成

Interfacial
molecular recognition
界面分子認識

3. Assembly
組み立て

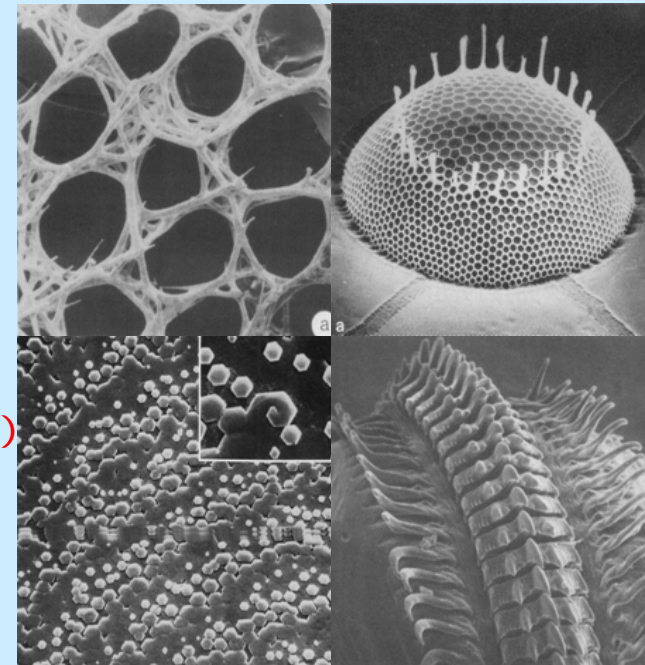
Crystal growth &
termination
結晶成長と終結

Vectorial regulation
ベクトル (大きさ・方向)
規制

4. Networking
連結・システム化

Higher order
Architectures
高次構造

Cellular processing
細胞加工



Nature's Nanotechnology for Materials Synthesis

- ***Molecular assemblies***

0D~3D architecture

Template (Molecular recognition)

**Nano/Micro Structure,
Morphology Synthesis**

***in Molecular
Environment***

Function Generation

- ***Exert molecules***

(Protein, Polysaccharide)

Structure-directing agent

Self-assembly, Hierarchical
structure, Polymorph control

- ***Enzyme-assisted***

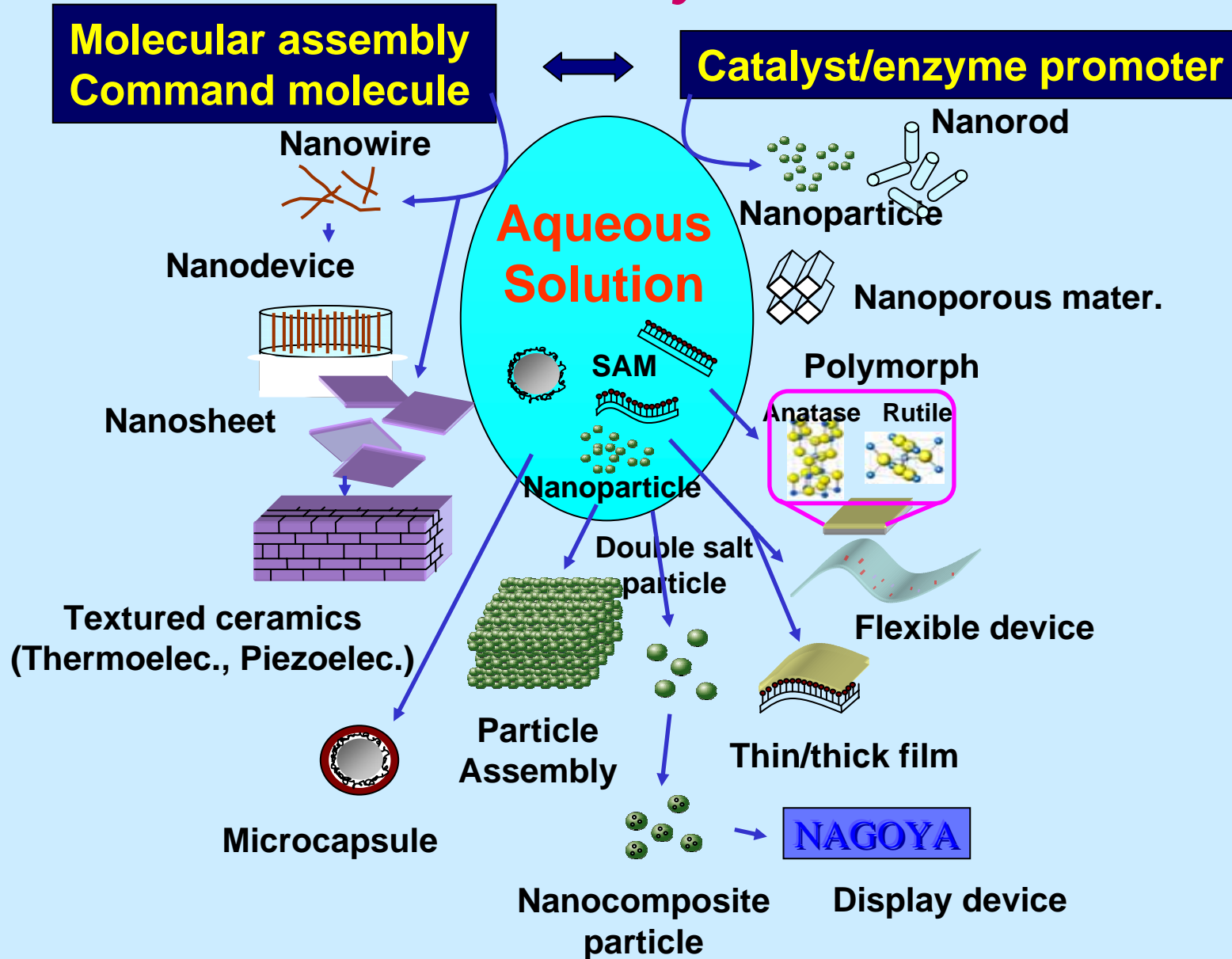
Matrix-selective reaction,

Regio-selective reaction

Ionic transport,

Supersaturation control

Chemical Nanotectonics for Morphogenetic Materials Synthesis



1. Nano/Micropatterning of Inorganic Thin Films on Self-assembled Monolayer Templates

- **Three major mechanisms for micropatterning**
- **Micropatterning on a PET Film**

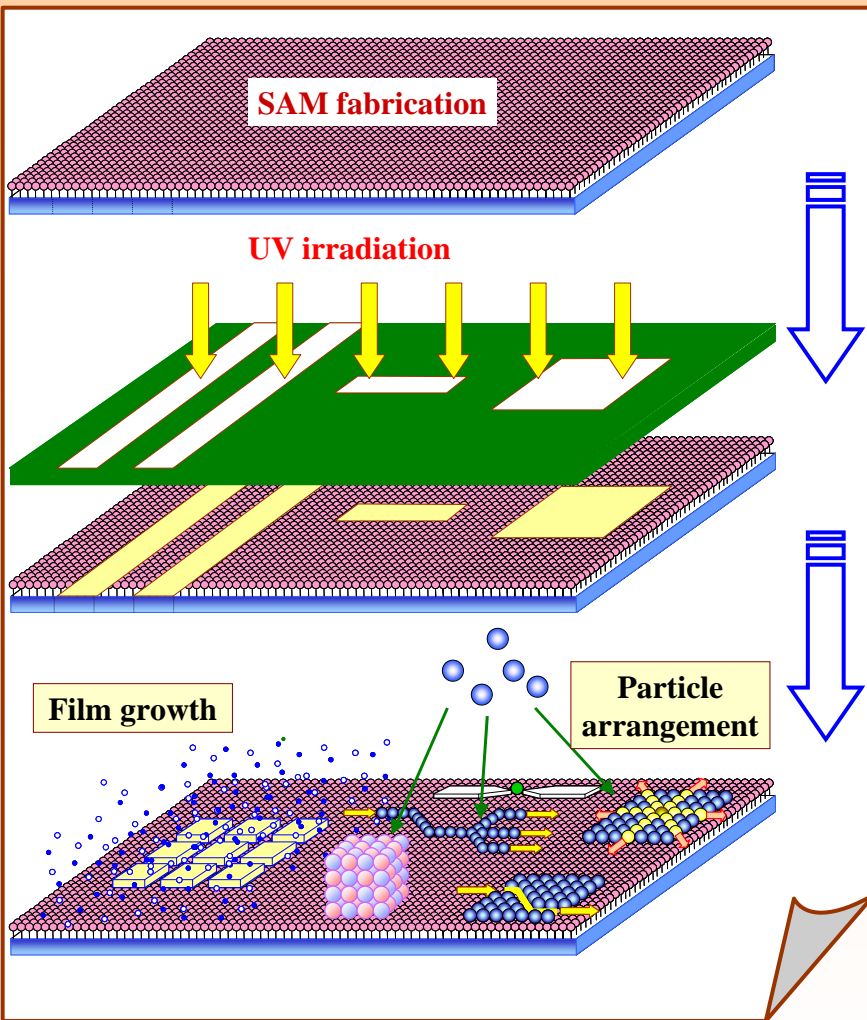
2. Particle assembly through self-organization

3. Catalyst/Enzyme-assisted Synthesis

- **TiO₂ anatase fibers, ribbons, plates**

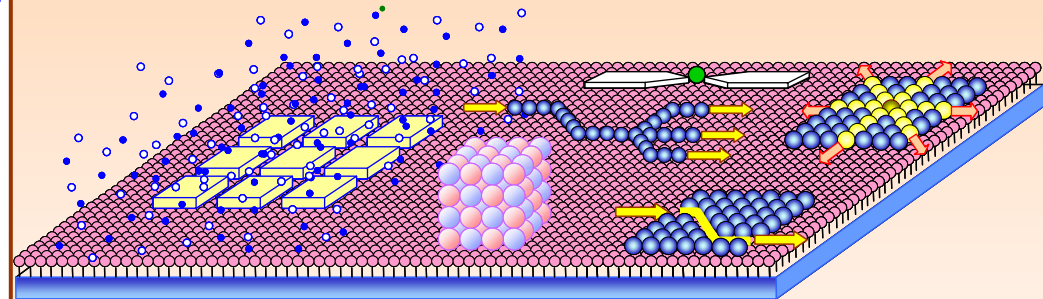
4. Synthesis of BaTiO₃ nanowires in alcohol

Micropatterning via Selective Deposition on SAM Template



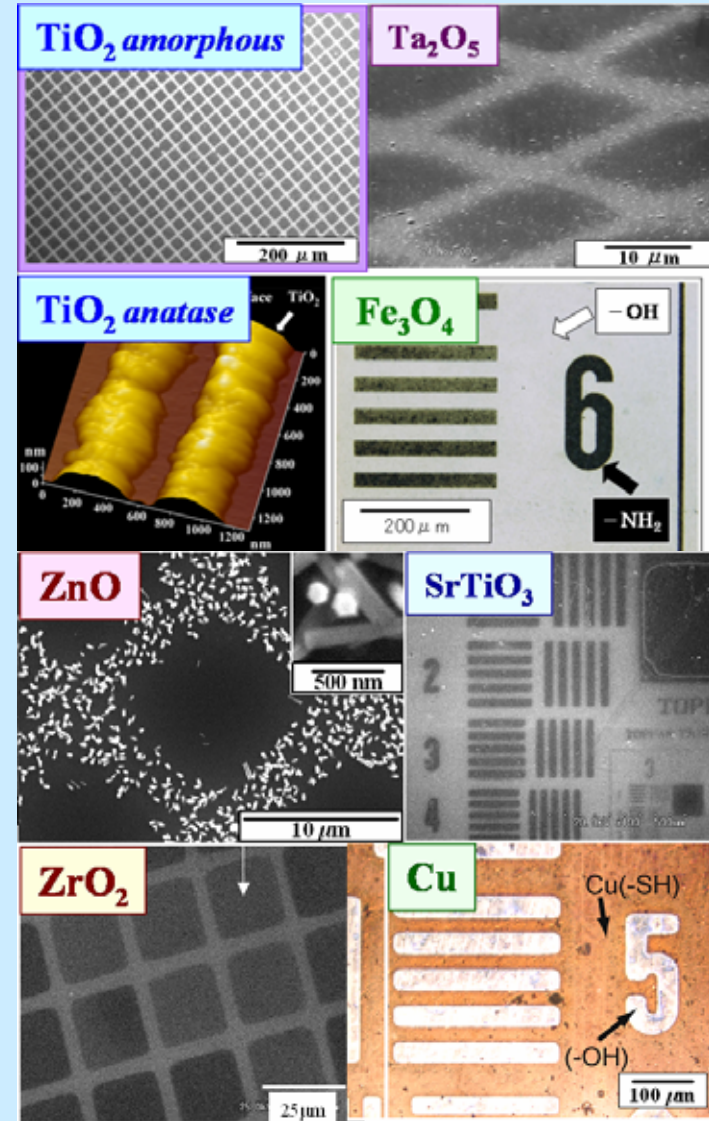
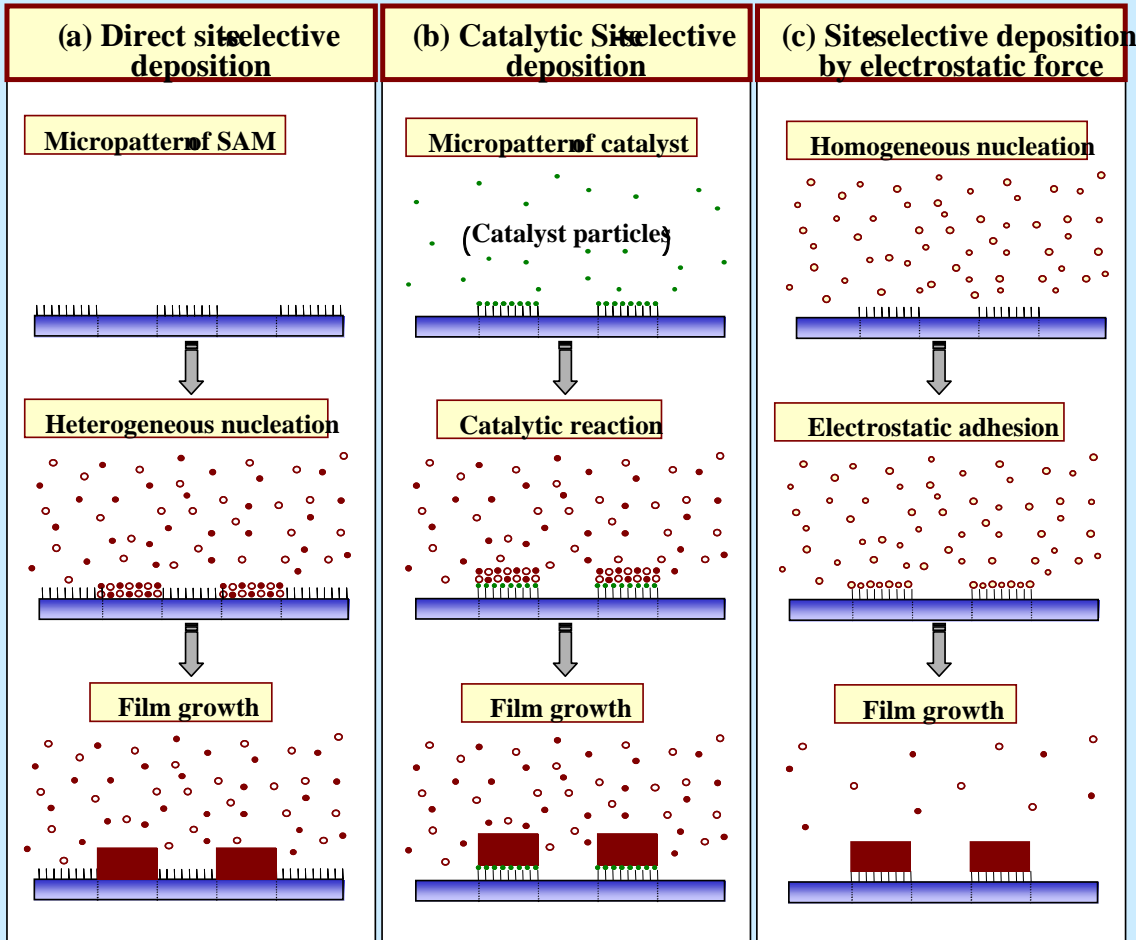
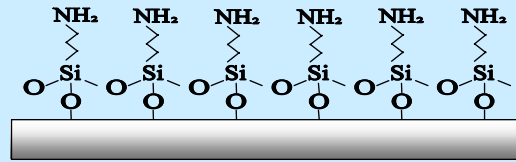
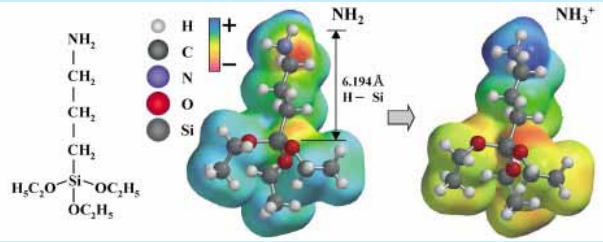
Quantum dot
Quantum wire
Single electron devices

Magnetic Memory
Semiconductor Memory
Photonic crystals

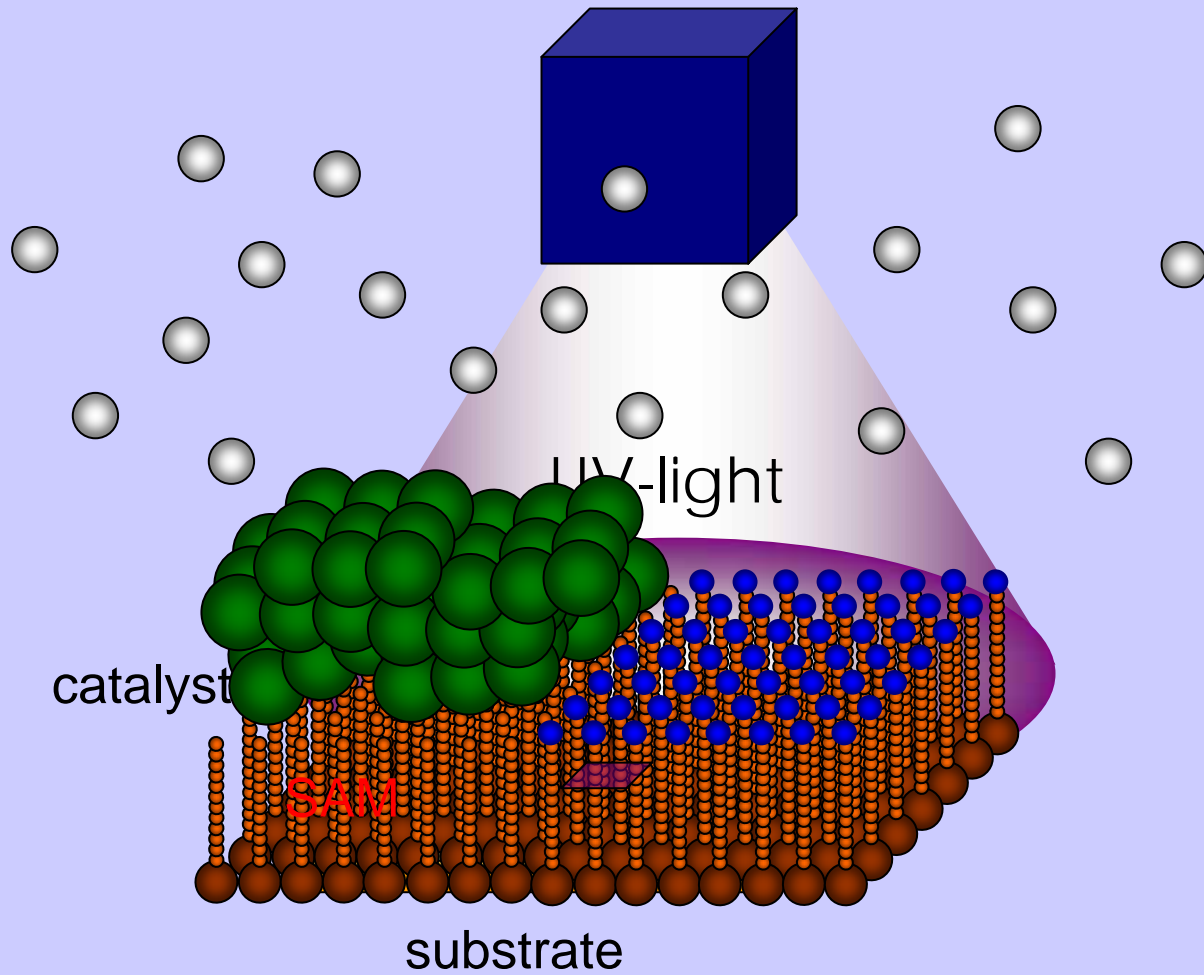


**Microelectronic, Optoelectronic,
Bio-electronic devices**

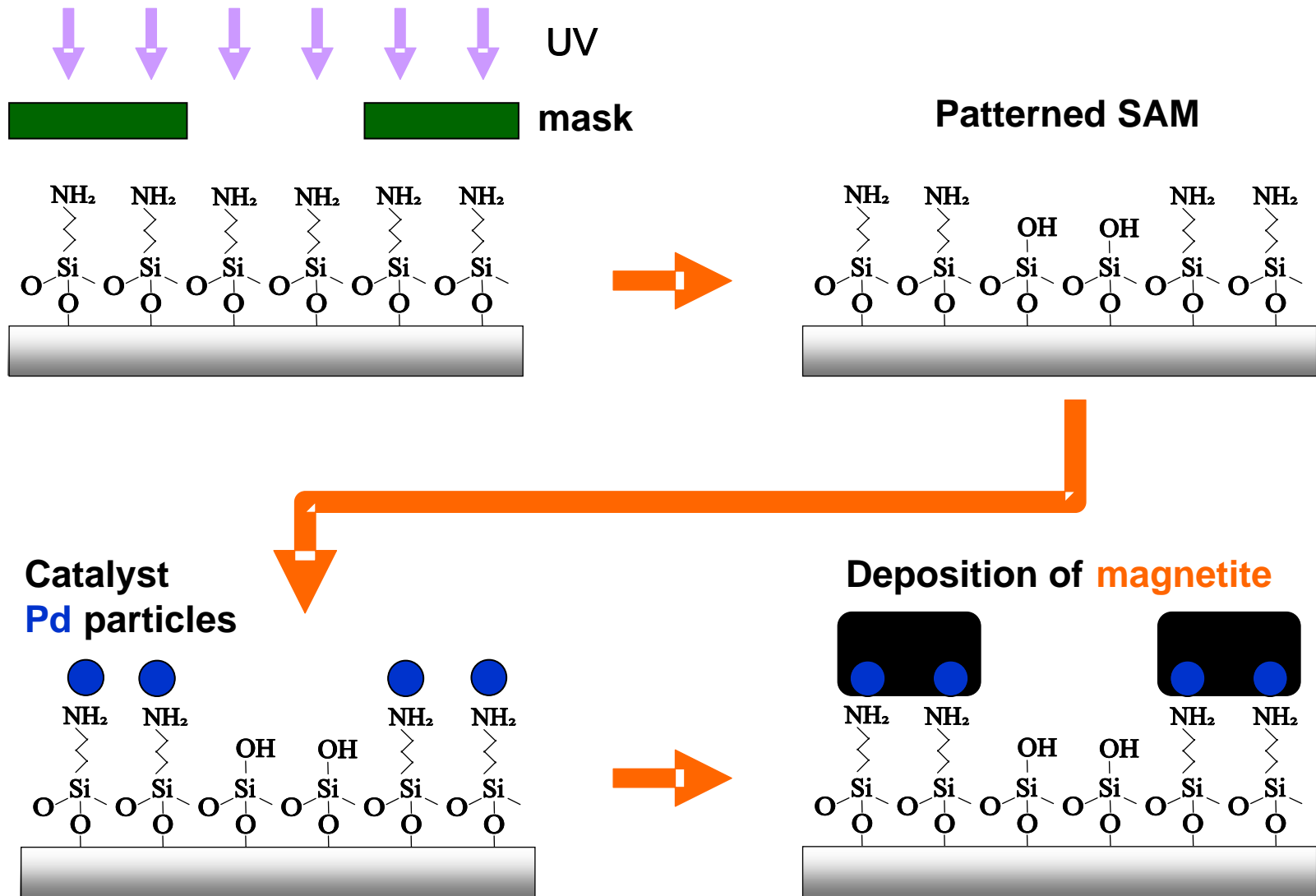
Micropatterning of Functional Materials on SAM Templates



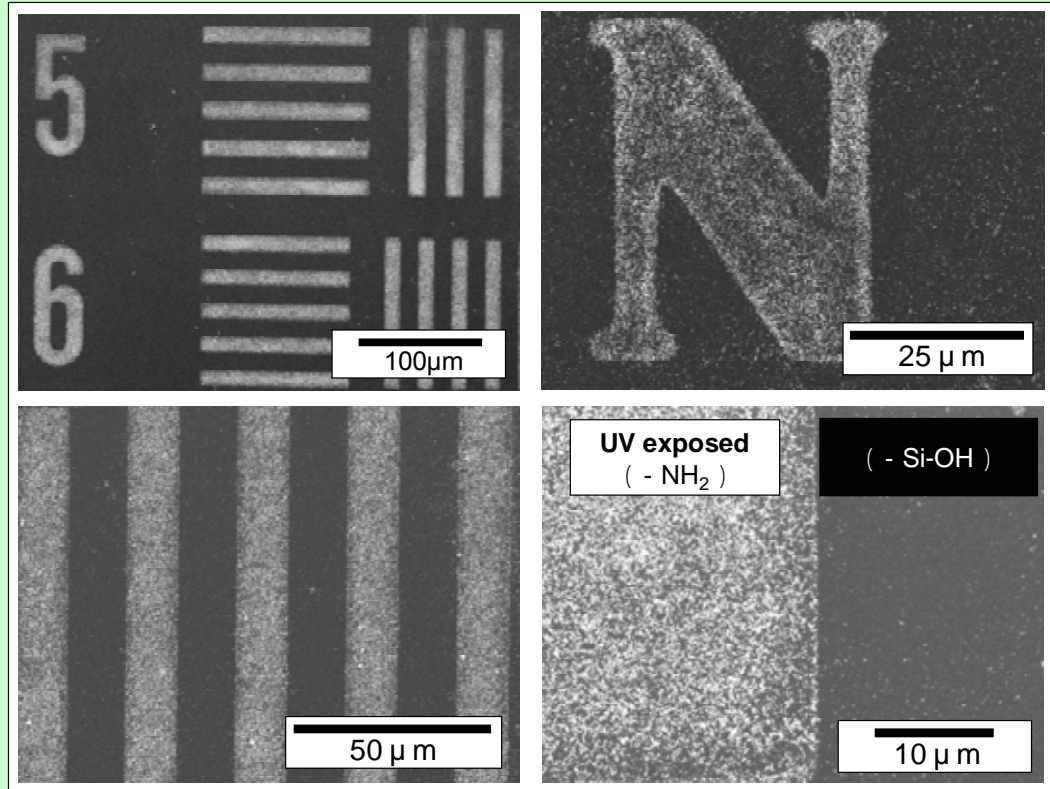
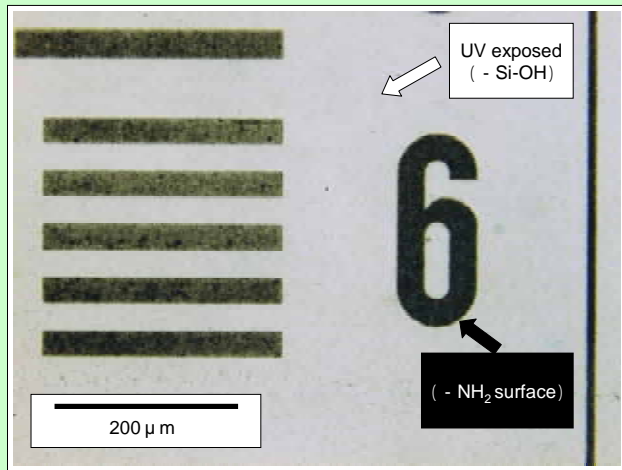
Site-selective deposition: Catalytic reaction



Micropatterning of Magnetite Fe_3O_4

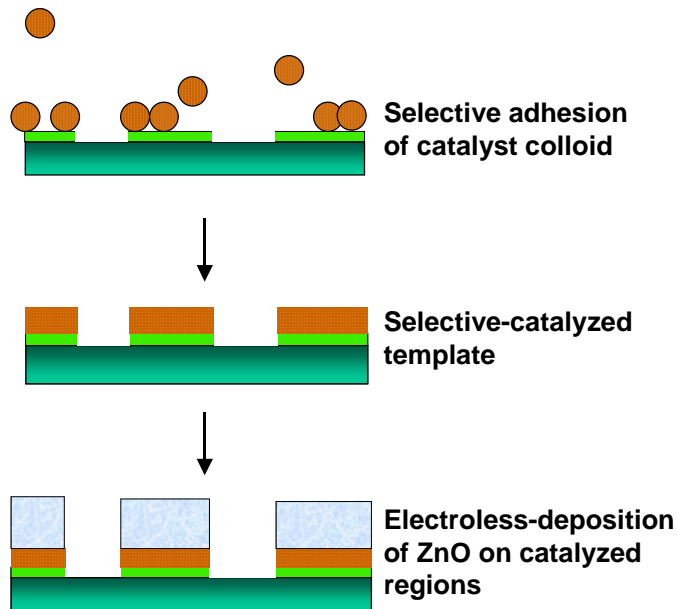


Micropattern of magnetite Fe_3O_4

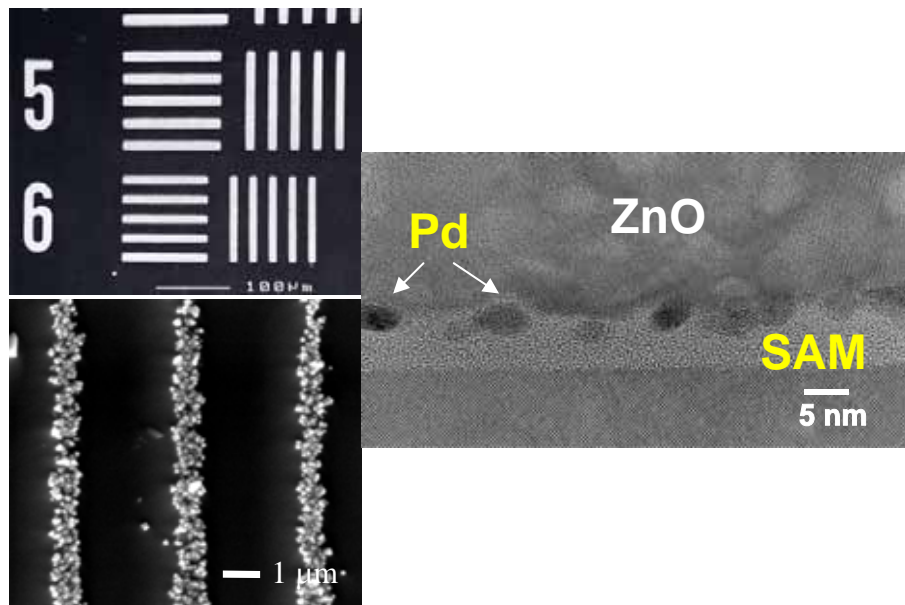
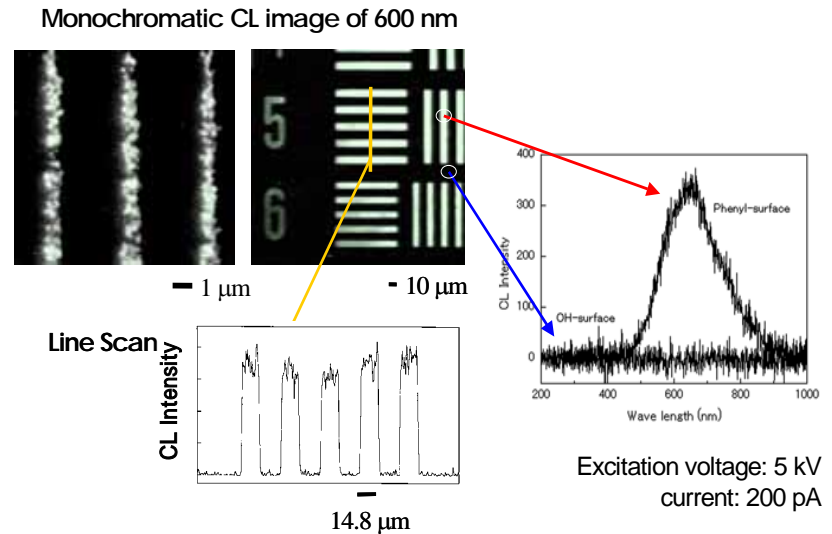


Nakanishi , Masuda, Koumoto, *Chem. Mater.*, 16, 3484 (2004).

Micropatterning of ZnO phosphor



Cathodoluminescence

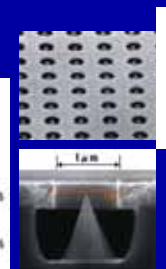
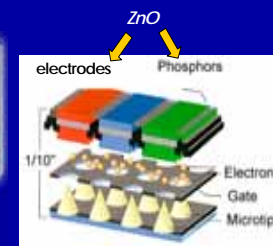
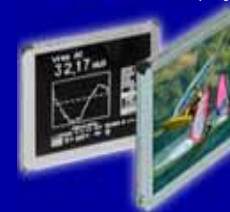


Selective Deposition of ZnO Ceramics

Direct Patterning

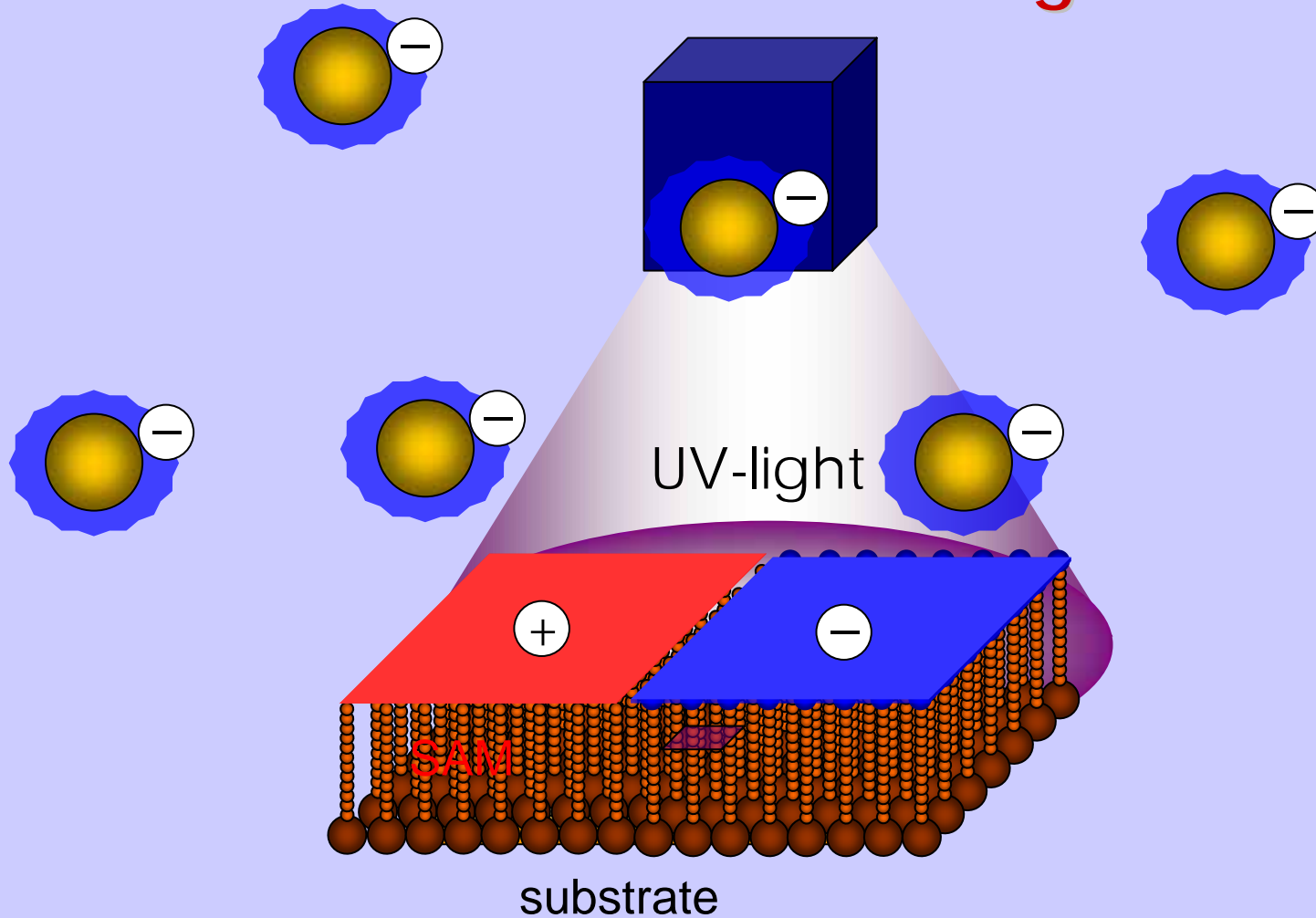
Integration of Functional Ceramics

Ex.: Field Emission Display



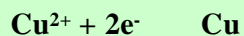
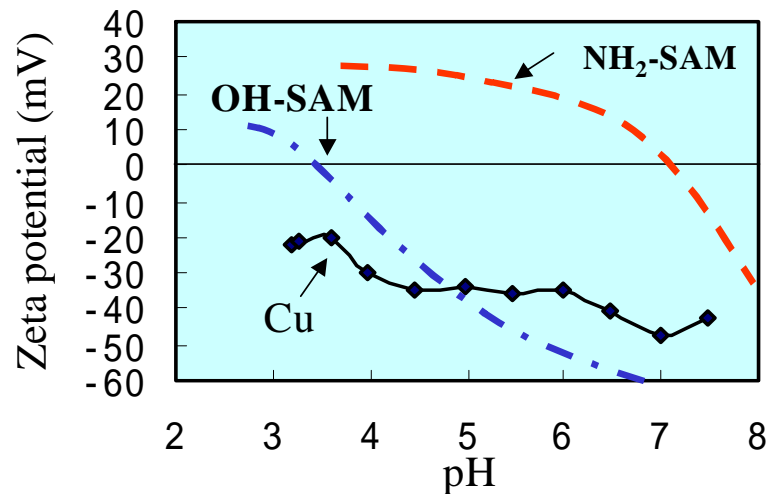
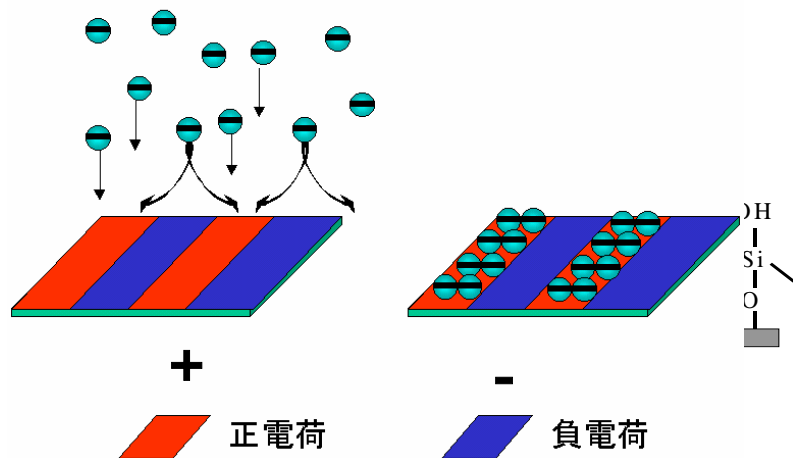
<http://www.futaba.com/>

Site-selective deposition: Electrostatic adhesion & growth



Micropatterning of Cu Electrode

静電作用によるパターンの作製



Soaking conditions R.T ~ 80 pH values

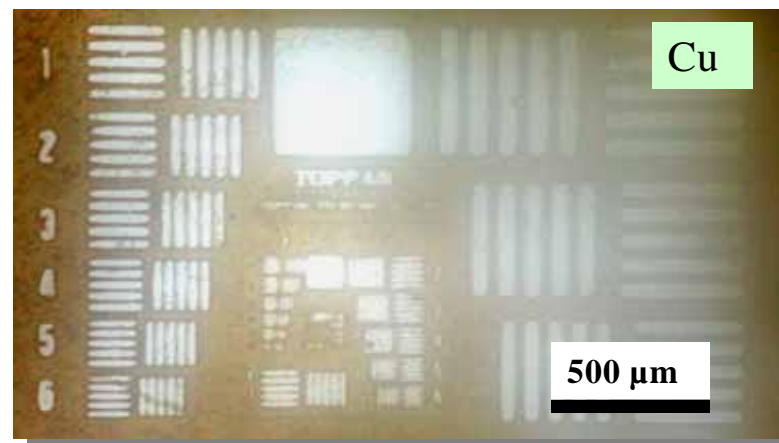
CuCl₂: 0.05

Sodium citrate (complex): 0.1

Dimethylamineborane (DMAB): 0.1

Additive (H₃BO₃): 0.1

Reaction in solutions



Organic/Inorganic Co-existing Devices

OLED (TV, Display)

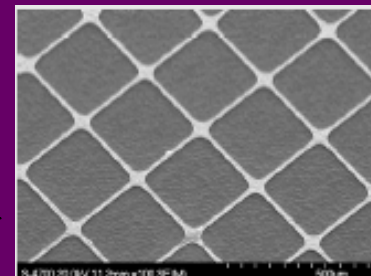


Electronic circuit

Photonic device



Nano/Micro Flexible Devices



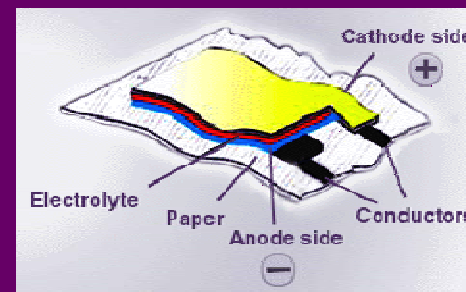
Flexible EMS



Electronic paper

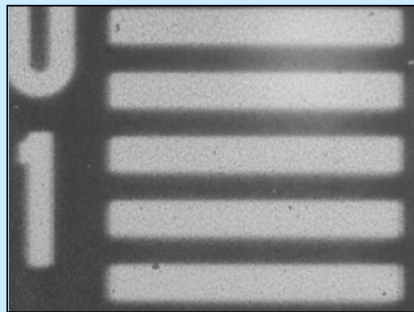
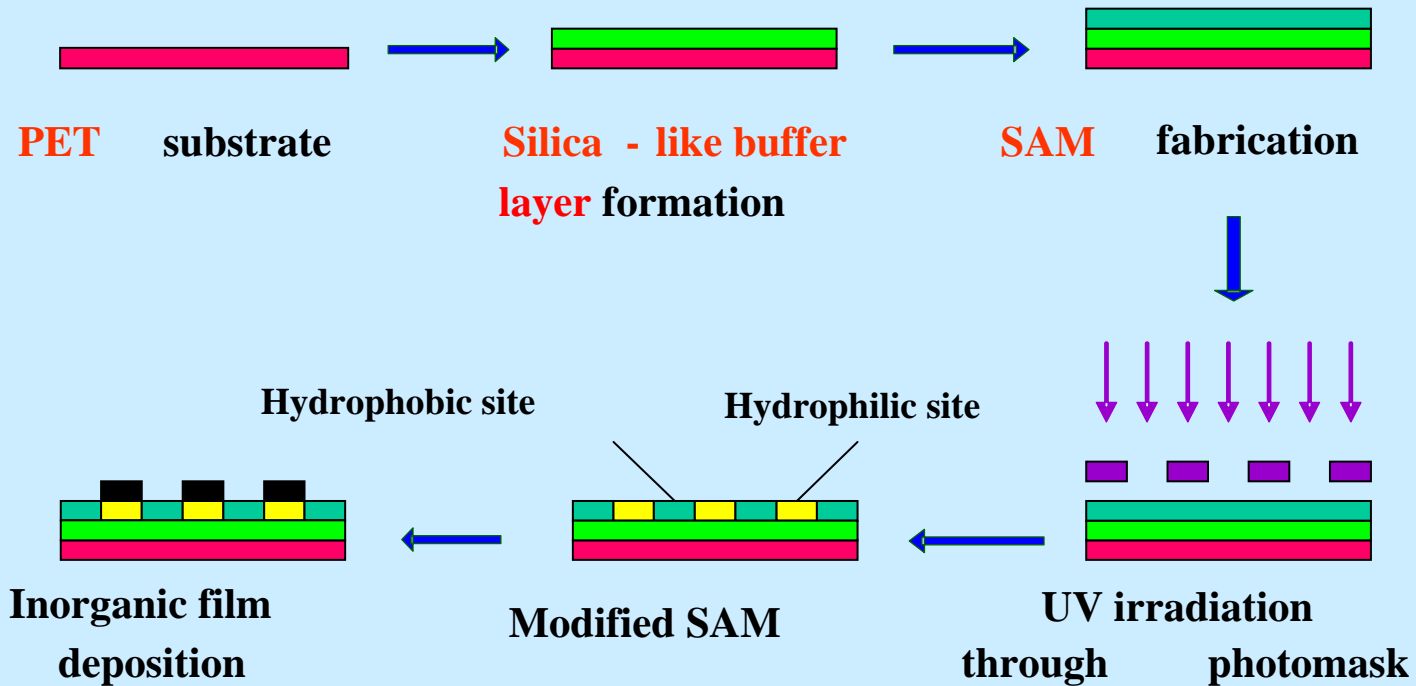
Flexible display

Solar cell



Flexible battery

Micropatterning on a PET Film



TiO₂ (anatase) micropattern



Cu micropattern

Line width < 1 μm
Resolution < 0.1 μm
Roughness < 2 nm rms
 $\sim 8 \times 10^4 \text{ Scm}^{-1}$

1. Nano/Micropatterning of Inorganic Thin Films on Self-assembled Monolayer Templates

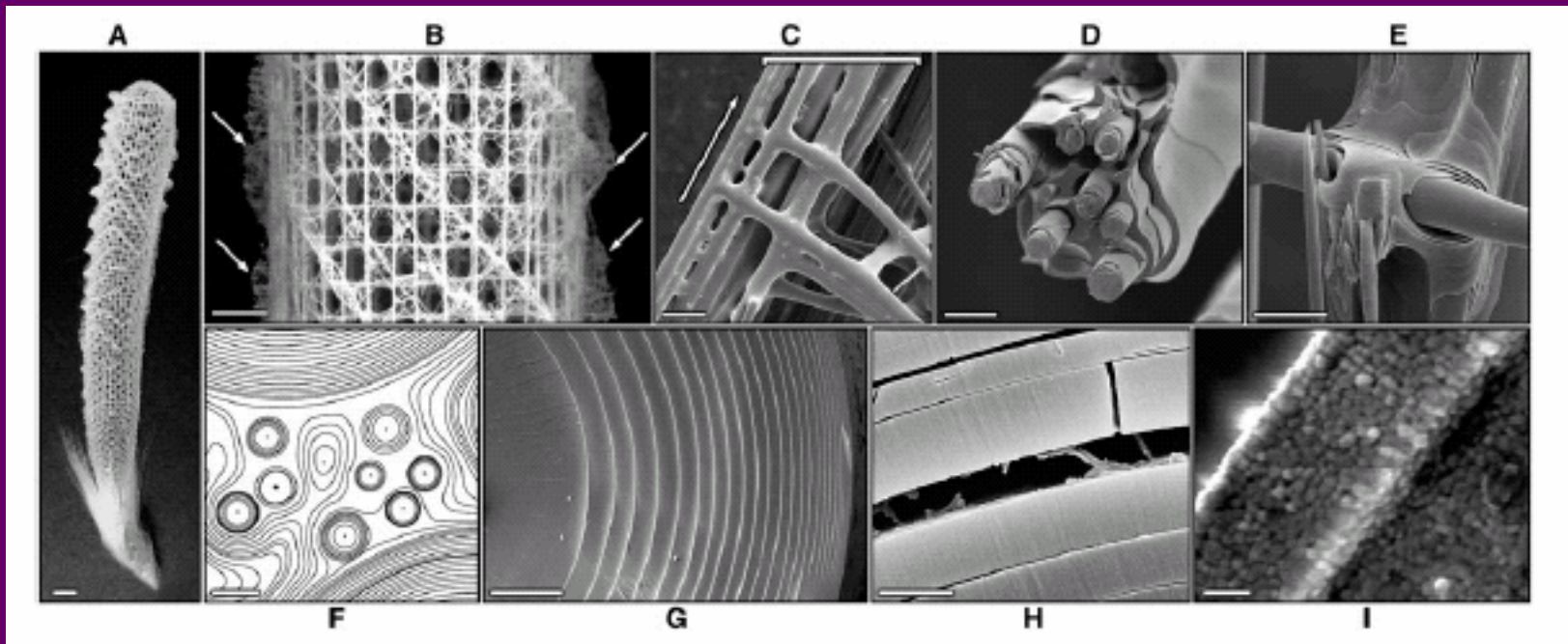
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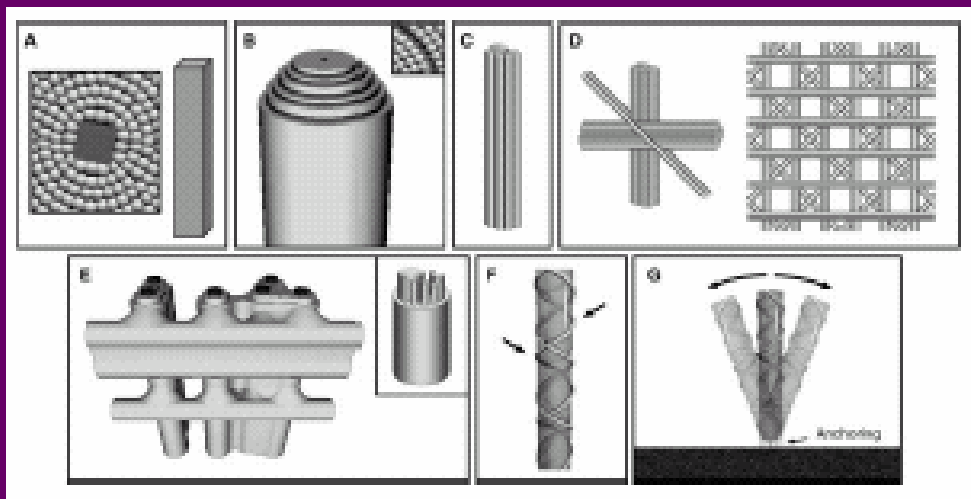


Hierarchical Structure

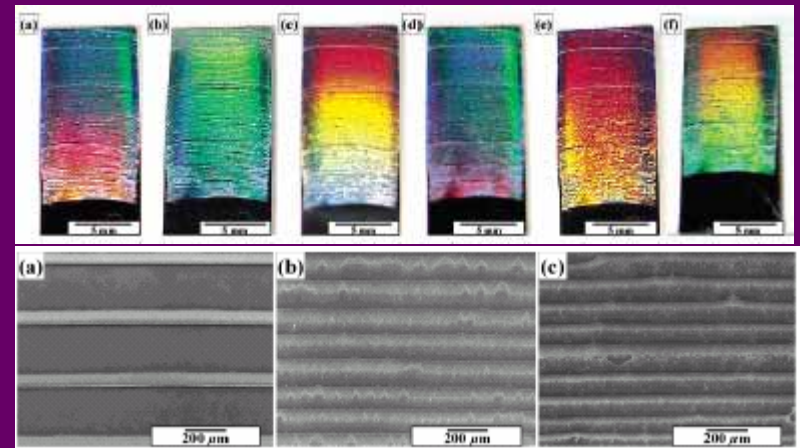
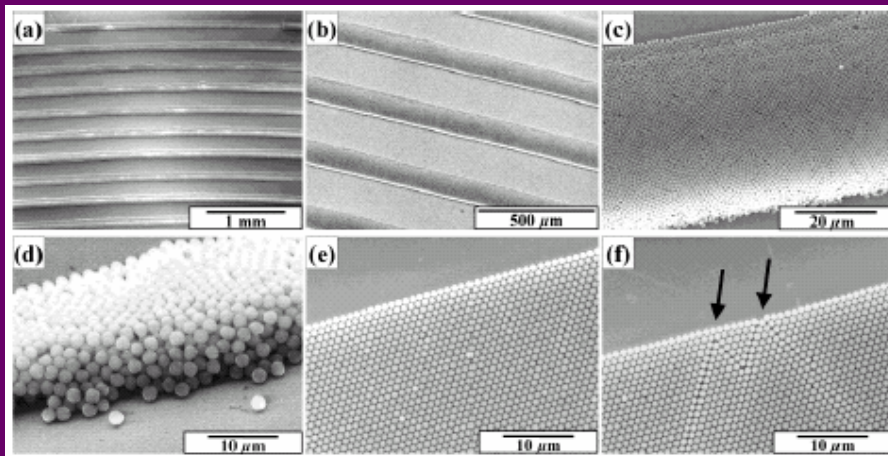
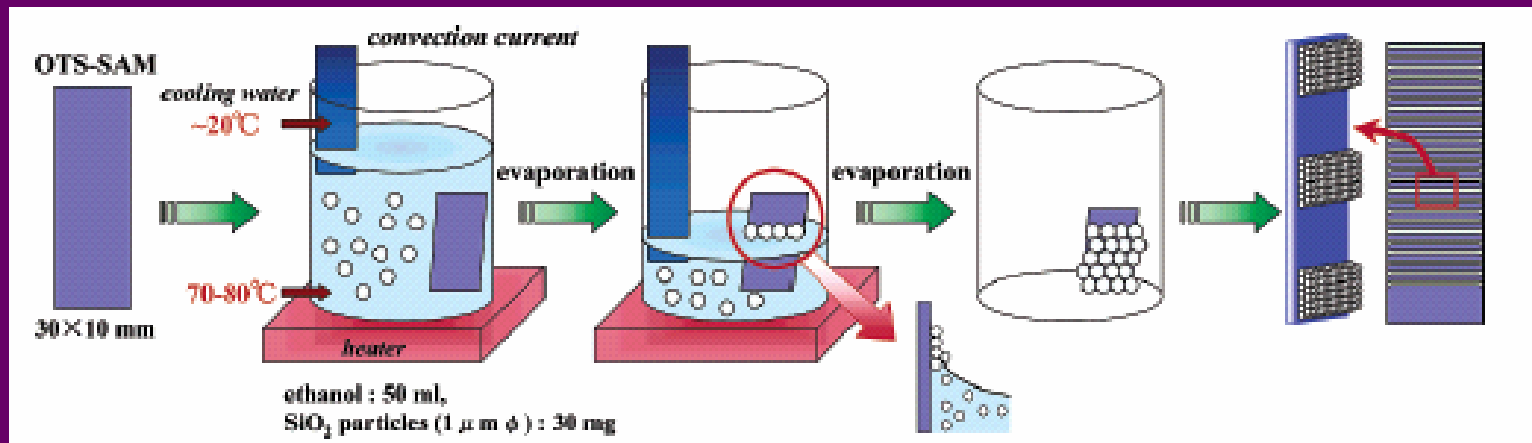
Skeleton of *Euplectella* sp.: Structural Hierarchy from the Nanoscale to the Macroscale

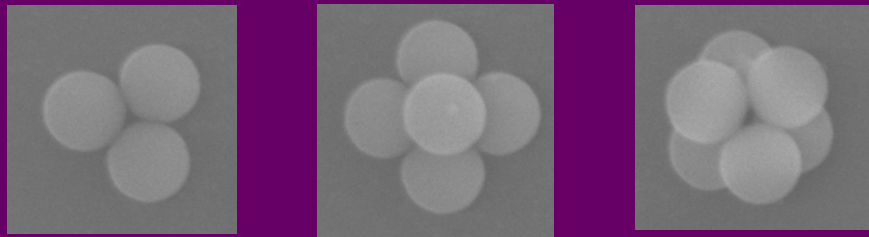
Joanna Aizenberg,^{1*} James C. Weaver,² Monica S. Thanawala,¹
Vikram C. Sundar,¹ Daniel E. Morse,² Peter Fratzl³

www.sciencemag.org SCIENCE VOL 309 8 JULY 2005

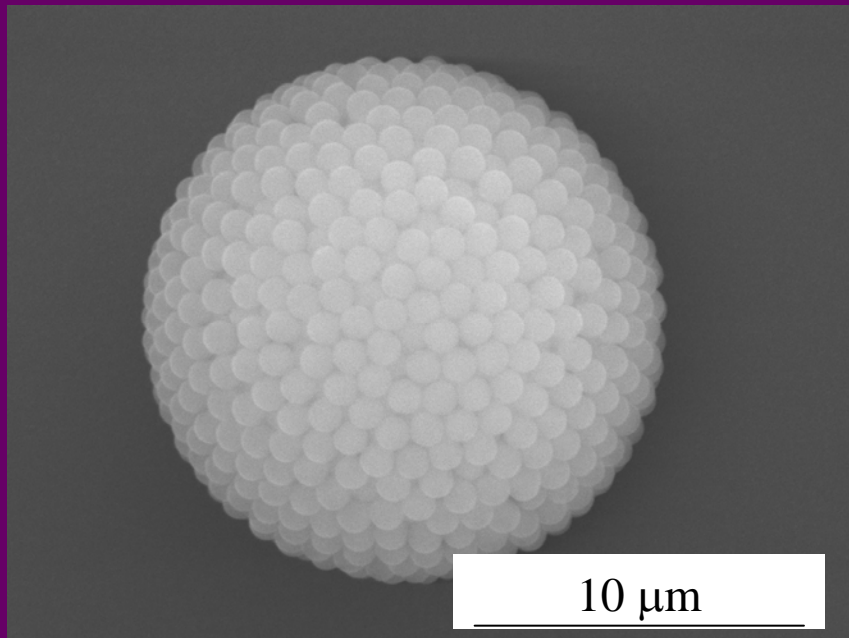
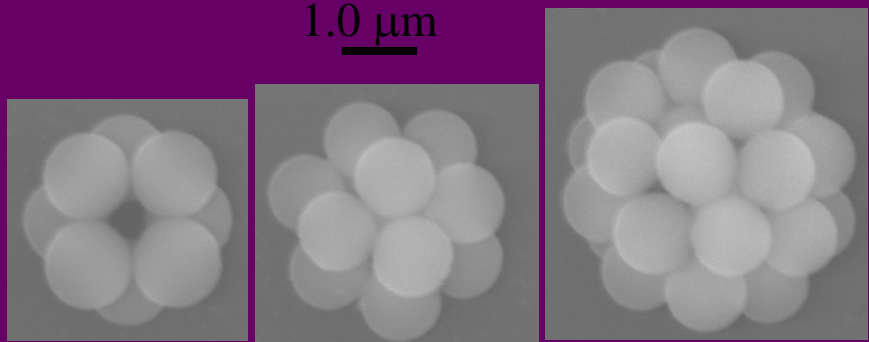


Particle assembly through self-organization on SAM

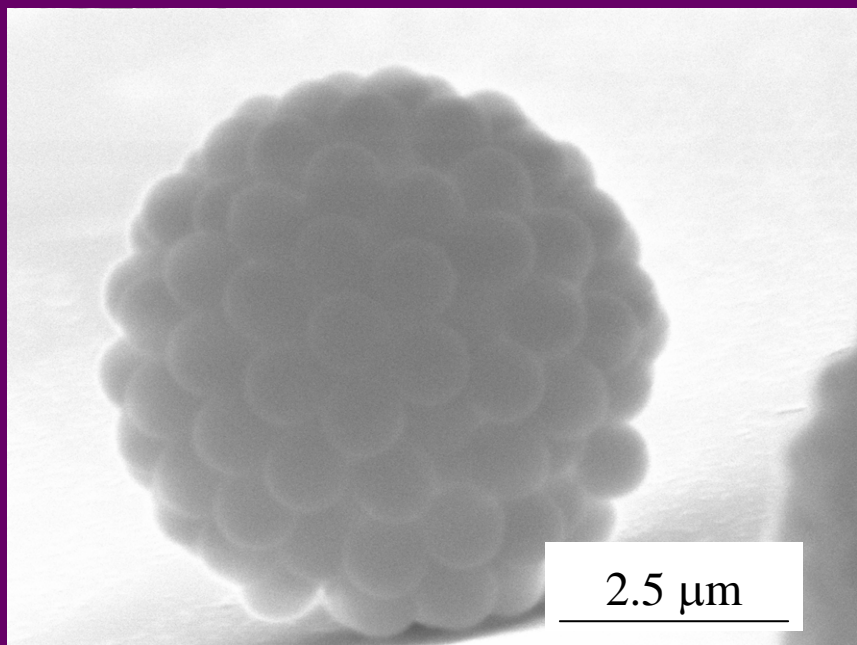




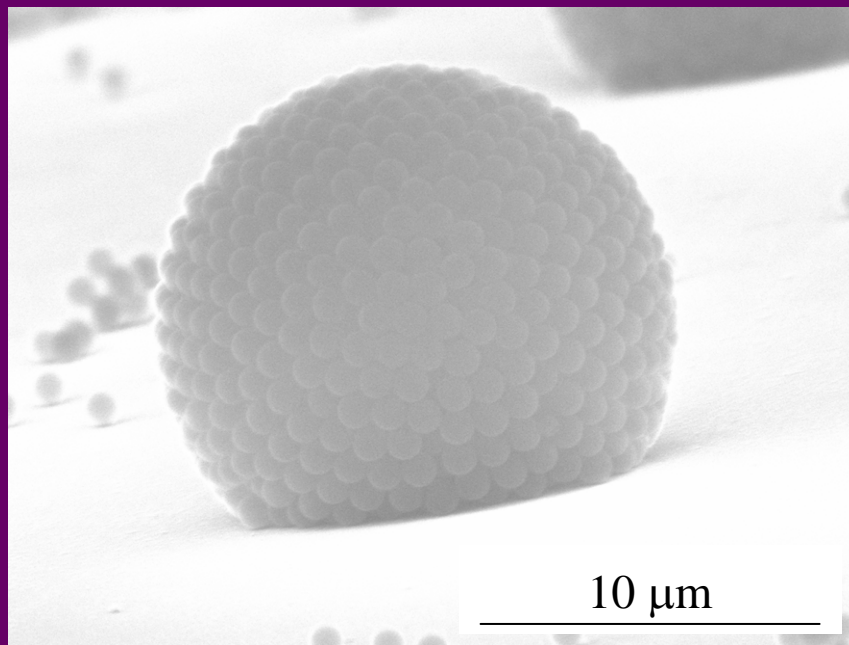
1.0 μm



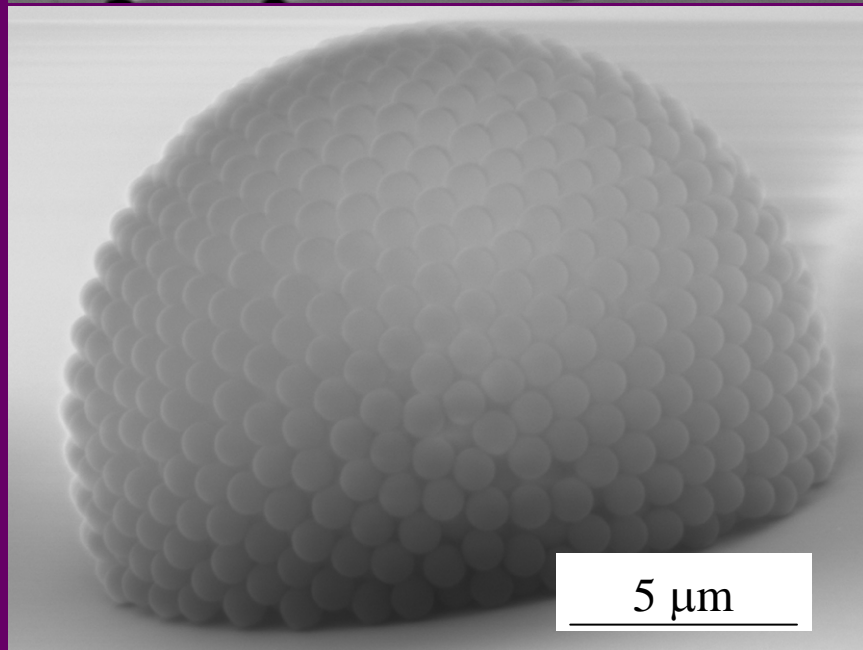
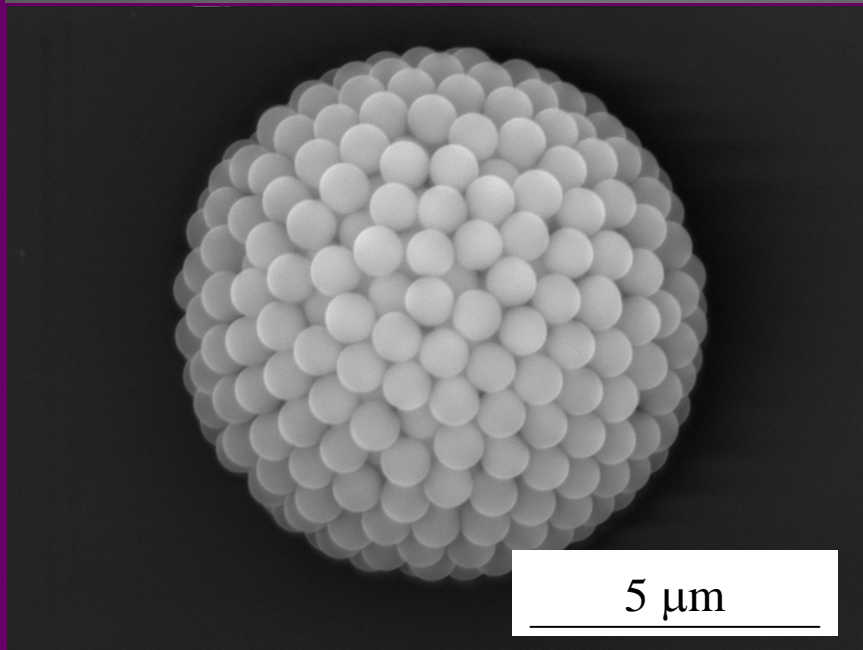
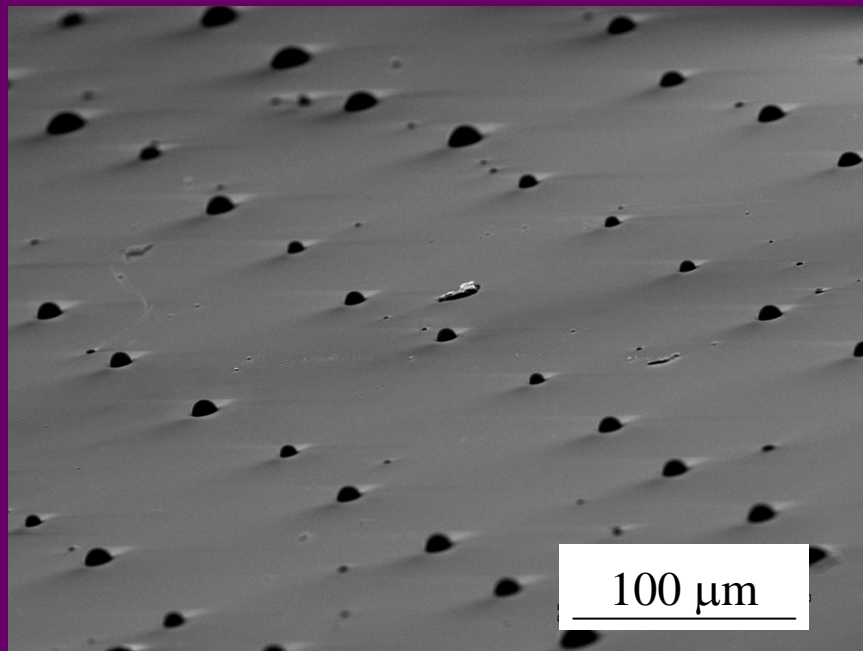
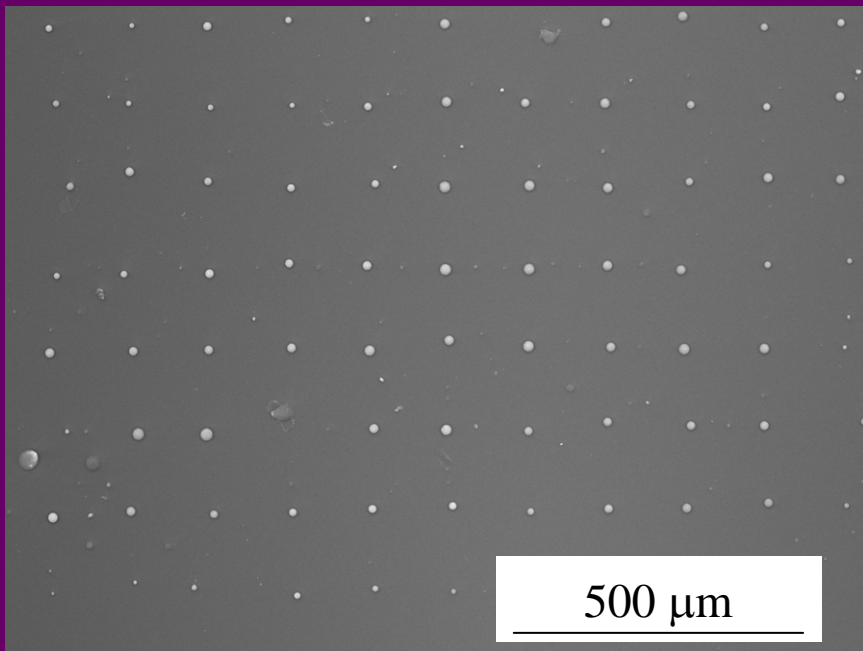
10 μm



2.5 μm



10 μm



1. *Nano/Micropatterning of Inorganic Thin Films on Self-assembled Monolayer Templates*

- Three major mechanisms for patterning
- Micropatterning on a PET Film

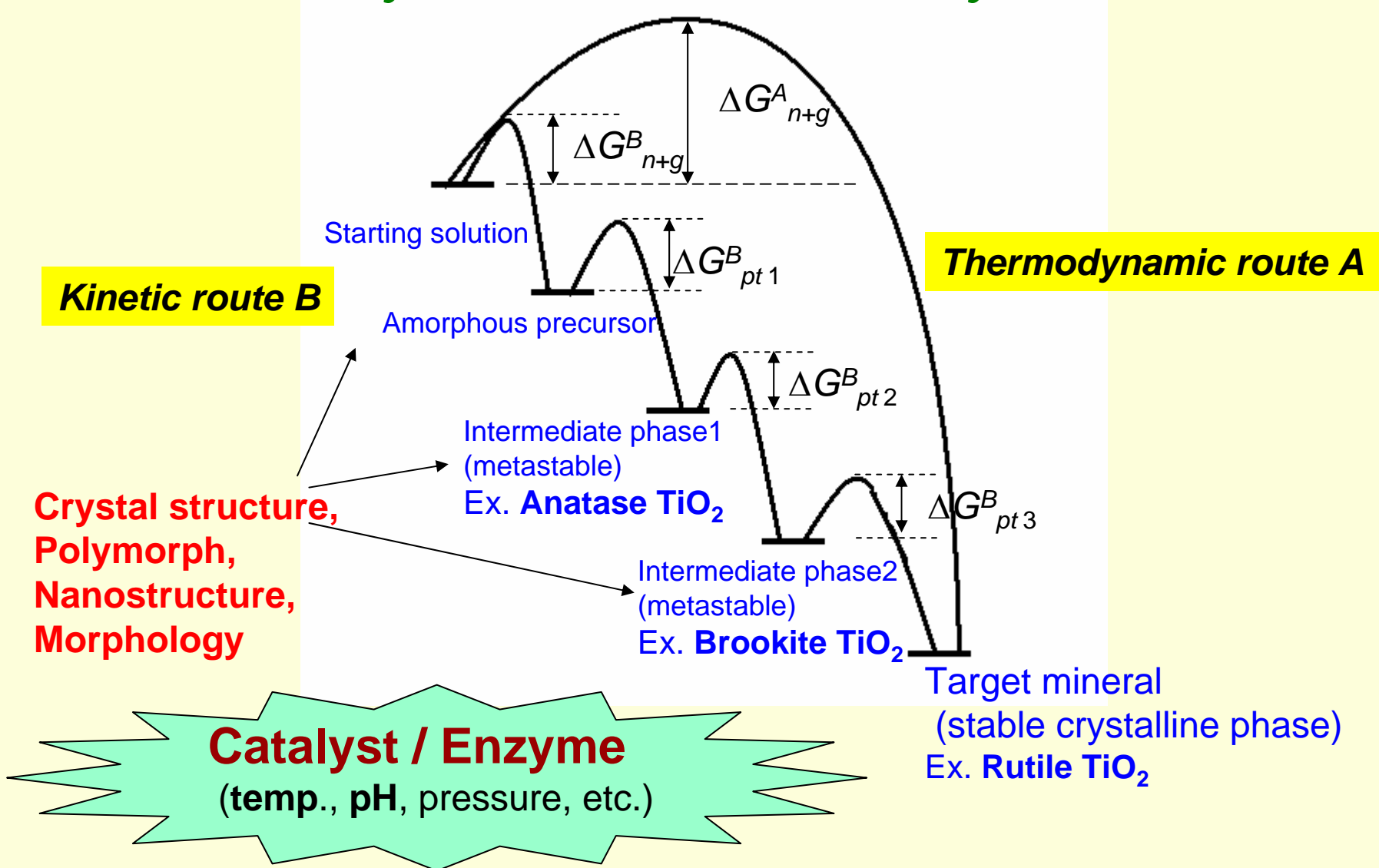
2. *Particle assembly through self-organization*

3. **Catalyst/Enzyme-assisted Synthesis**

- **TiO₂ anatase fibers, ribbons, plates**

4. *Synthesis of BaTiO₃ nanowires in alcohol*

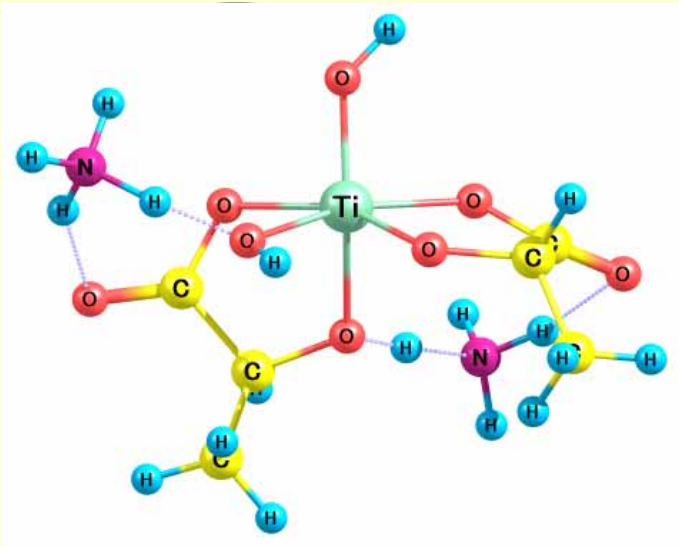
Activation-energy diagram of thermodynamically & kinetically-controlled routes for crystallization



Anisotropy in complex assembly can be controlled by **regio-selective** reaction

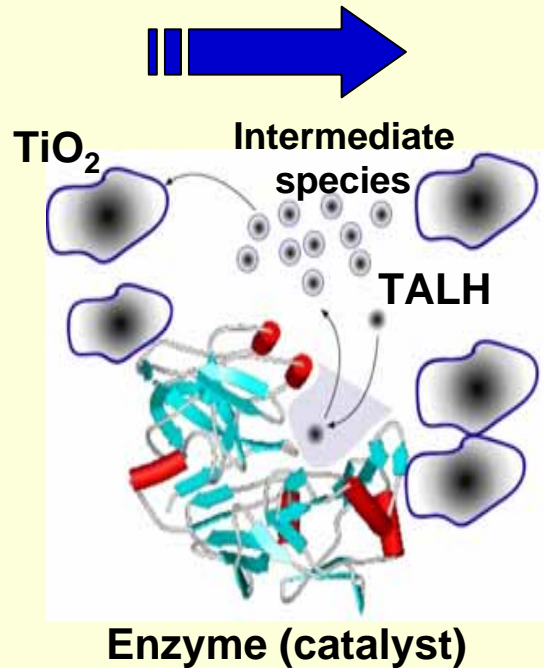
TALH

Titanium(IV) bis(ammonium lactato) dihydroxide

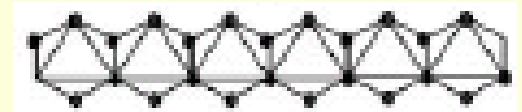


Ligand (species, configuration)
Isomer, Oligomer

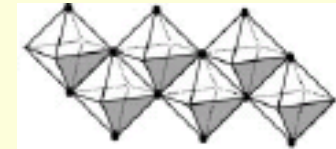
Nanostructure
Morphology



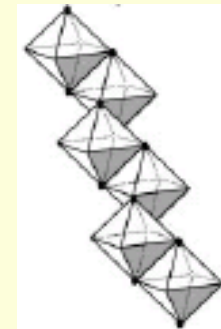
Nanoblock for Rutile

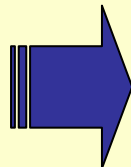
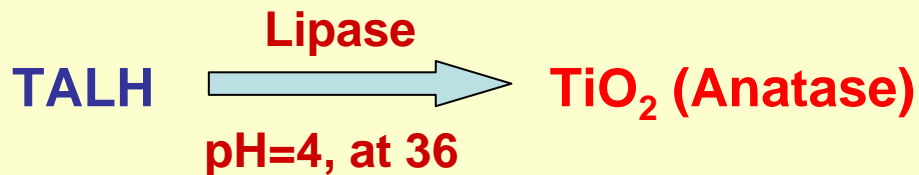


Nanoblock for Anatase

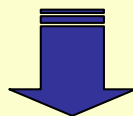
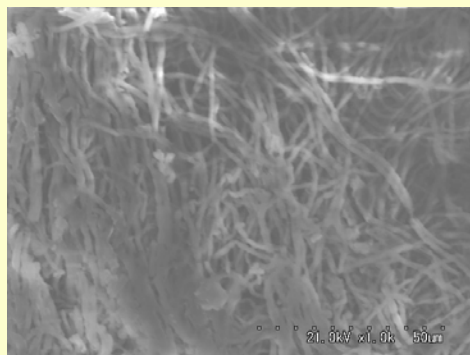


Nanoblock for Brookite

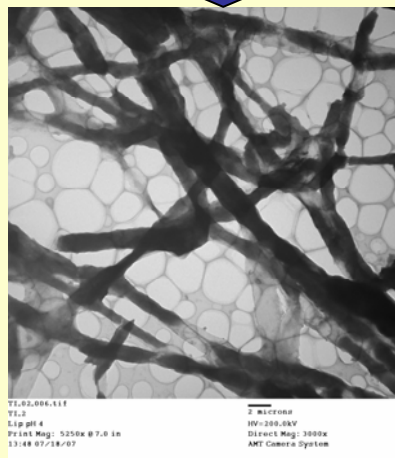




SEM: As-prepared



TEM: fired at 500



TEM: As-prepared

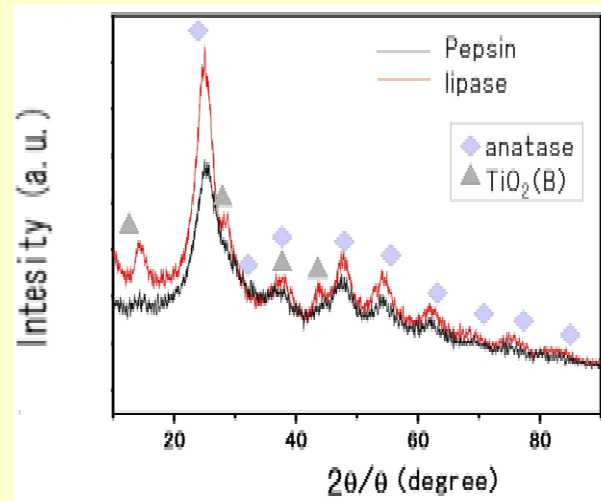
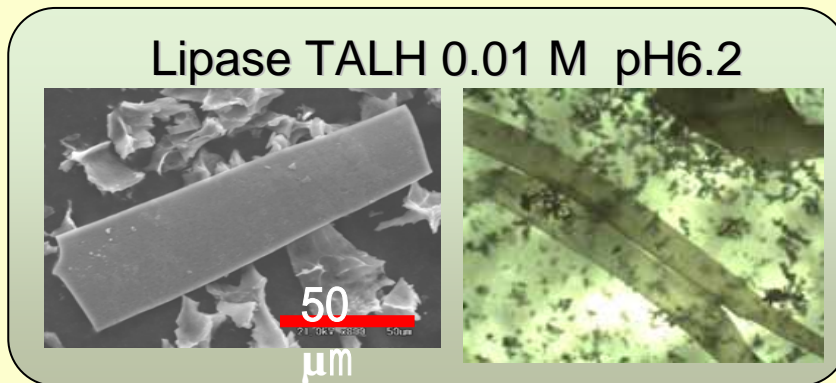


Fig. 2. XRD patterns of precipitates obtained from TALH solutions containing pepsin and lipase. The pHs of the reaction solutions are 2.0 and 6.2 for pepsin and lipase, respectively.



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- Three major mechanisms for patterning
- Micropatterning on a PET Film

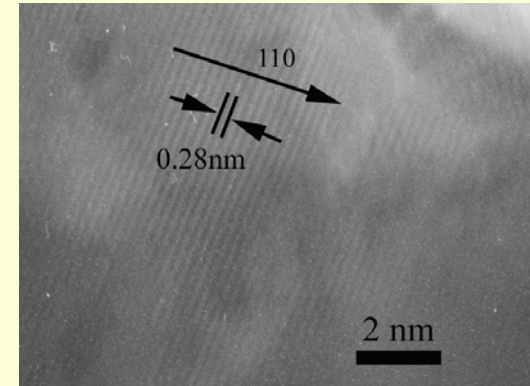
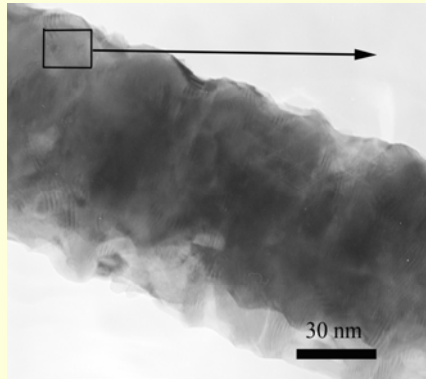
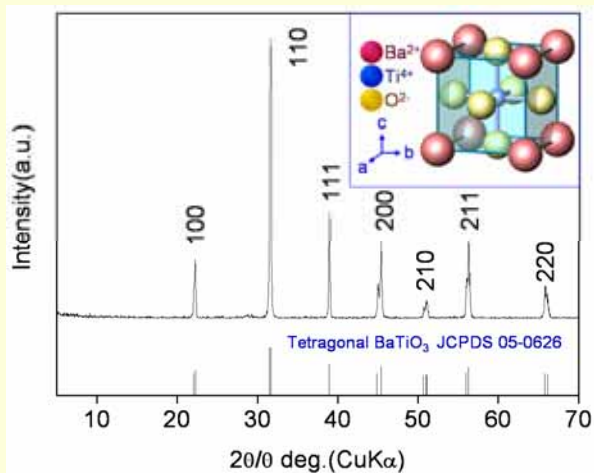
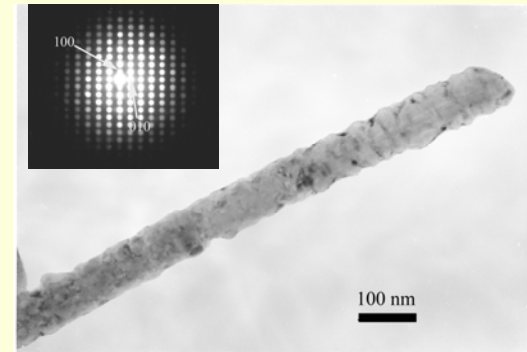
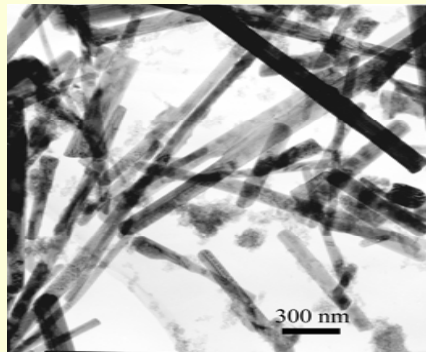
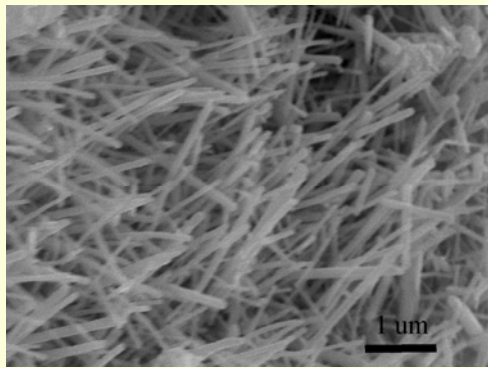
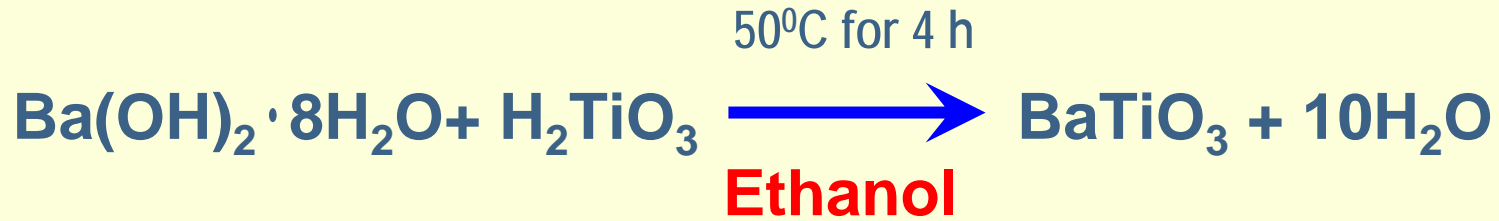
2. Catalyst/Enzyme-assisted Synthesis

- TiO₂ anatase fibers, ribbons, plates
- magnetic microcapsules

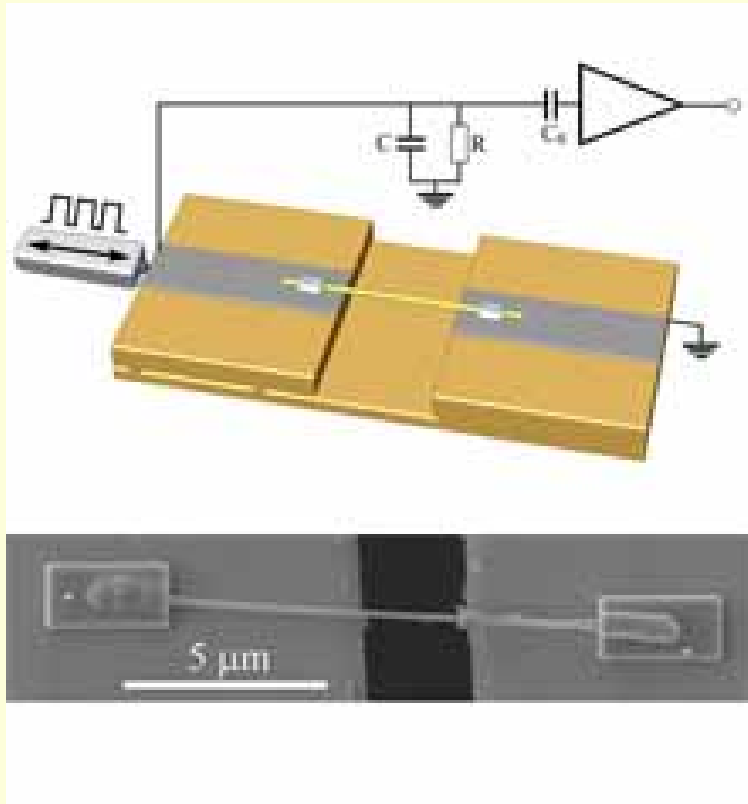
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Synthesis of BaTiO₃ Nanowires in Alcohol



Voltage Generation from Individual BaTiO_3 Nanowires Under Periodic Tensile Mechanical Load



Biomedical sensors powered by blood flow or muscle contractions

Tiny gas sensors that run on wind or acoustic waves

Pathogen monitors powered by water flow

etc.

Z. Wang et al., *Nano Lett.*, 7 (10), 2966-2969 (2007)

Holy Grails of Chemistry

By David Young

Holy Grail (聖杯) ---the cup used by Jesus at the last supper.
now that which is most highly sought after.

The ability to observe single atoms

The ability to manipulate individual atoms to synthesize any compound

The exact analytic solution of the Schroedinger equation

The ability to observe chemical reactions taking place

Self assembling machines

.

.

Holy Grails of Materials Chemistry

The ability to produce any inorganic material in water

A way of recycling 100% of arbitrary material

.

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