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Promotion Data

Morphology Control of Transition Metal Oxides by Liquid-phase Process and their Material Development

(Case of ZnO)

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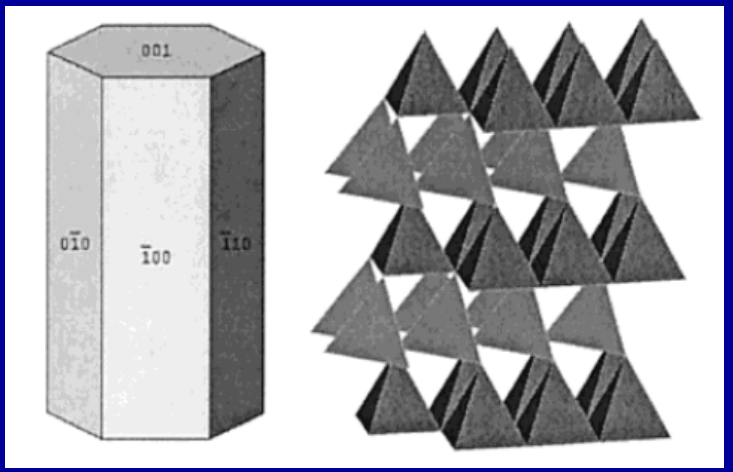
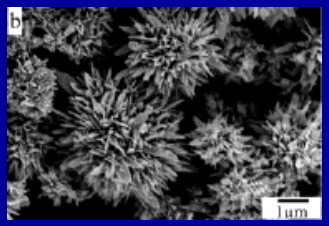
Introduction

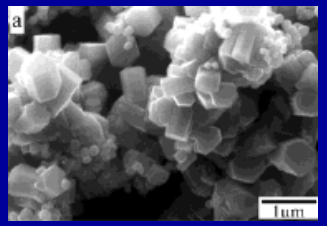
ZnO has wide applications in photocatalytic reaction, solar cell, sensor, pigments, UV shielding material, etc. It is expected that the physical-chemical properties greatly change with the morphology of the zinc oxide crystals. It is important to synthesize ZnO with high specific surface area and controllable morphology.



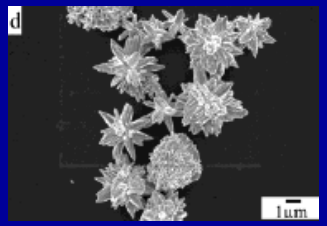
Control of ZnO Morphology via a Simple Solution Route: $Zn(OH)_4^{2-}$ at 100-180°C for 0.1-13h *



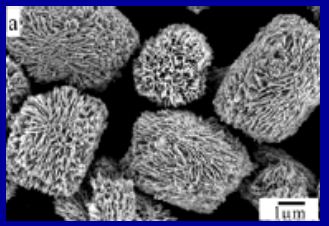
Prickly sphere-like



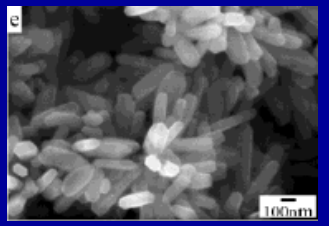
Prism-like



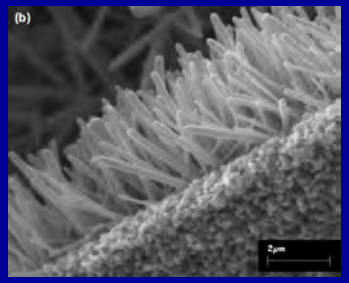
Flower-like



Sheet-like branch



Rod-like



Growth of Arrayed Nanorods and Nanowires of ZnO from Aqueous Solutions: in Zn^{2+}- HMT solution at 90-95°C for 1-10h**

*C.Yan, et al, Mater.Chem., **14**, 4172-4177, 2002

L.Vayssieres, et al, Adv. Mater., **15, 464-466, 2003

Experimental

Effect of zinc concentration, reaction time, reaction media, kinds of precipitates

Precursor: $Zn(NO_3)_2 \cdot 6H_2O$: 0.1 mM-1 M $[Zn^{2+}]$

Precipitants: Hexamethylenetetramine (HMT, $C_6H_{12}N_4$) ; Urea(N_2H_4CO)

$[Zn^{2+}]$: [HMT] or [urea]= 1:1

Reaction Media: Aqueous solution

50% organic solvent-50% aqueous solutions

(e.g. MeOH, EtOH, i-PrOH, Hexane, Ethylene Glycol et.al.)

Reaction Conditions: **95°C, 3-192 h, Together with a glass substrate**

$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3$ **(Hydrolysis)** **(1)**

$N_2H_4CO + H_2O \rightarrow CO_2 + 2NH_3$ **(Hydrolysis)** **(2)**

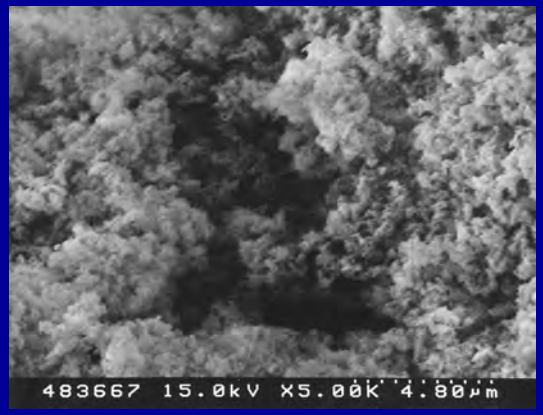
$Zn^{2+} + 4NH_3 + 4H_2O \rightarrow Zn(OH)_2 + 4NH_4^+ + 2OH^-$

$\rightarrow [Zn(NH_3)_4]^{2+} + 4H_2O \rightarrow ZnO + 2OH^- + 4NH_4^+ + H_2O$ **(Precipitation & Crystallization)** **(3)**

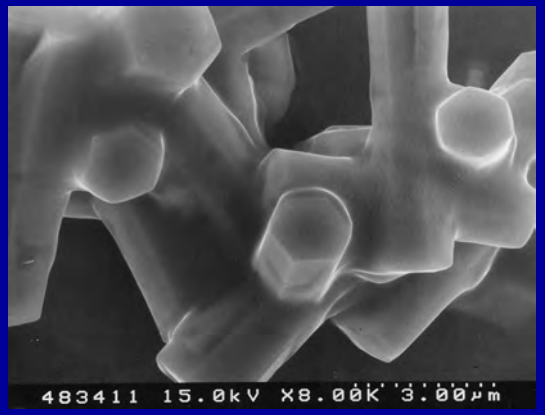
→realize the morphological control by a low-temperature heating process using various organic solvents;

→clarify the crystalline growth mechanism of ZnO with nano structures.

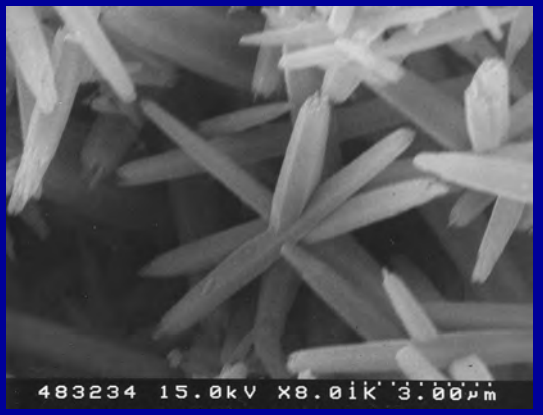
Results: Effect of Zn^{2+} concentration ---- Aqueous reaction system



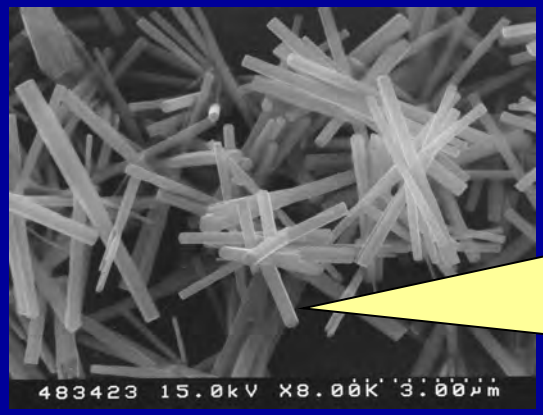
1M [Zn^{2+}]



0.1M [Zn^{2+}]



0.01M [Zn^{2+}]



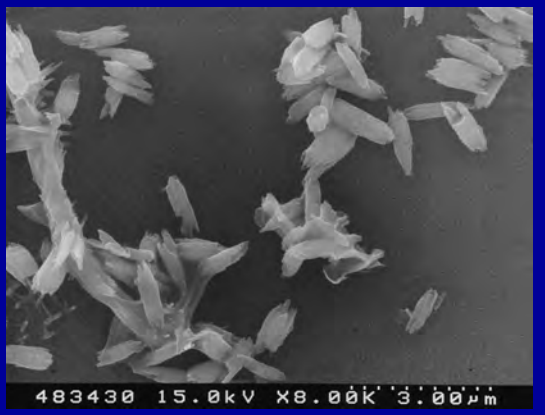
0.001M [Zn^{2+}]

0.001M [Zn^{2+}]

Homogeneous ZnO film on substrate

with

well -dispersed fine hexagonal particles



0.0001M [Zn^{2+}]

Fig. SEM photographs of ZnO powders prepared by heating various concentration of Zn^{2+}-HMT aqueous solution at 95°C for 3 h.

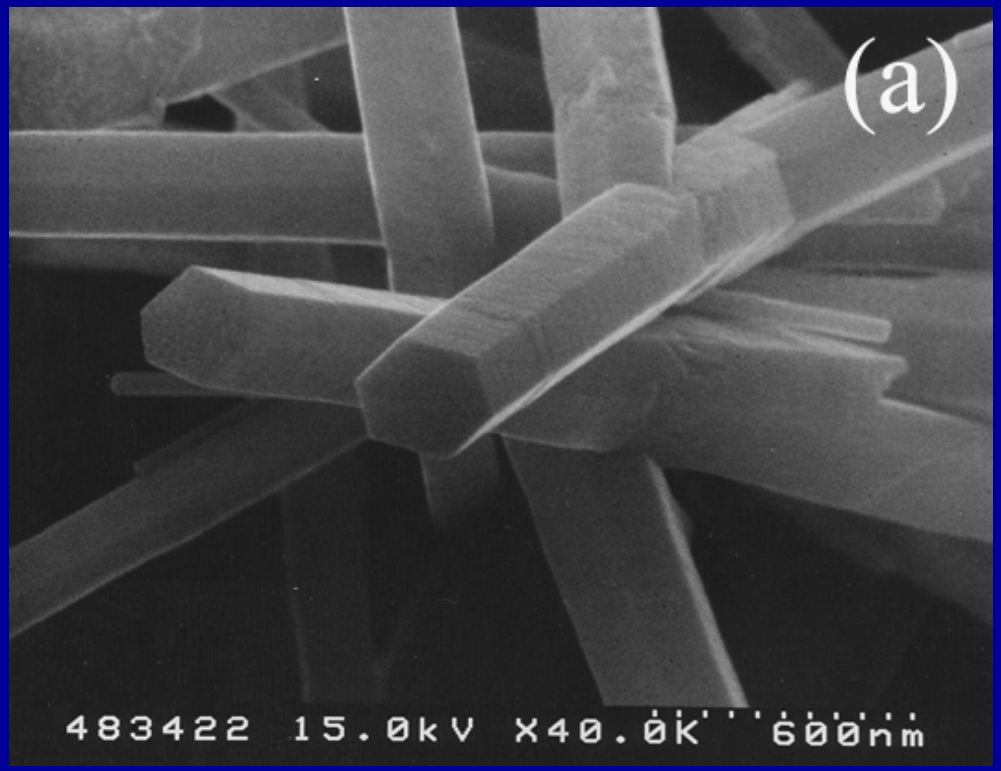
ZnO nano-rod can not be produced at high zinc concentration [Zn^{2+}] > 1 M

- Low concentration/precipitation rate prefer to form perfect crystalline structure

The crystalline size & aspect ratio of nano-rod decreased with [Zn^{2+}] concentration

Morphological Contral ---- in Aqueous reaction system

95°C, 3h



95°C, 76h

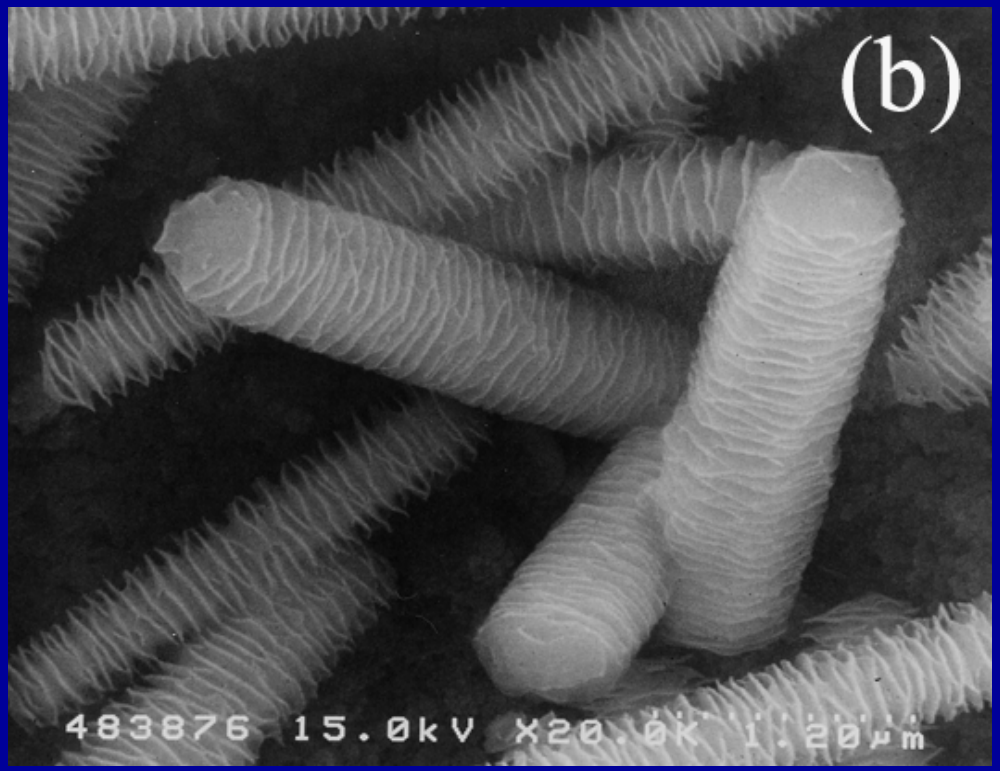
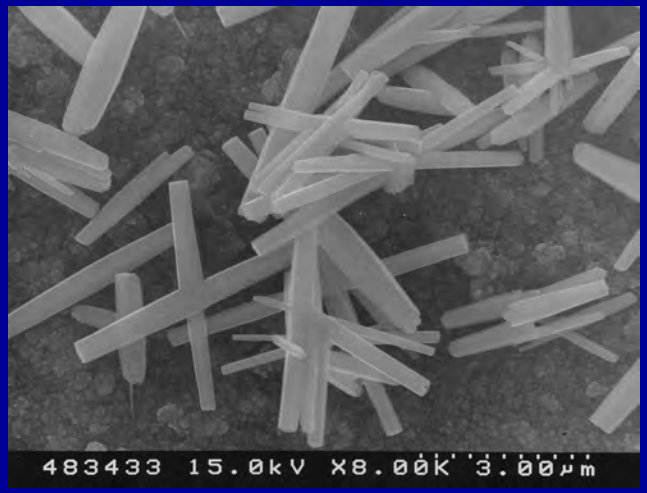


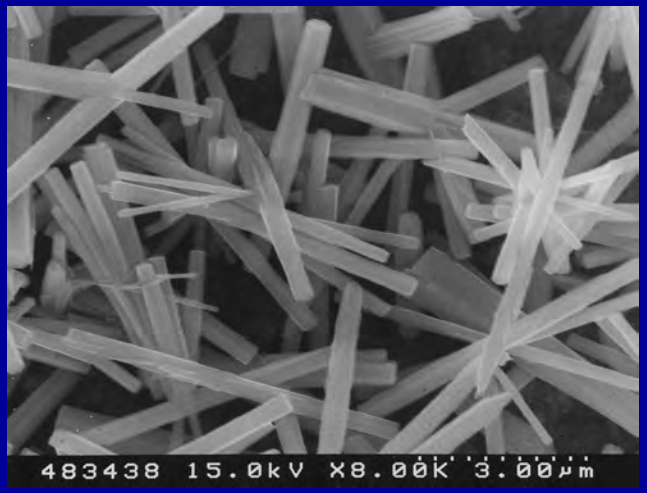
Fig. SEM images of (a)hexagonal and (b)screw-like ZnO nano rod prepared by heating Zn^{2+}-HMT aqueous solution at 95°C for 3 and 76 h, respectively.

Microstructure of ZnO also changed with treatment time

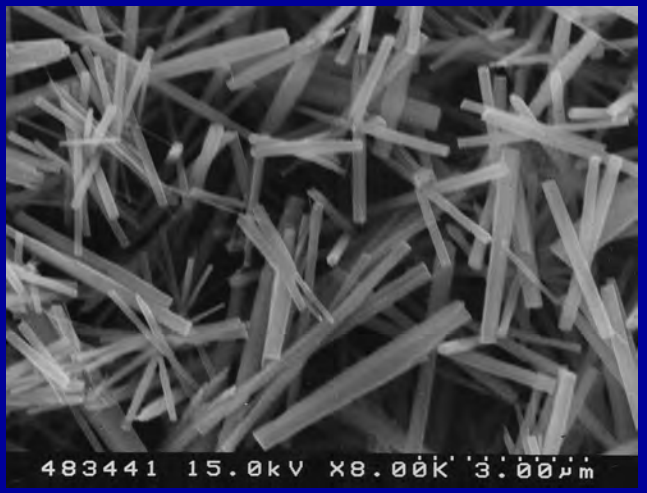
Effect of reaction time on the microstuucture of ZnO



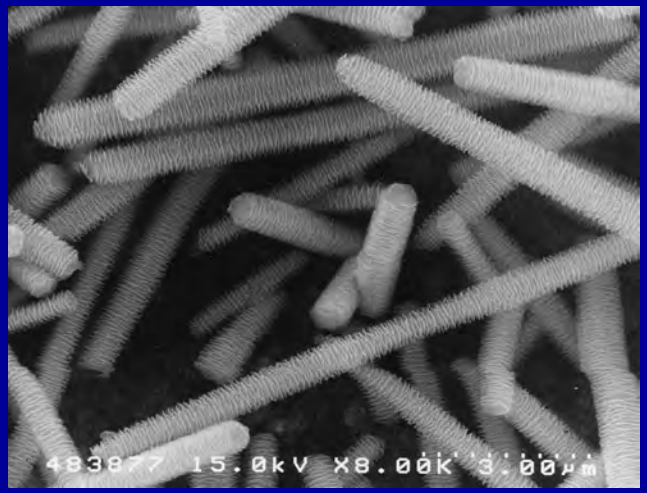
3.0 h



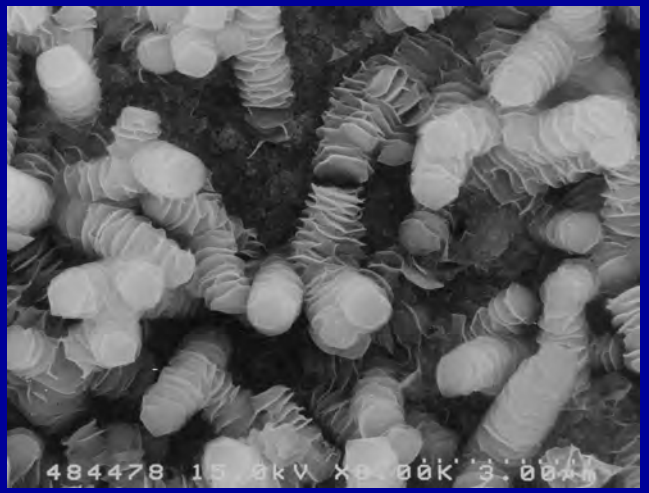
16 h



24 h



76 h



171 h

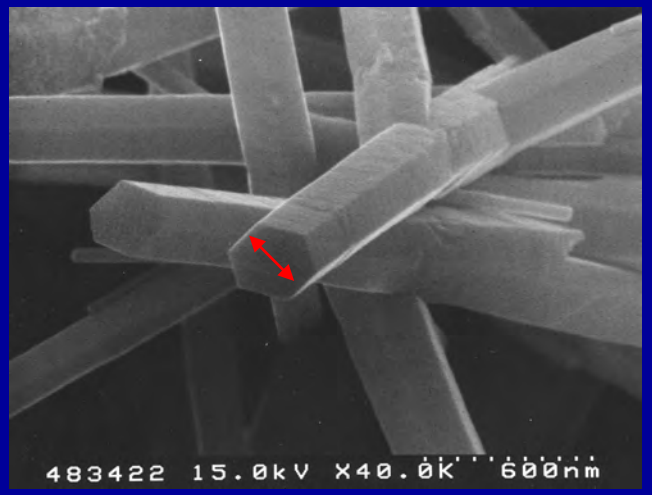
192 h

Fig. SEM images of ZnO nano particles prepared by heating Zn^{2+}-HMT aqueous solution at 95°C for different reaction time.

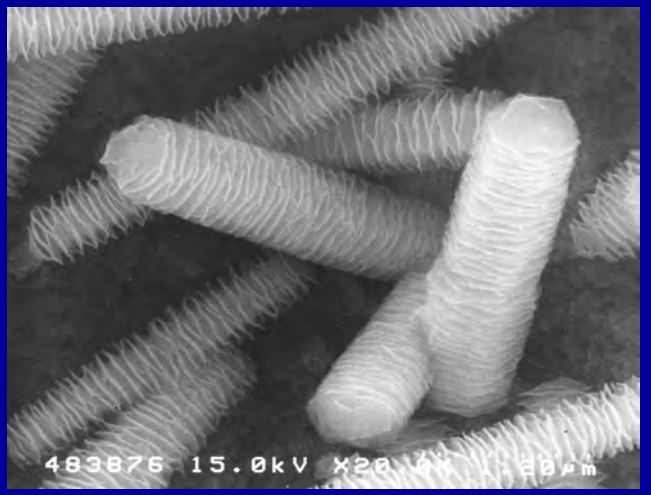
With the reactant concentration decreasing gradually during a further extension of reaction time, the effect of diffusion process affects the morphology and microstructure.

Formation mechanism of ZnO nano screw

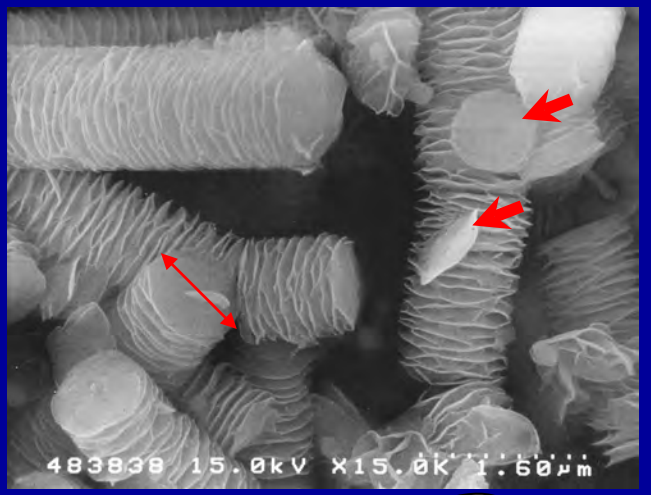
3.0 h

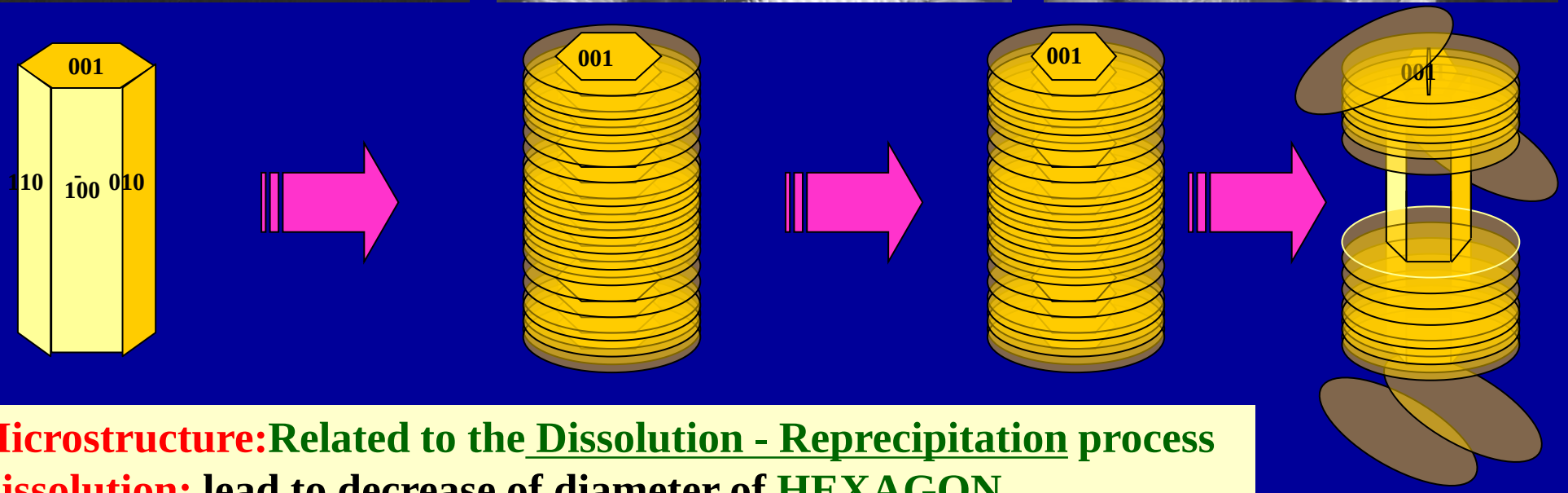


76 h



192 h





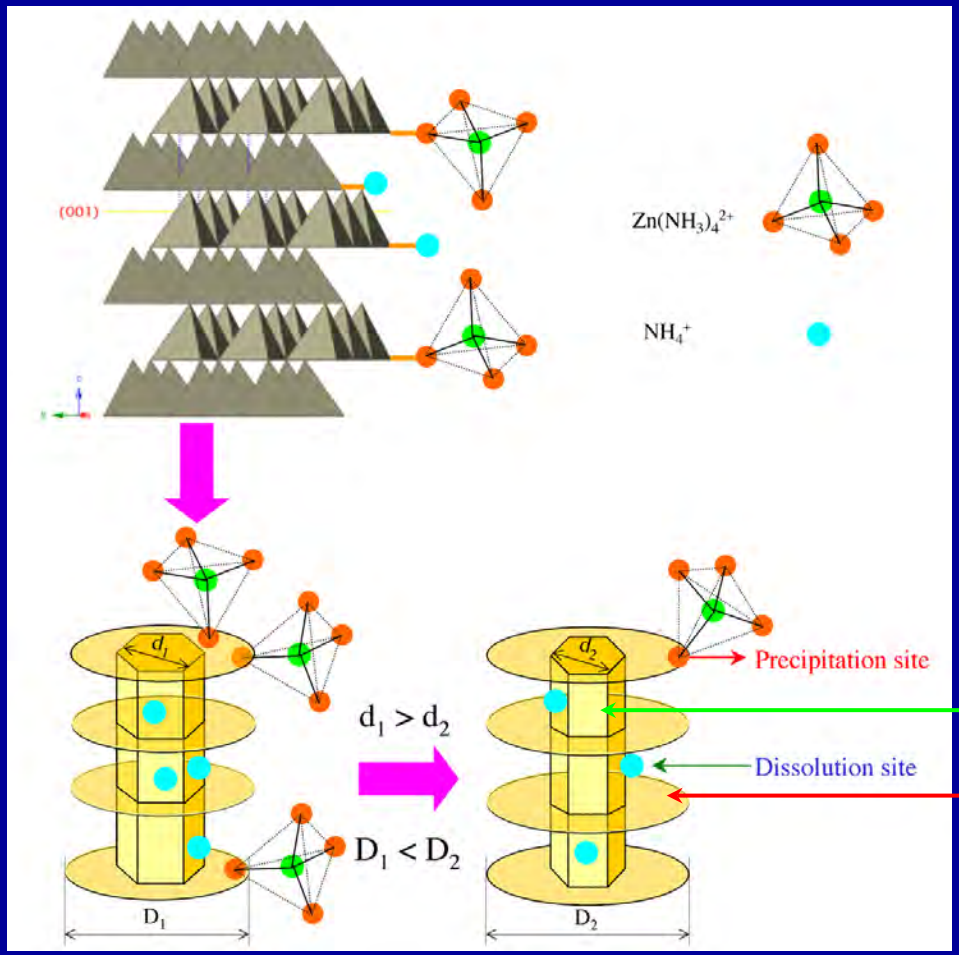
Microstructure: Related to the Dissolution - Reprecipitation process

Dissolution: lead to decrease of diameter of HEXAGON

Reprecipitation [at very low Zn^{2+} concentration]:

Lead to increase of diameter of SCREW & surface area

Formation mechanism of the nanoscrews from nanorods



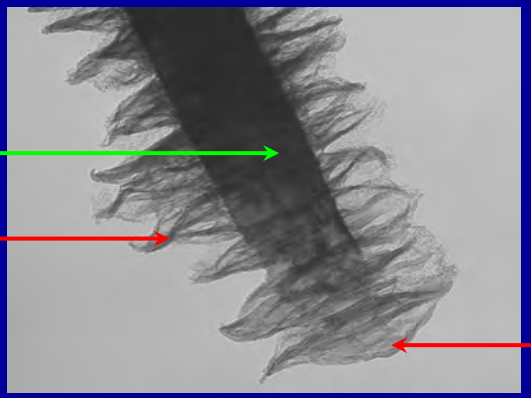
During the "Dissolution - Reprecipitation" process:

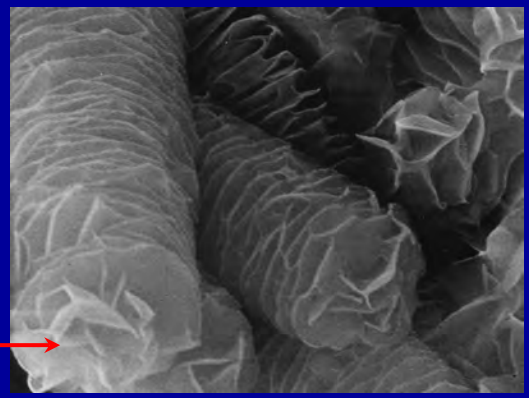
The existence of complex and molecules may affect the precipitation position

NH_4^+ adsorption site : Dissolution Site

$[Zn(NH_3)_4]^{2+}$ complex site : Precipitation Site

Selective precipitation on different direction /surface

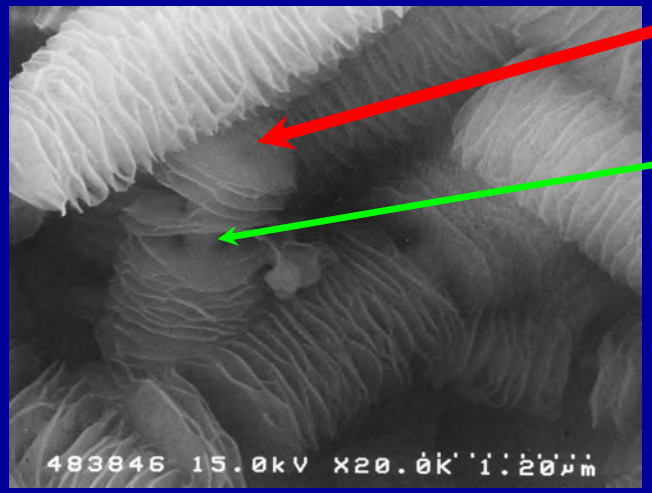


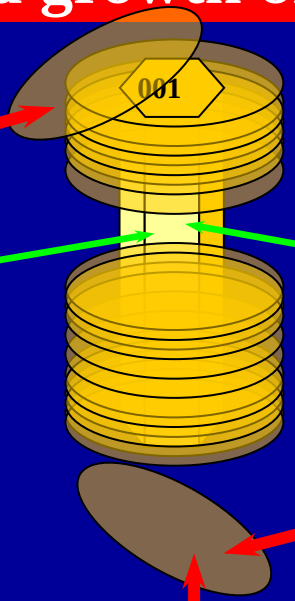


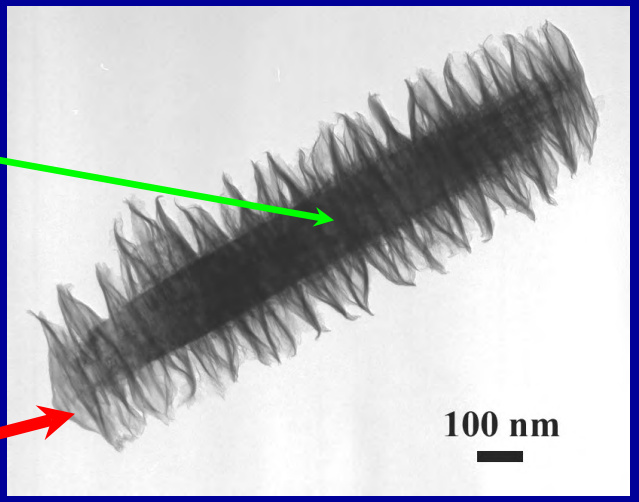
In most case, because of the repulsion force among the disks, $[Zn(NH_3)_4]^{2+}$ complex preferred to be adsorbed on the edge of the disks and crystallized to form large (001) area and lead to the "Formation of Parallel Disks".

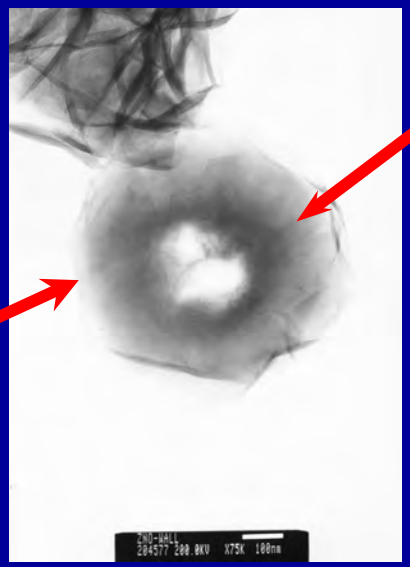
-- Low concentration prefers to form thin and large circle structure ?

ZnO Nano Screw --- Oriented growth of Zinc Oxide









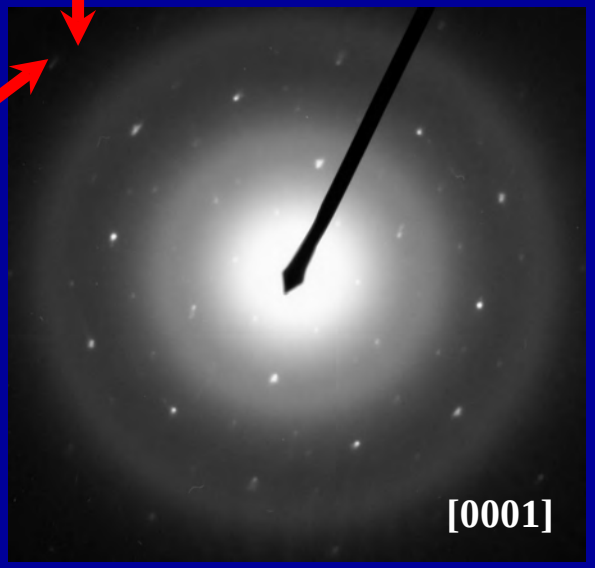
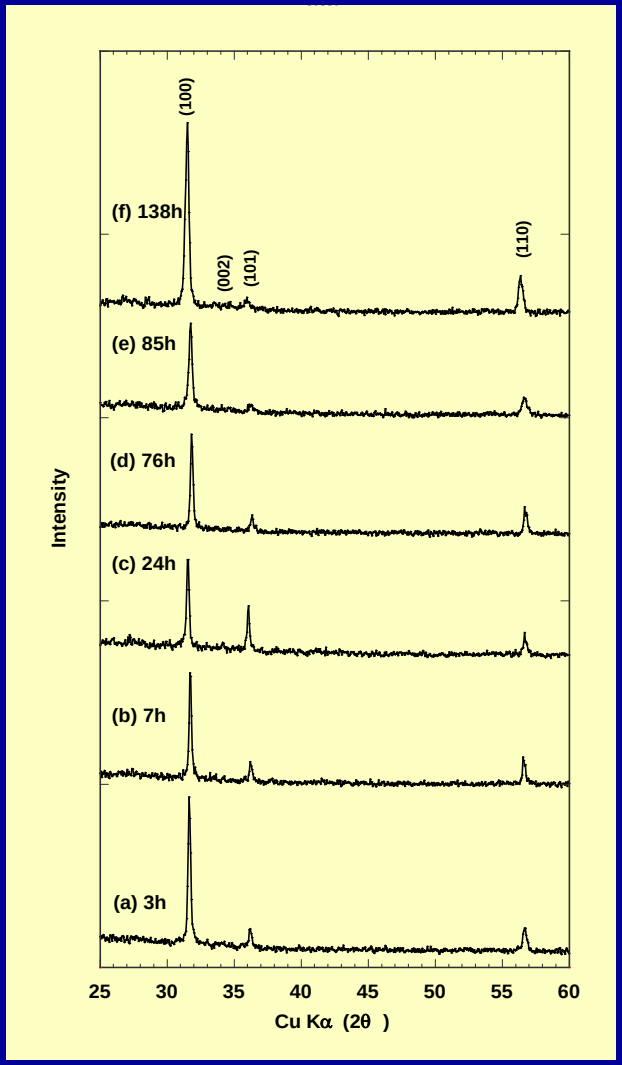
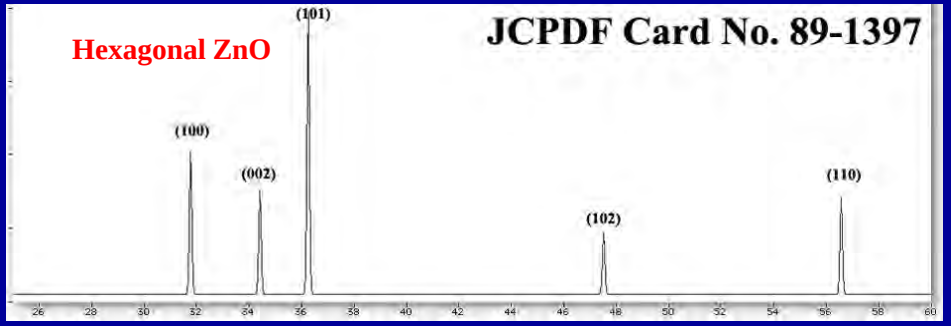
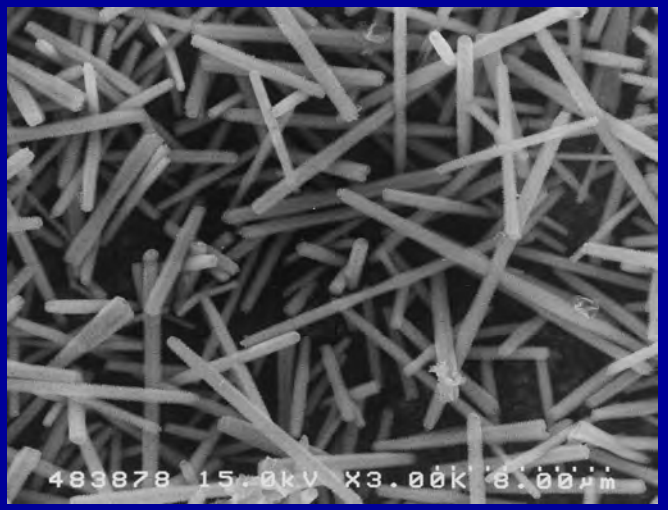


Fig. SEM, TEM, and electronic diffraction pattern of the screw-like ZnO nano particles prepared by heating Zn^{2+}-HMT aqueous solution at 95°C for 192h.

XRD of ZnO film on glass substrate ---- Aqueous reaction system







Aspect ratio = 10-25

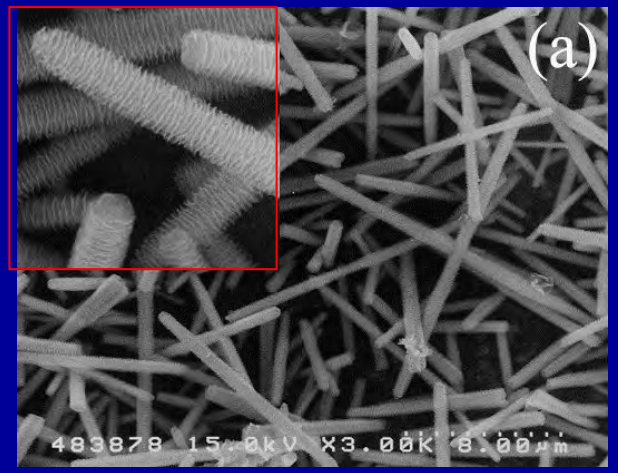
Almost no (002) peak can be observed by XRD analysis,

indicating nano-rod and nano-screw with large aspect ratio

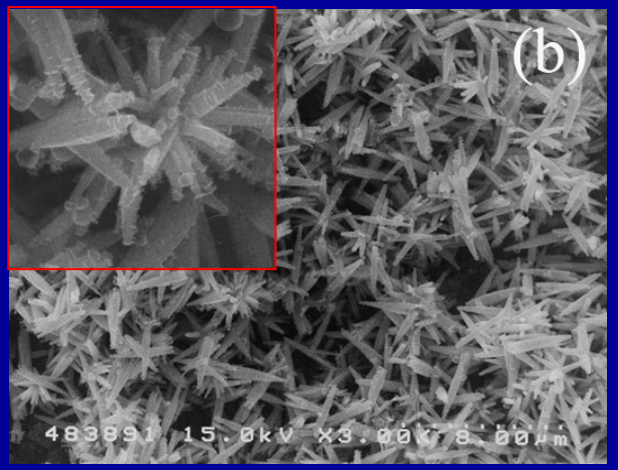
Lay down on the surface of substrate

(100) peak intensity increases with the development of nanostructure ZnO

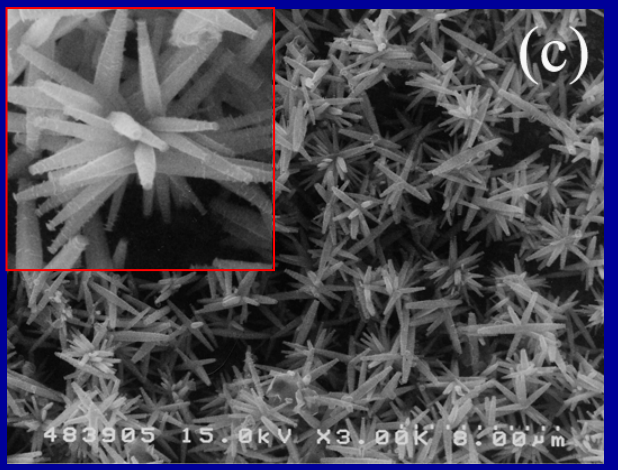
Effect of solvents: 50% organic solvent-50%aqueous solution system



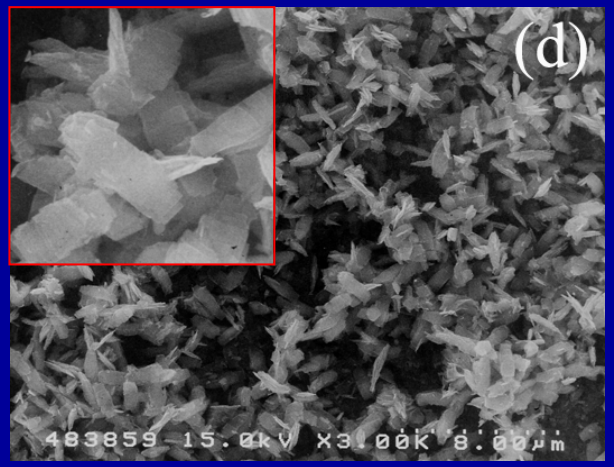
Aqueous



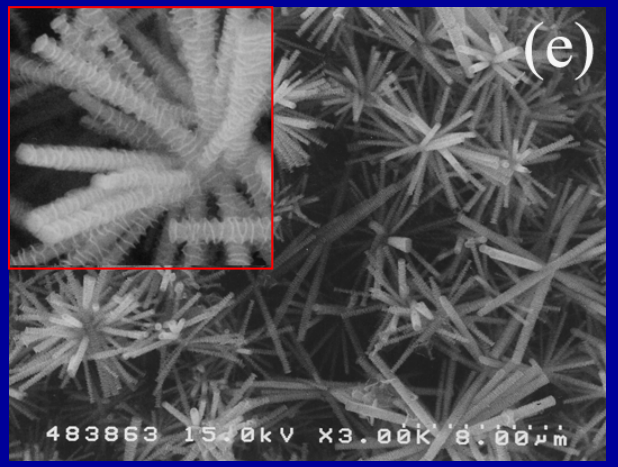
50% MeOH



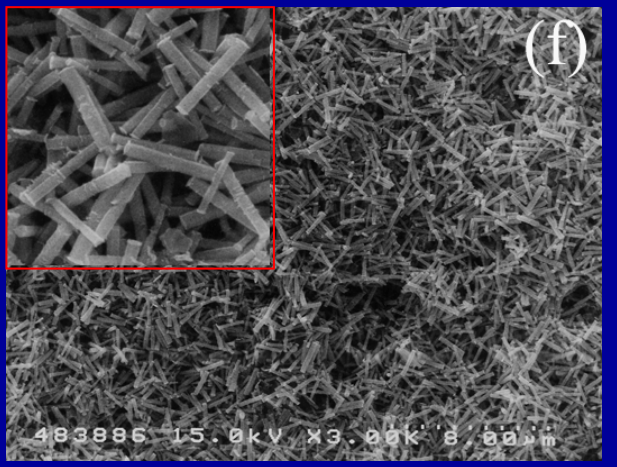
50% EtOH



50% i-PrOH



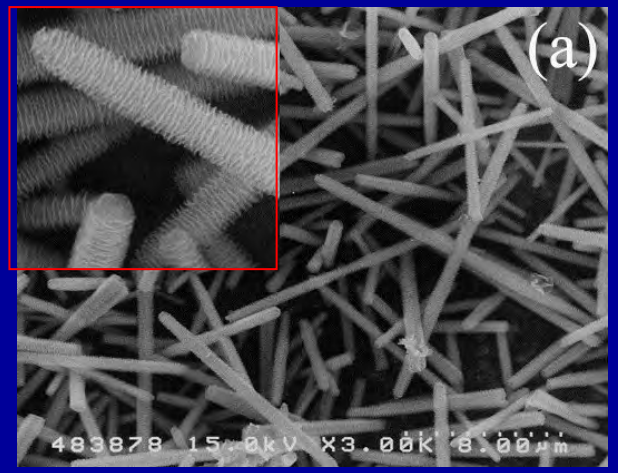
50% Hexane



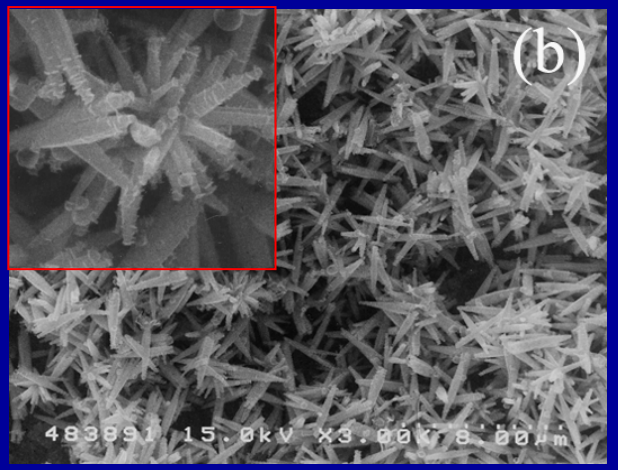
50% Ethylene Glycol

Fig. SEM images of the zinc oxide prepared by heating 1 mM Zn^{2+}-HMT aqueous solution(a), 50% methanol aqueous solution (b), 50% ethanol aqueous solution (c), 50% i-propanol aqueous solution (d), 50% hexane aqueous solution (e), and 50% ethylene glycol aqueous solution (f) at 95°C for 76h.

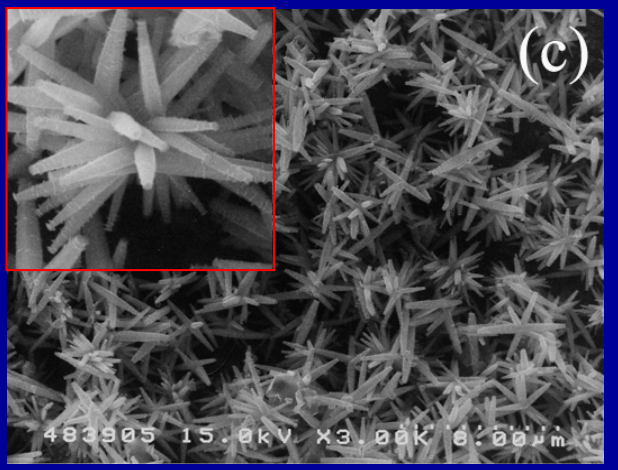
Effect of solvents: 50% organic solvent-50%aqueous solution system



Aqueous



50% MeOH



50% EtOH

Aqueous: Monodispersed nano screw with large aspect ratio

---> Larger precipitation rate on (002) direction

50% MeOH / EtOH : Symbiotic nano-rod with small aspect ratio

---> Low solubility lead to small particle size

& smaller precipitation rate on (002) direction

Fig. SEM images of the zinc oxide prepared by heating 1 mM Zn^{2+}-HMT aqueous solution(a), 50% methanol aqueous solution (b), 50% ethanol aqueous solution (c), 50% i-propanol aqueous solution (d), 50% hexane aqueous solution (e), and 50% ethylene glycol aqueous solution (f) at 95°C for 76h.

Effect of solvents: 50% organic solvent-50%aqueous solution system

50% i-PrOH: Similar structure to that of weak Zn^{2+} aqueous solution

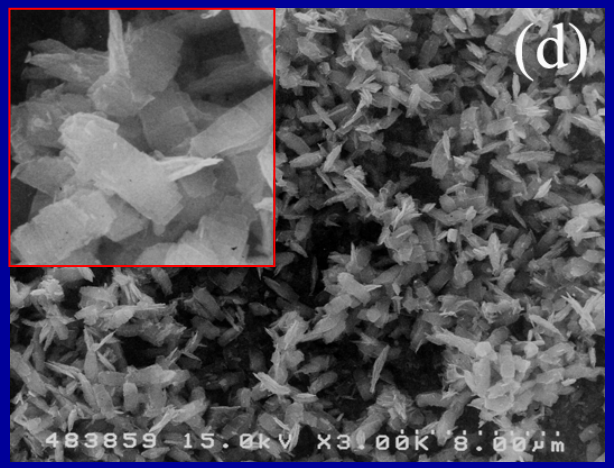
---> Low solubility lead to poor crystalline structure

50% Hexane: Symbiotic nano-screw with large aspect ratio

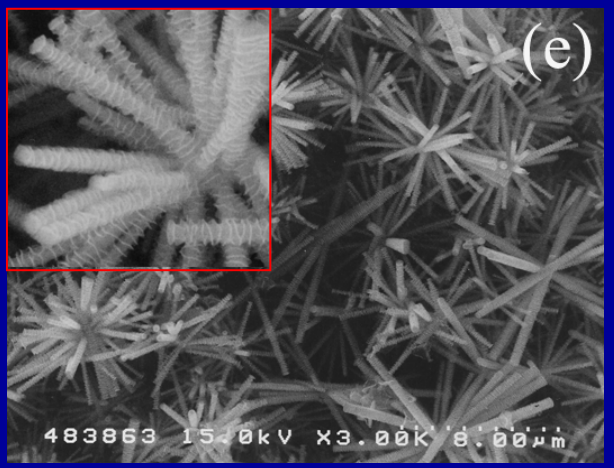
---> Hydrophobic property of hexane lead to
the same structure with that obtained in 2 mM aqueous solution

50% Ethylene Glycol: Monodispersed nano rod with small aspect ratio

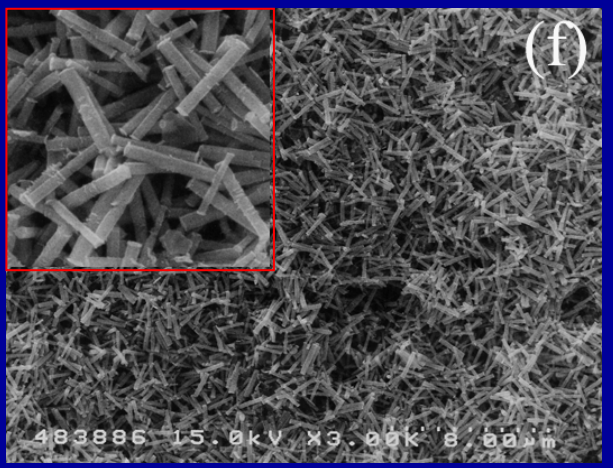
---> EG depress the growth on (002) direction of ZnO crystalline



50% i-PrOH



50% Hexane

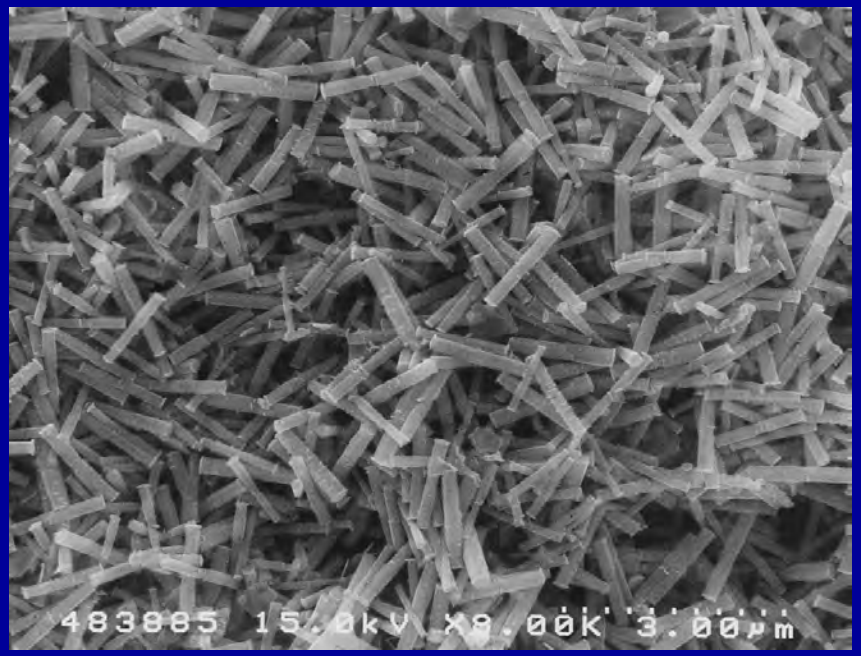


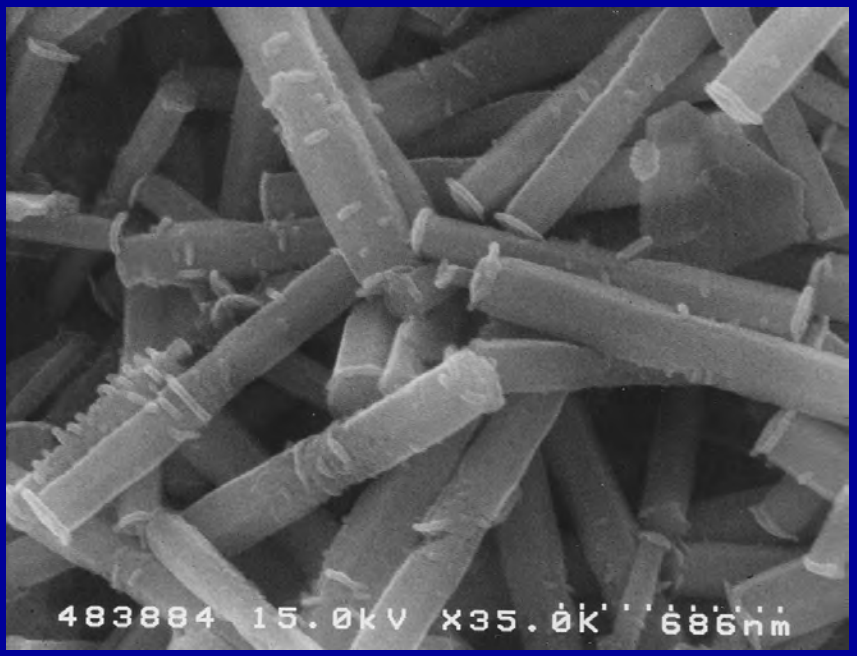
50% Ethylene Glycol

Fig. SEM images of the zinc oxide prepared by heating 1 mM Zn^{2+}-HMT aqueous solution(a), 50% methanol aqueous solution (b), 50% ethanol aqueous solution (c), 50% i-propanol aqueous solution (d), 50% hexane aqueous solution (e), and 50% ethylene glycol aqueous solution (f) at 95°C for 76h.

Effect of solvents: 50% organic solvent-50%aqueous solution system

50% Ethylene Glycol: Monodispersed nano rod with small aspect ratio

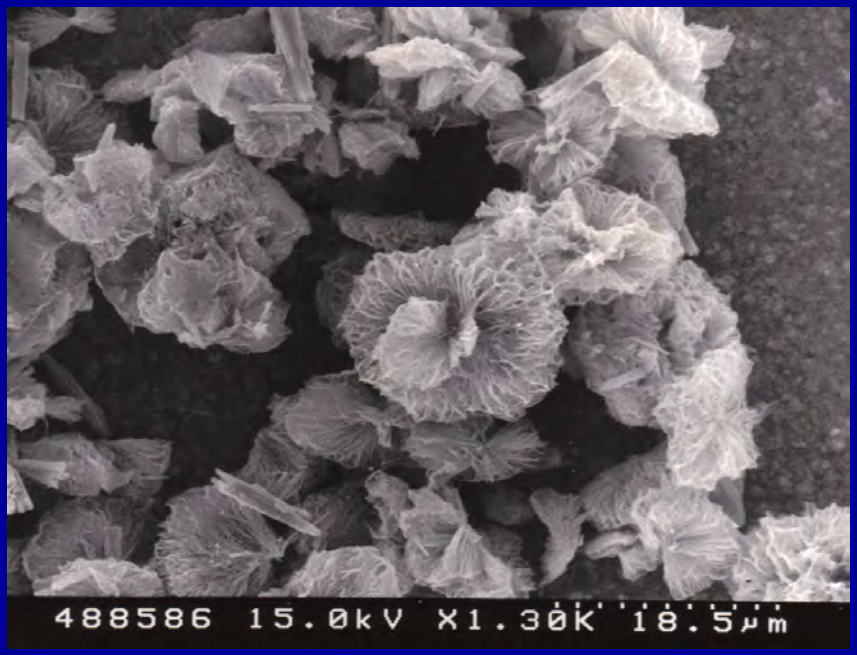




Homegeneous Particle Size, Diameter and Aspect ratio

Length ≒ 1.35 μ; Diameter≒0.19 μ ; Aspect ≒ 7,

Effect of Precipitant ---- Urea Aqueous Solution System



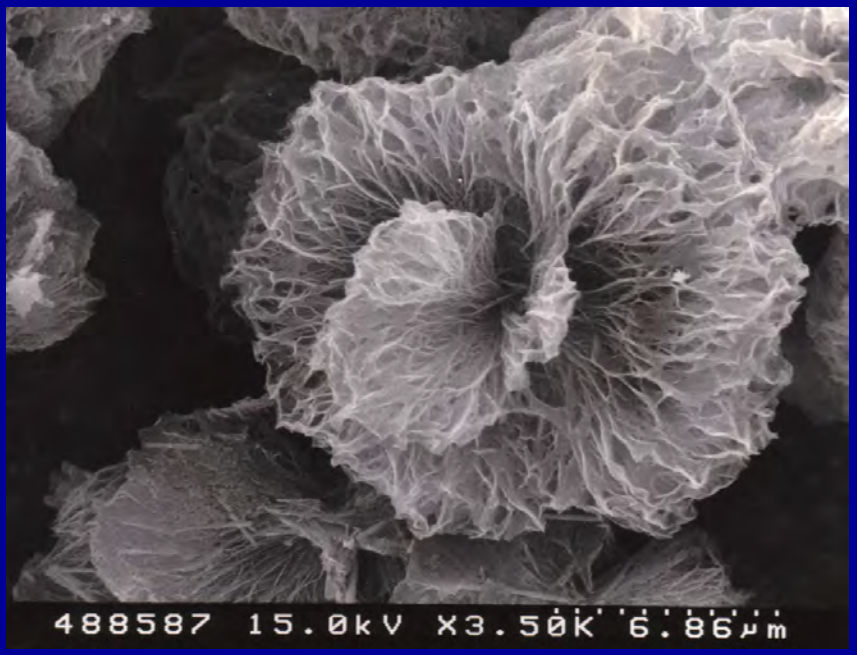


Fig. SEM images of the zinc oxide prepared by heating 1 mM Zn^{2+}-Urea aqueous solution at 95°C for 76h.

Instead of nano-rod and nanoscrew, another type of micro-folwer with superstructure can be formed in urea system.

---- No rod-like particles can be produced.

Effect factors on the microstructure of ZnO particles:

Solvent effect:

different dielectric constant
viscosity
shows different diffusion coefficient
different solubility of ZnO
lead to different nuclear formation rate
different morphology
during the dissolution-reprecipitation process.

Zinc complex formation:

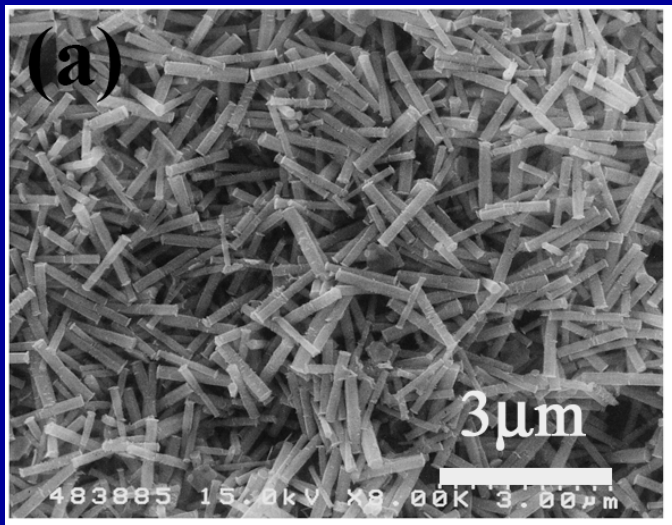
affect the nuclear growth during the reprecipitation

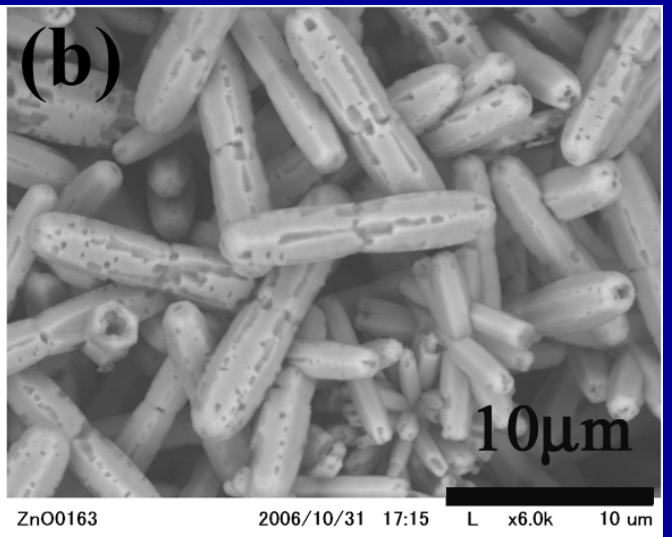
Zinc ion: easy to form 4-coordinated tetrahedron structure
6-coordinated octahedron structure

Structure of zinc complex: affected by the existence of
ammonia, HCHO, CO_2 and solvent (e.g. EG)

Effect of Precursors: 50% EG-50%aqueous solution system

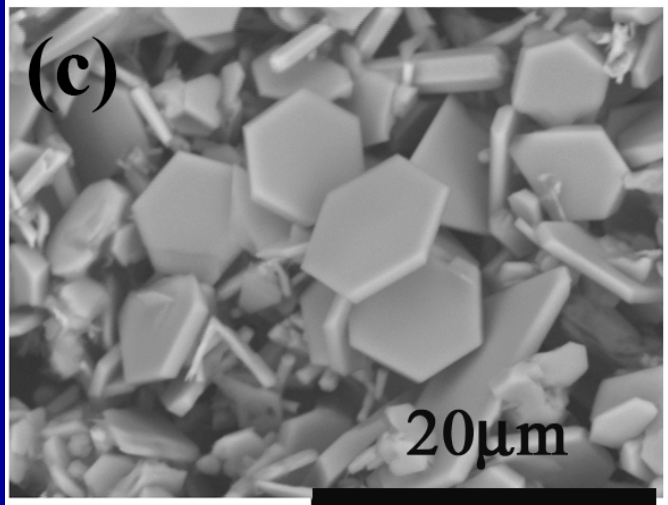
ZnO:
Monodispersed nano rod
L ≒ 1.35 μ;
D≒0.19 μ ;
Aspect ≒ 7,
in
0.001M $ZnNO_3$

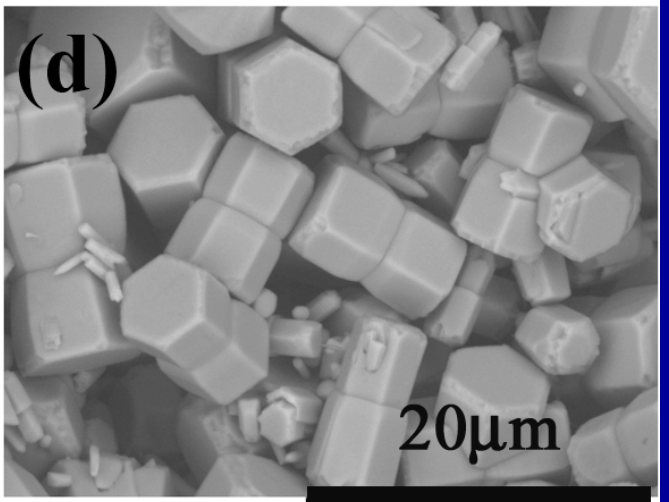




ZnO:
Porous Rod
in
0.05M $ZnNO_3$

$Zn_5(OH)_8Cl_2 \cdot H_2O$:
Simonkoleite
in
0.05M $ZnCl_2$





ZnO Nut:
in 0.05M $Zn(CH_3COO)_2$

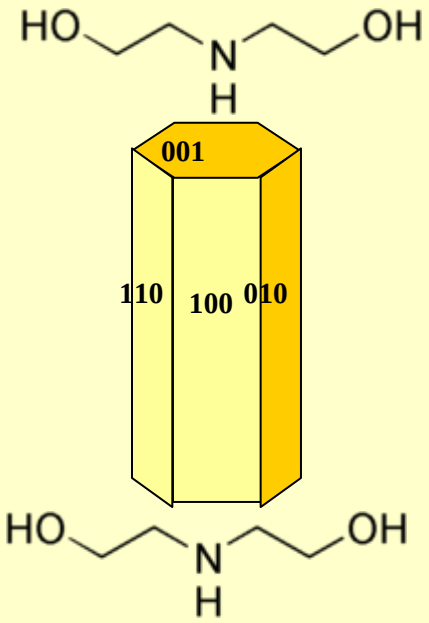
SEM photographs of ZnO particles prepared from (a)0.001M $Zn(NO_3)_2$, (b)0.05M $Zn(NO_3)_2$, (c) 0.05M $ZnCl_2$, (d)0.05M ($Zn(CH_3COO)_2$ solutions with 50% EG additive at 95°C for 3h.

Effect of aging treatment on the surface structure

Spherical particles:

Additive of surfactant

(Diethanolamine)



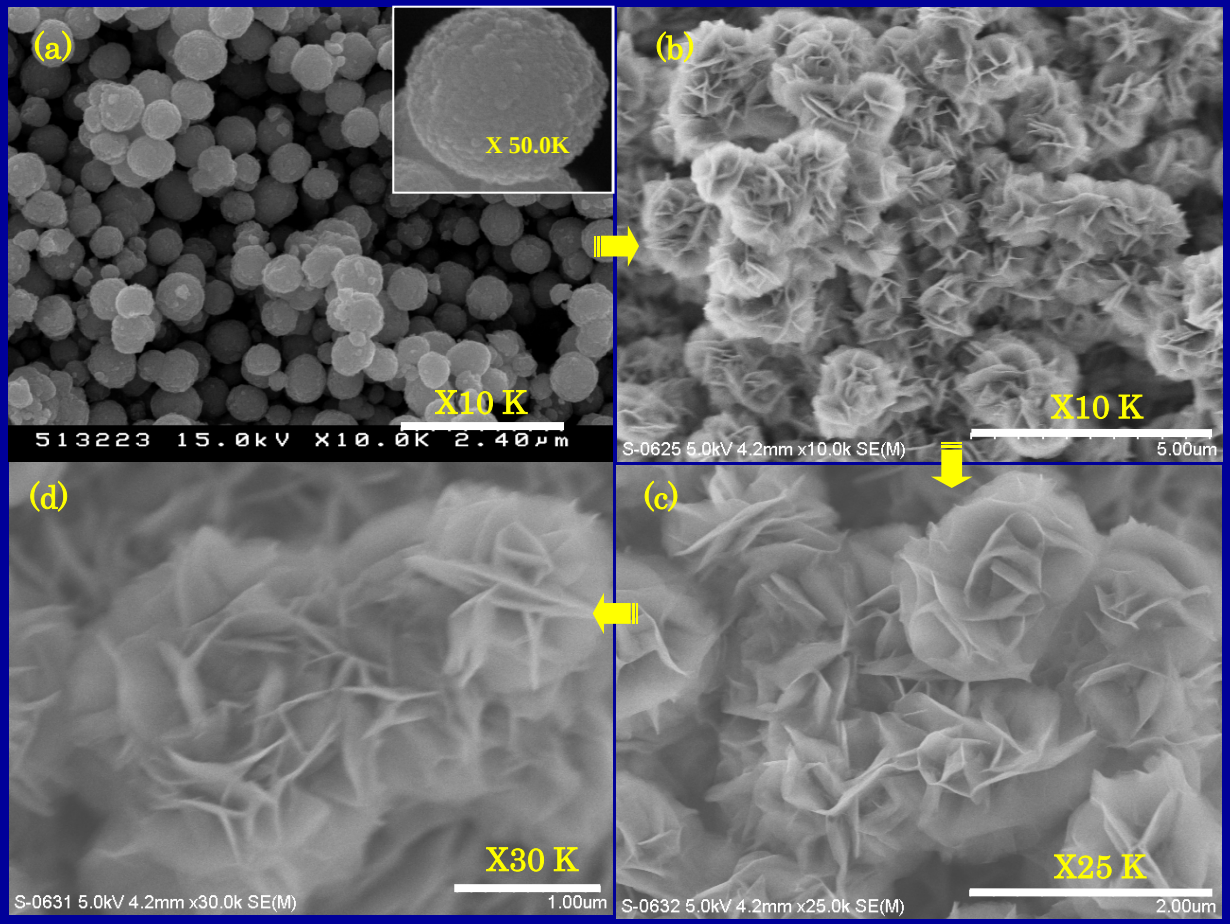
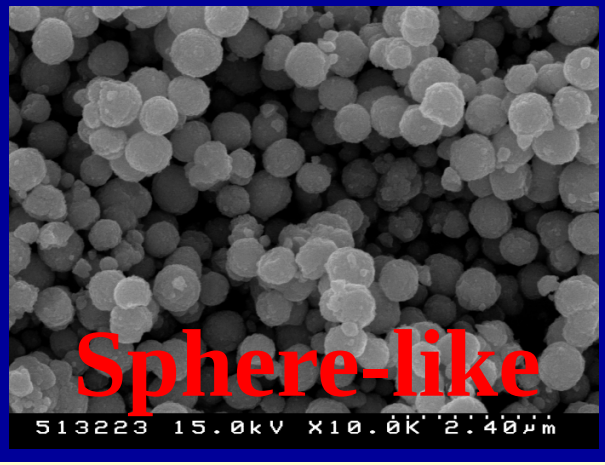
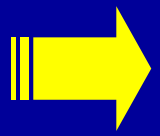


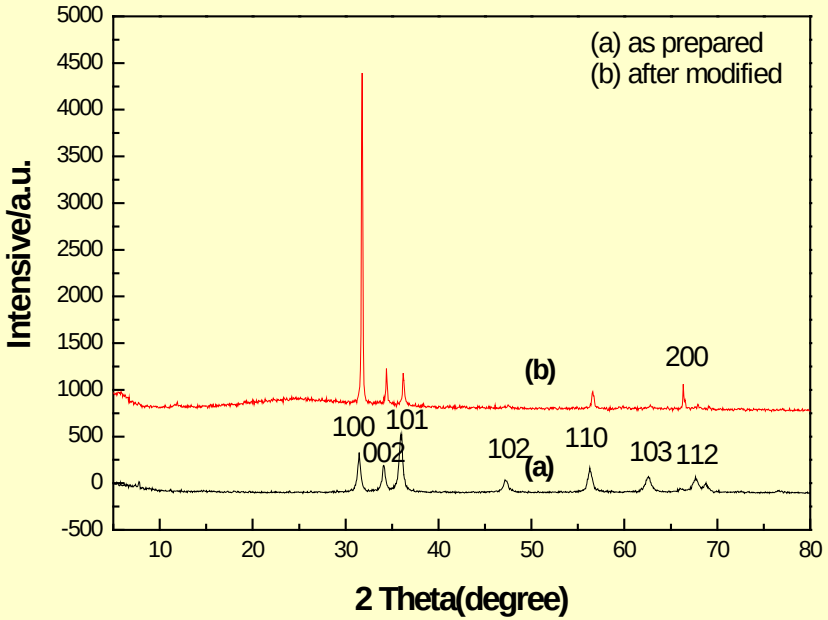
Fig. SEM images of ZnO films consisted of (a) sphere-like; (b, c, d) 3D flower-like superstructures with different magnifications

Not only the rod-like particles, but also spherical particles with developed superstructures could be formed by the dissolution - reprecipitation process

Physical-Chemical Properties







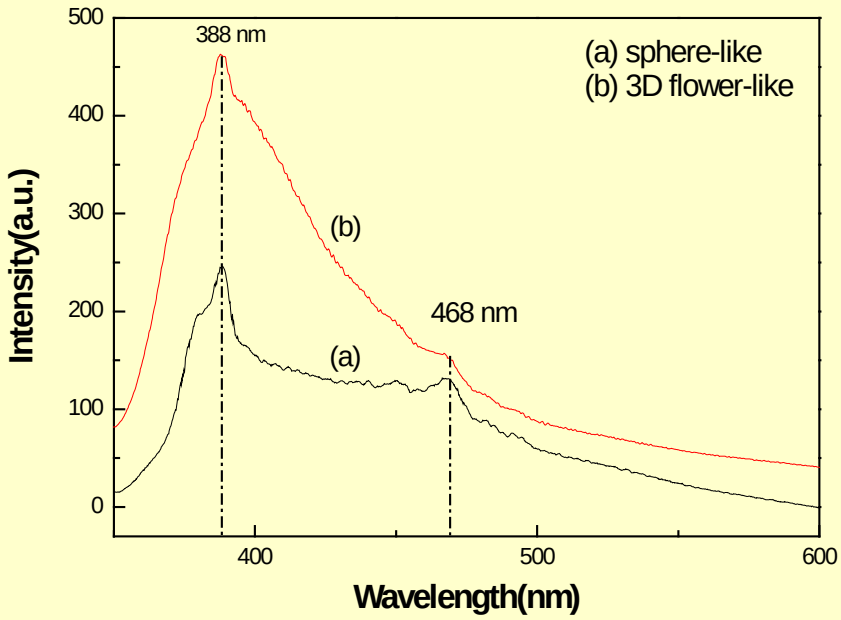
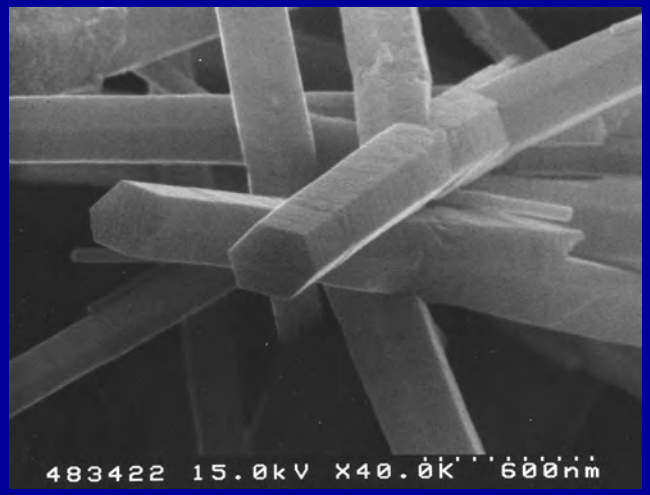
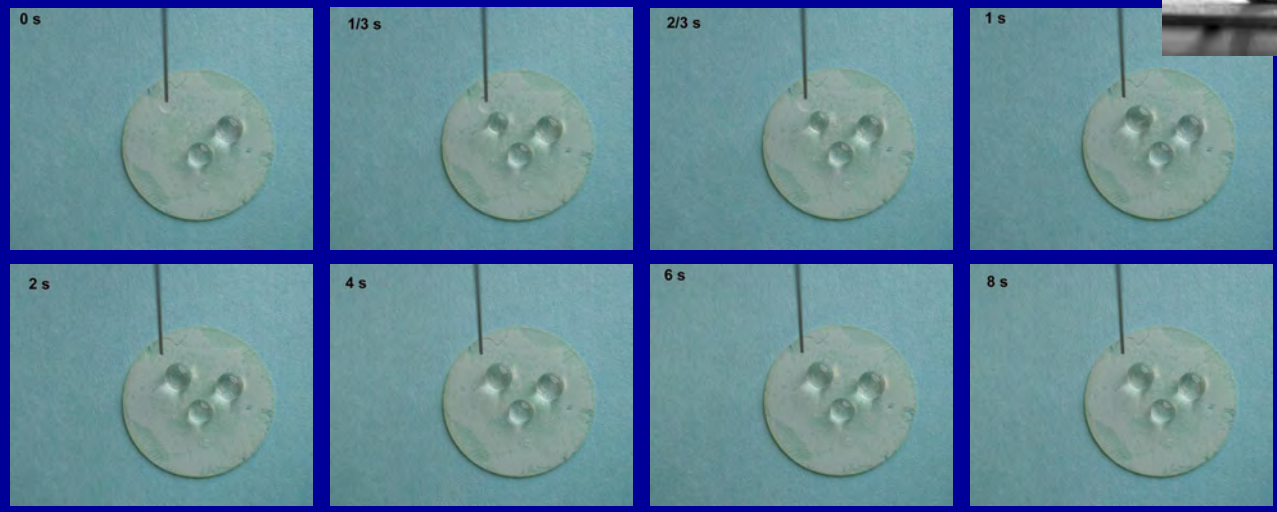


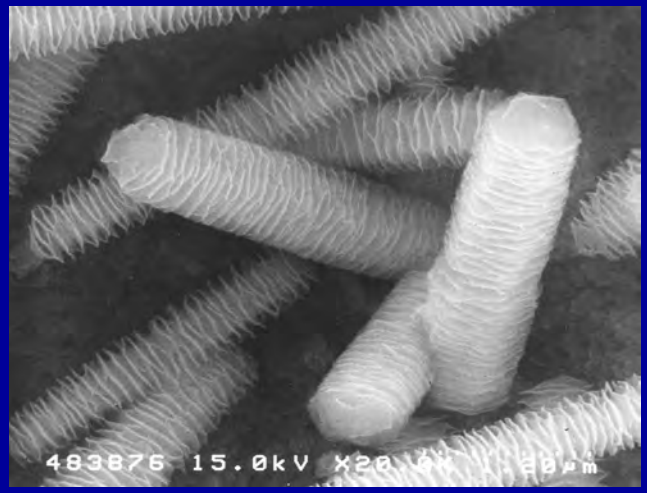
Fig. XRD patterns (Left) and room-temperature photoluminescence spectra (Right) of the ZnO thin films consisted of different superstructures. (a) sphere-like (b) 3D flower-like.

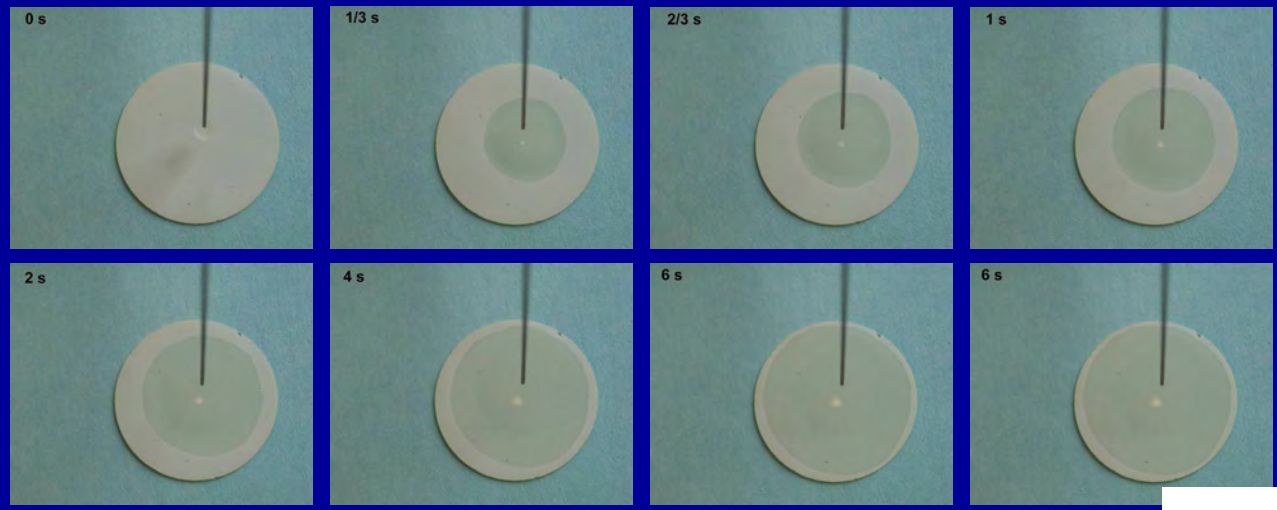
Hrdrophilicity of ZnO film with various morphologies





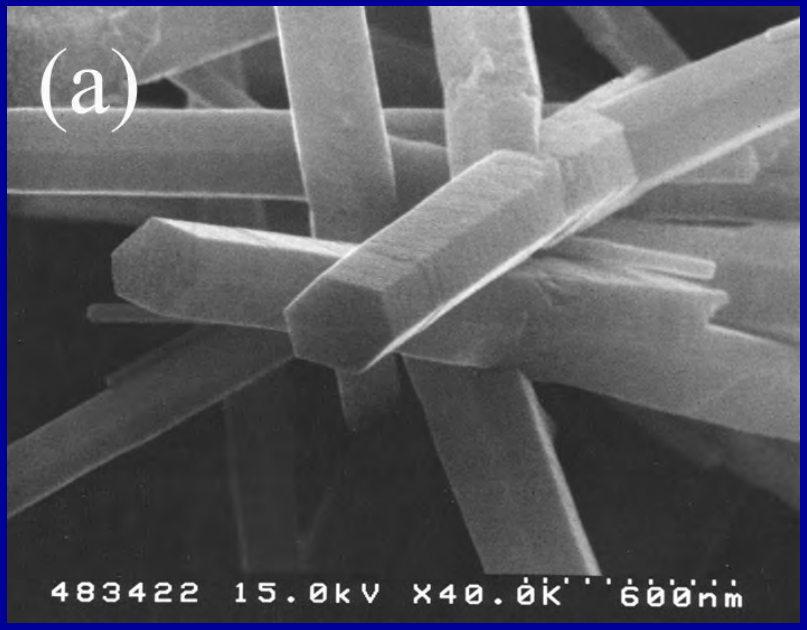
Superhydrophobic surface

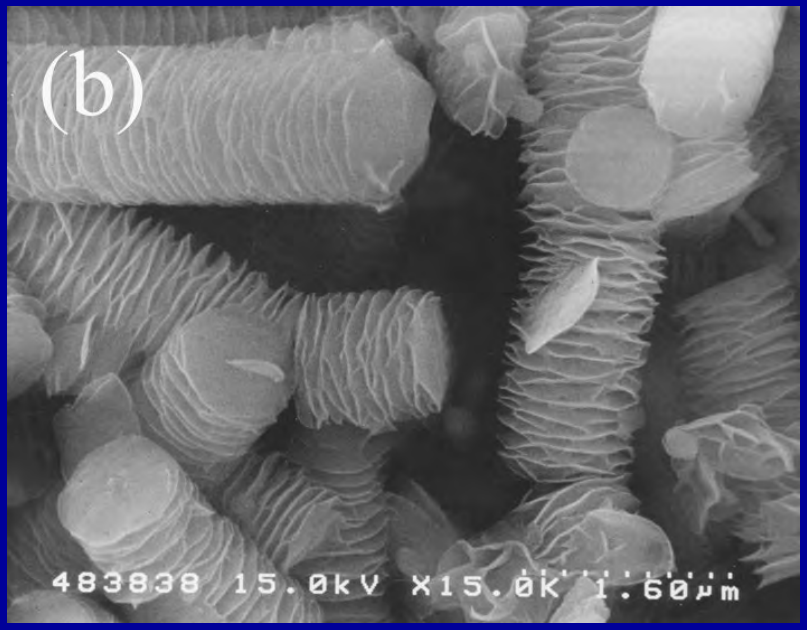


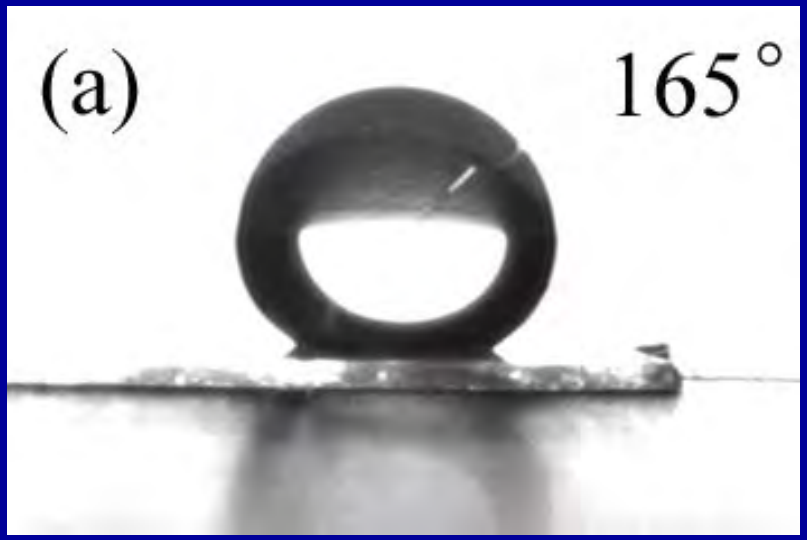


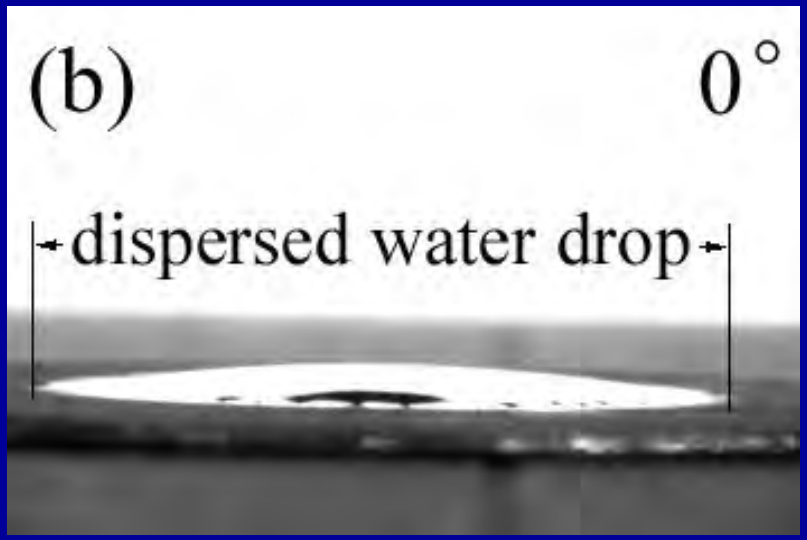
Superhydrophilic surface

Hydrophobicity and Hrdrophilicity of ZnO film with various morphologies







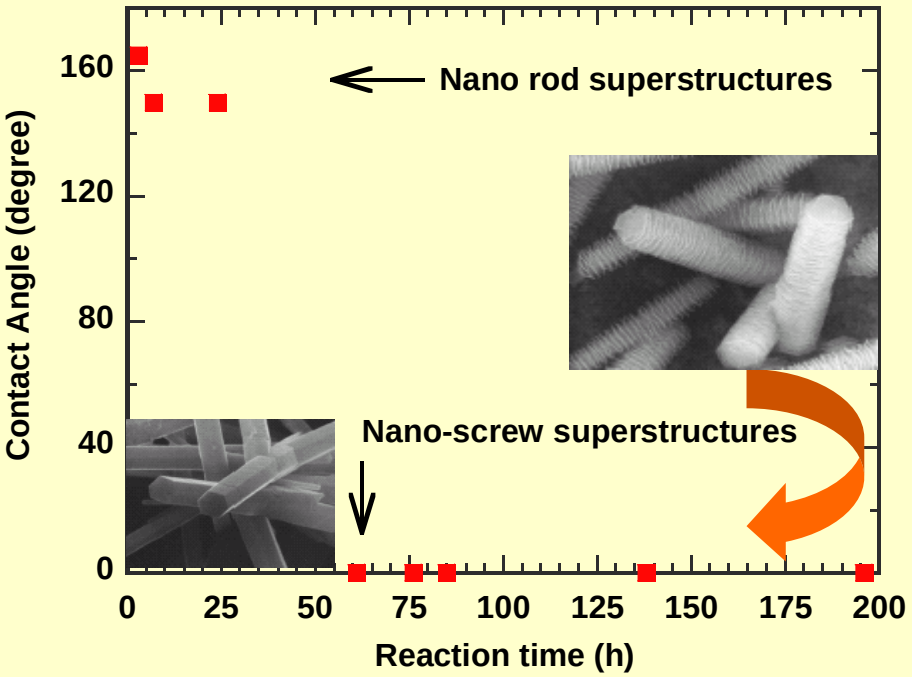


Superhydrophobic surface

Superhydrophilic surface

Physical-Chemical Properties

Contact angle



Active oxygen species

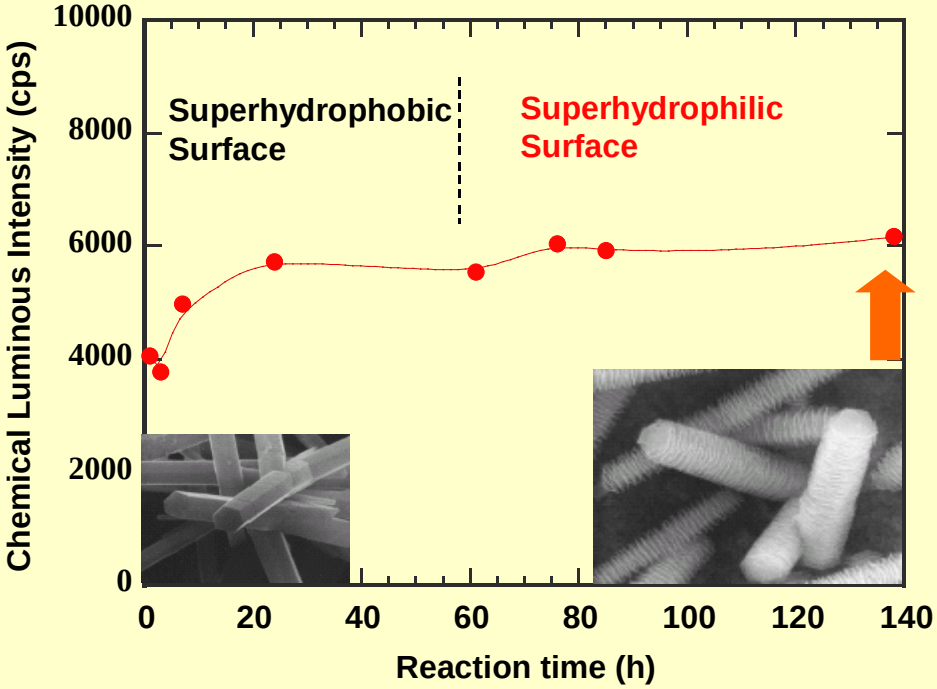
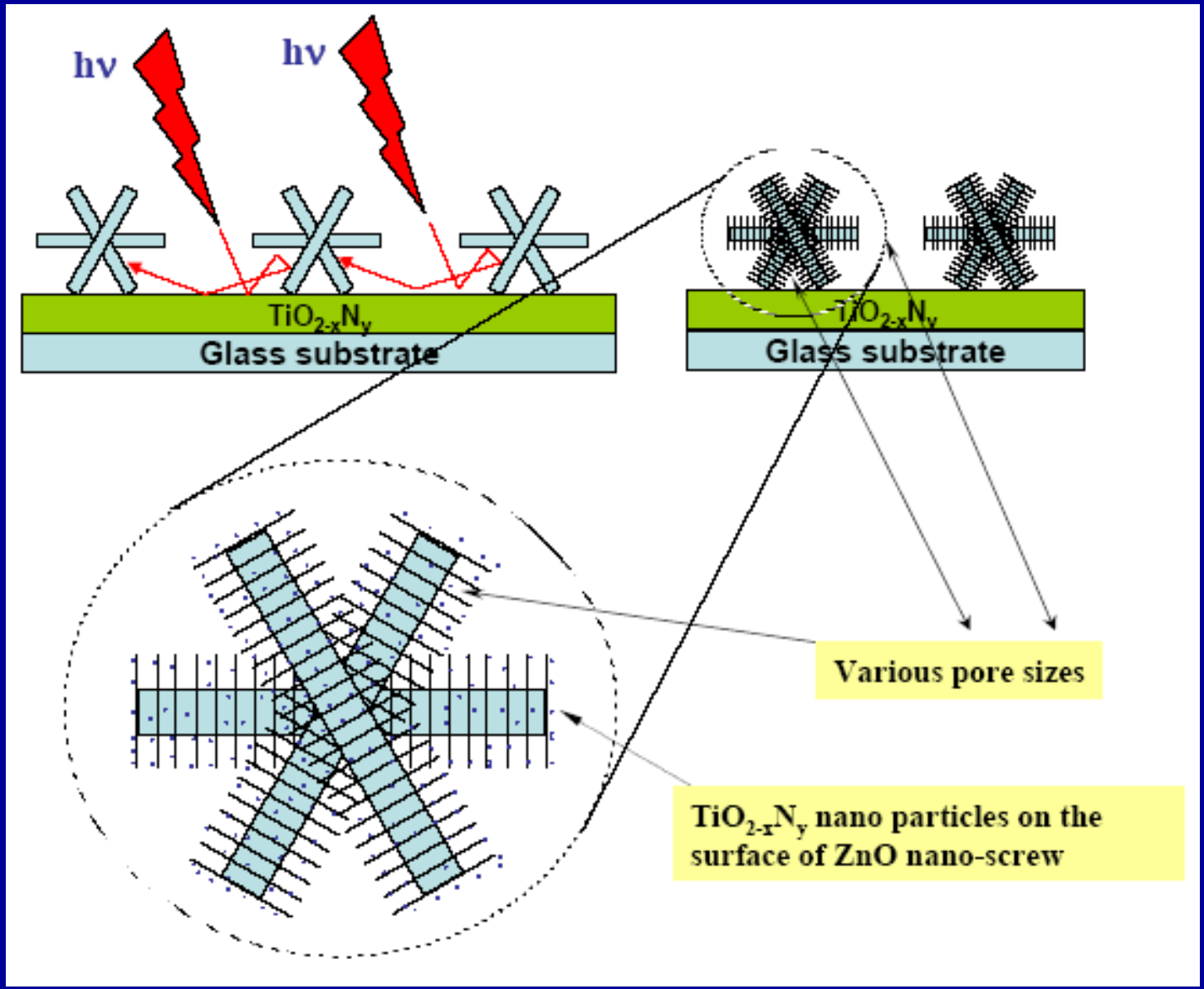


Fig. The contact angle and the chemical luminous intensity of water drops on the surface of ZnO films of ZnO films prepared by heating Zn^{2+}-HMT aqueous solution at 95°C for various reaction times.

Formation of Sandwich structure thin film



Synthesis and Photocatalytic Activity of $TiO_{2-x}N_y$ / ZnO Nano-screw / $TiO_{2-x}N_y$ composites

Formation of Sandwich structure thin film

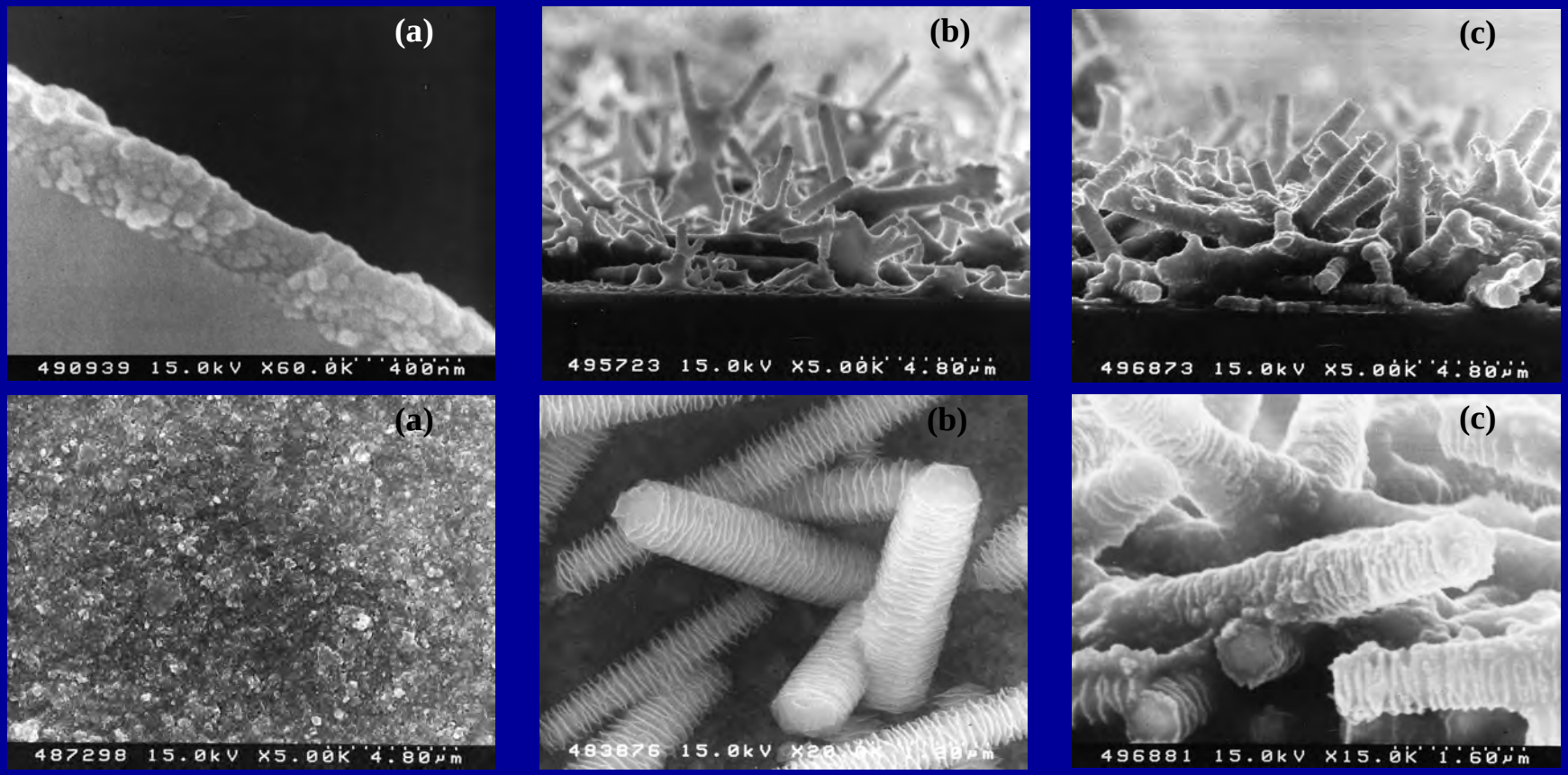
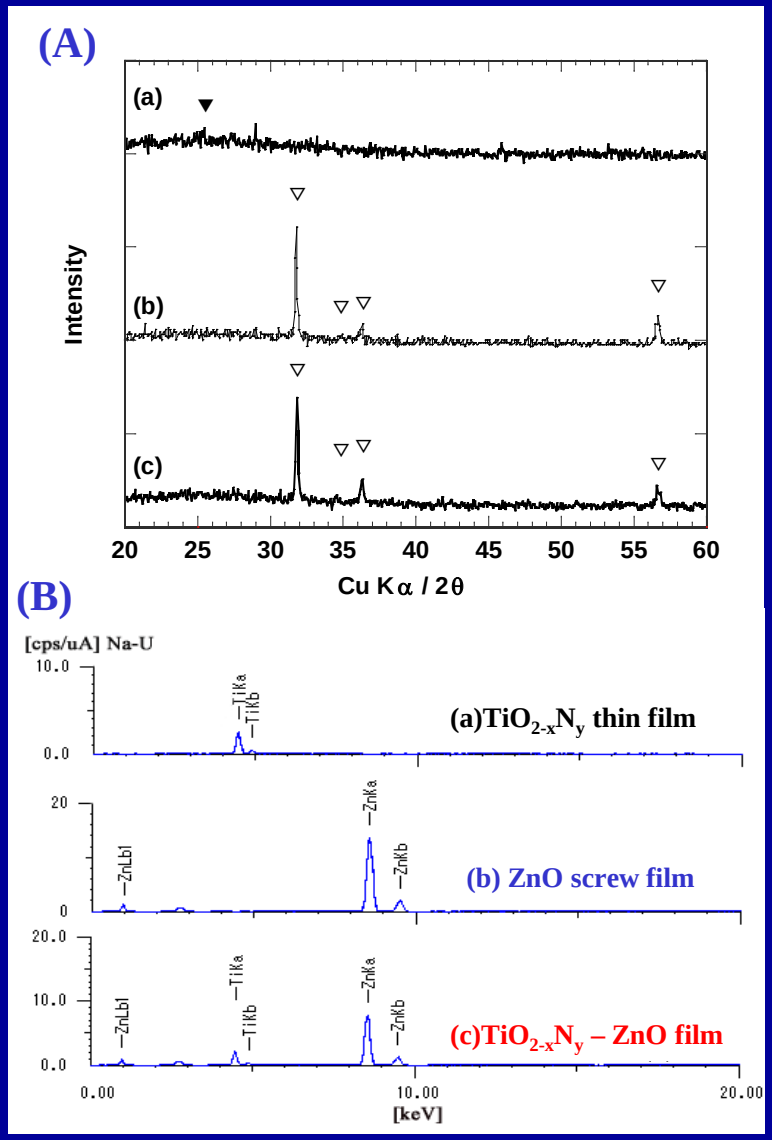


Fig. Scanning electron micrographs of (a)$TiO_{2-x}N_y$ thin film, (b)ZnO screw film, and (c)$TiO_{2-x}N_y$/ZnO composite film. Upper: cross section; Lower: Top view.

Formation of Sandwich structure thin film



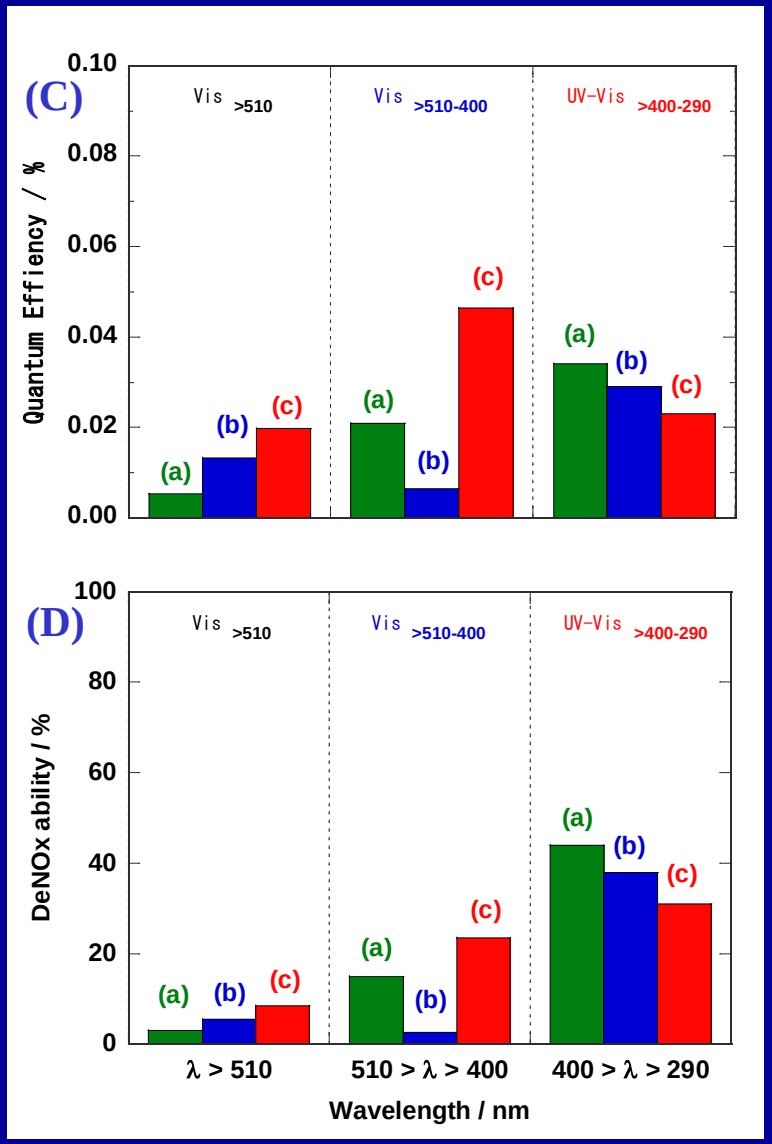
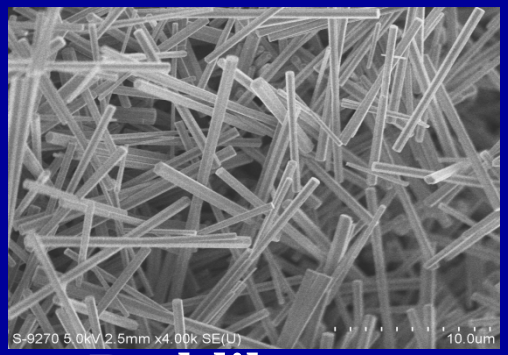


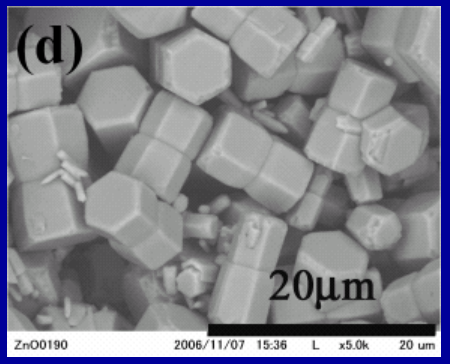
Fig. (A)XRD patterns, (B)EDX spectra, (C) Photocatalytic deNO$_x$ ability and (D) Quantum efficiency of (a)TiO$_{2-x}$N$_y$ thin film, (b)ZnO screw film, and (c)TiO$_{2-x}$N$_y$ – ZnO composite film.

The photocatalytic deNO$_x$ ability data were treated against various wavelength ranges.

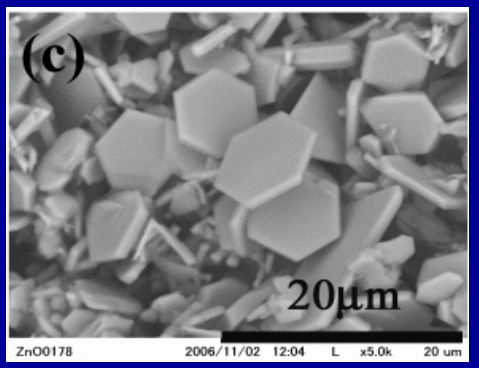
Morphologies of ZnO particles by Solution Process:



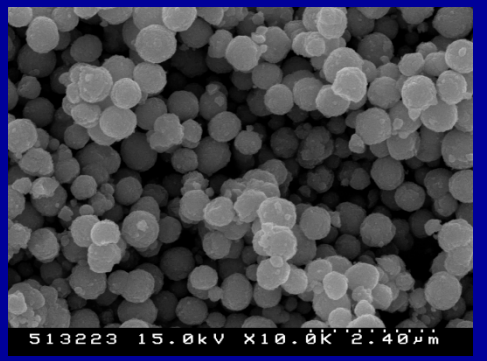
Rod-like



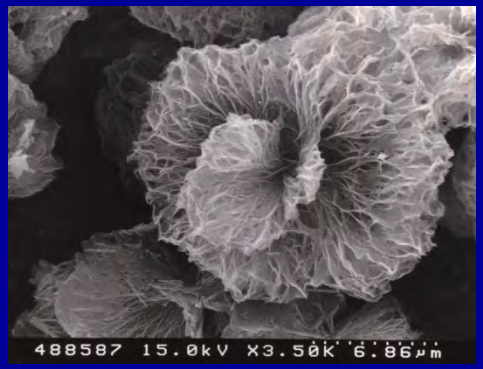
Nut Structure

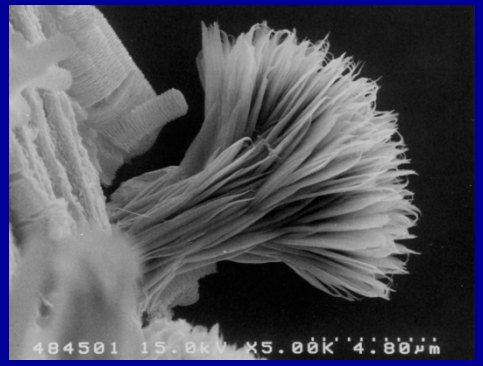


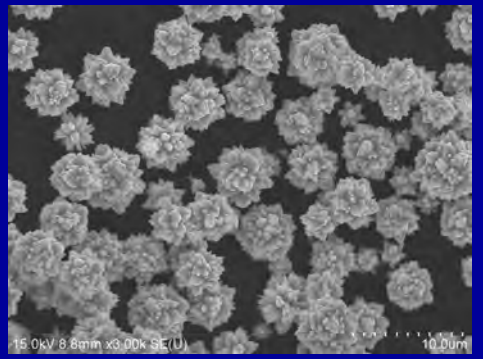
Disk

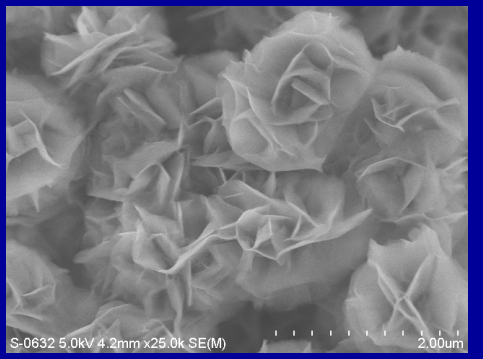


Spherical

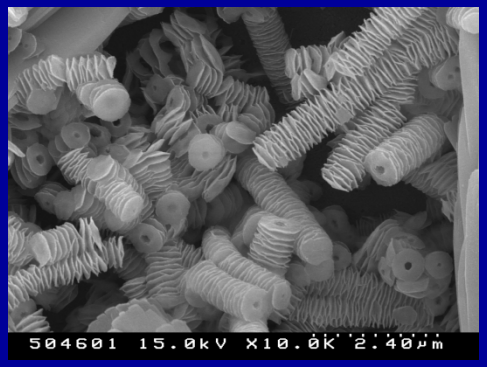


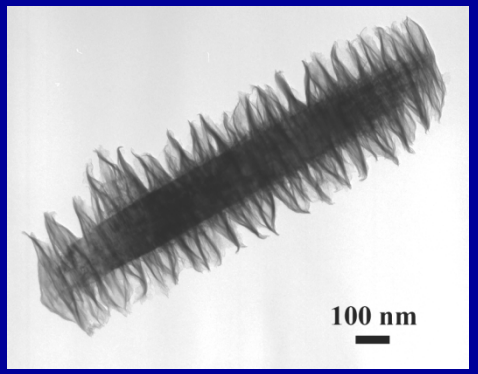


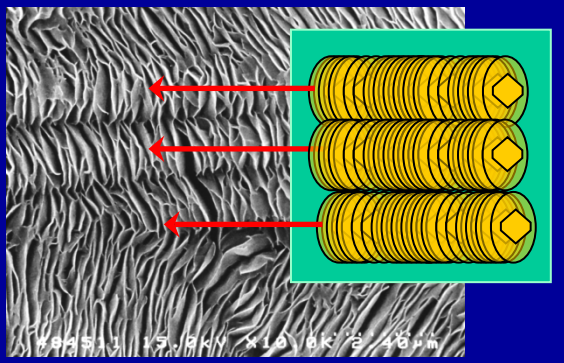




Nano-Flower

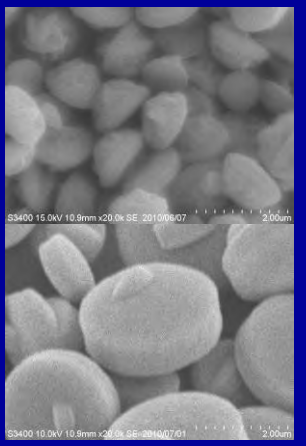




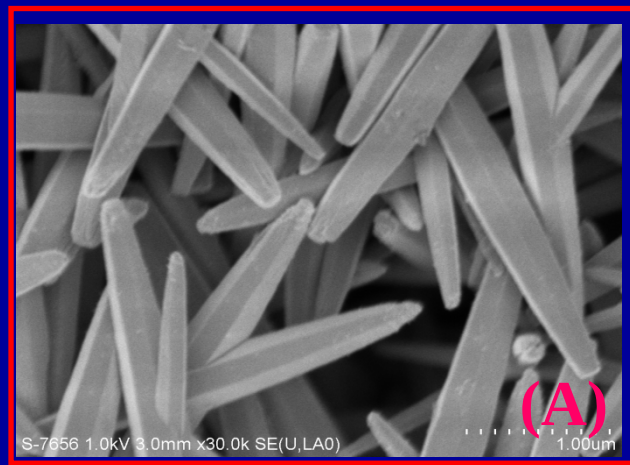


Nano-Screw

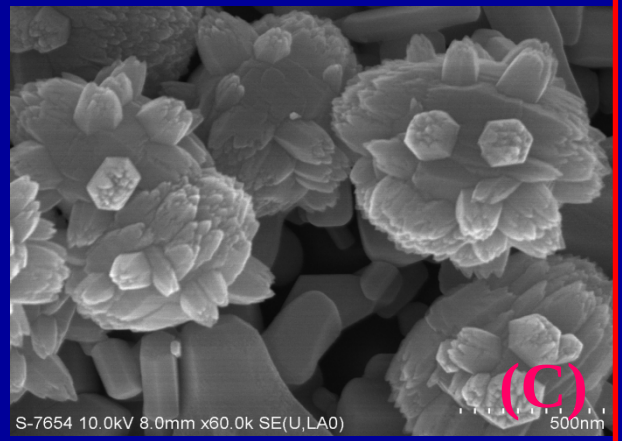
Nano-Carpet: consisted of nano-screws

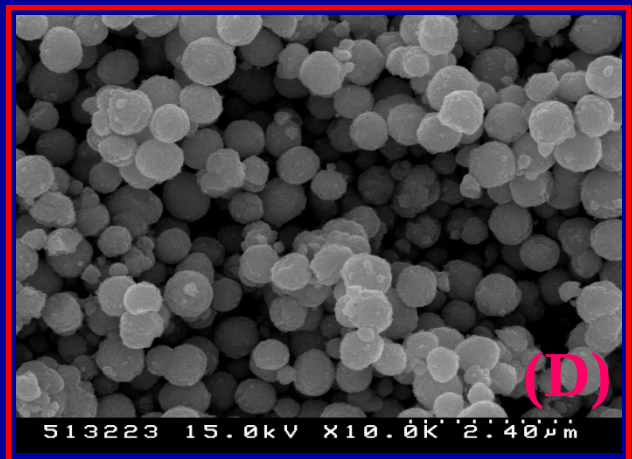


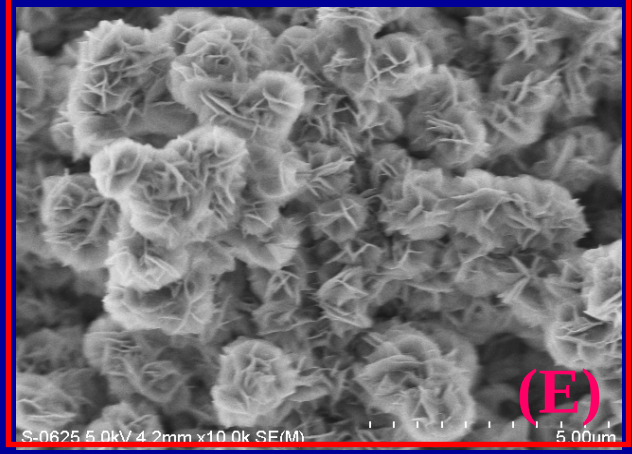
Tablet

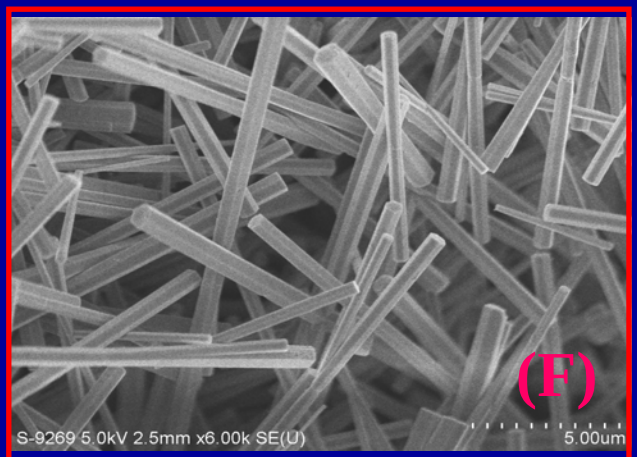

S-7656 1.0kV 3.0mm x30.0k SE(U,LA0)
1.00um
(A)


S-7121 3.0kV 2.1mm x30.0k SE(U)
1.00um
(B)

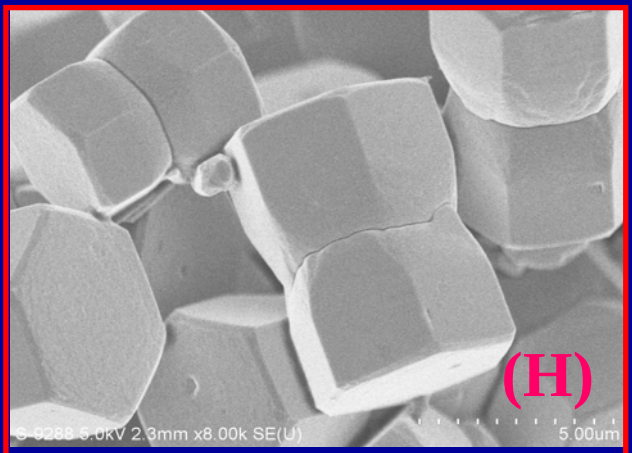

S-7654 10.0kV 8.0mm x60.0k SE(U,LA0)
500nm
(C)

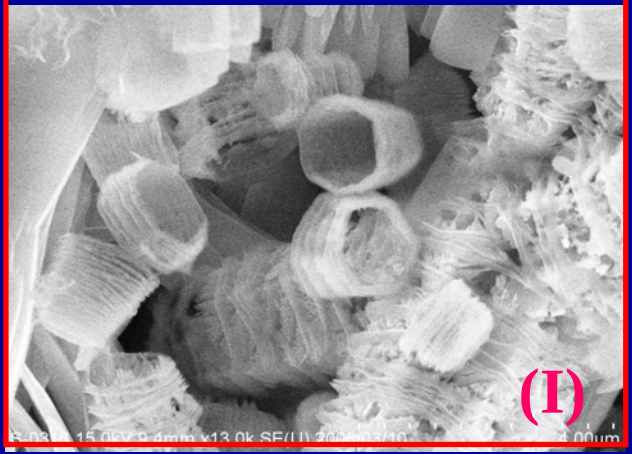

513223 15.0kV X10.0K 2.40um
(D)


S-0625 5.0kV 4.2mm x10.0k SE(M)
5.00um
(E)


S-9269 5.0kV 2.5mm x6.00k SE(U)
5.00um
(F)


S-0329 15.0kV 4.6mm x7.00k SE(M) 2008/06/10
5.00um
(G)


S-9288 5.0kV 2.3mm x8.00k SE(U)
5.00um
(H)


15.0kV 9.4mm x13.0k SE(U)
(I)

Photoluminescence spectrum

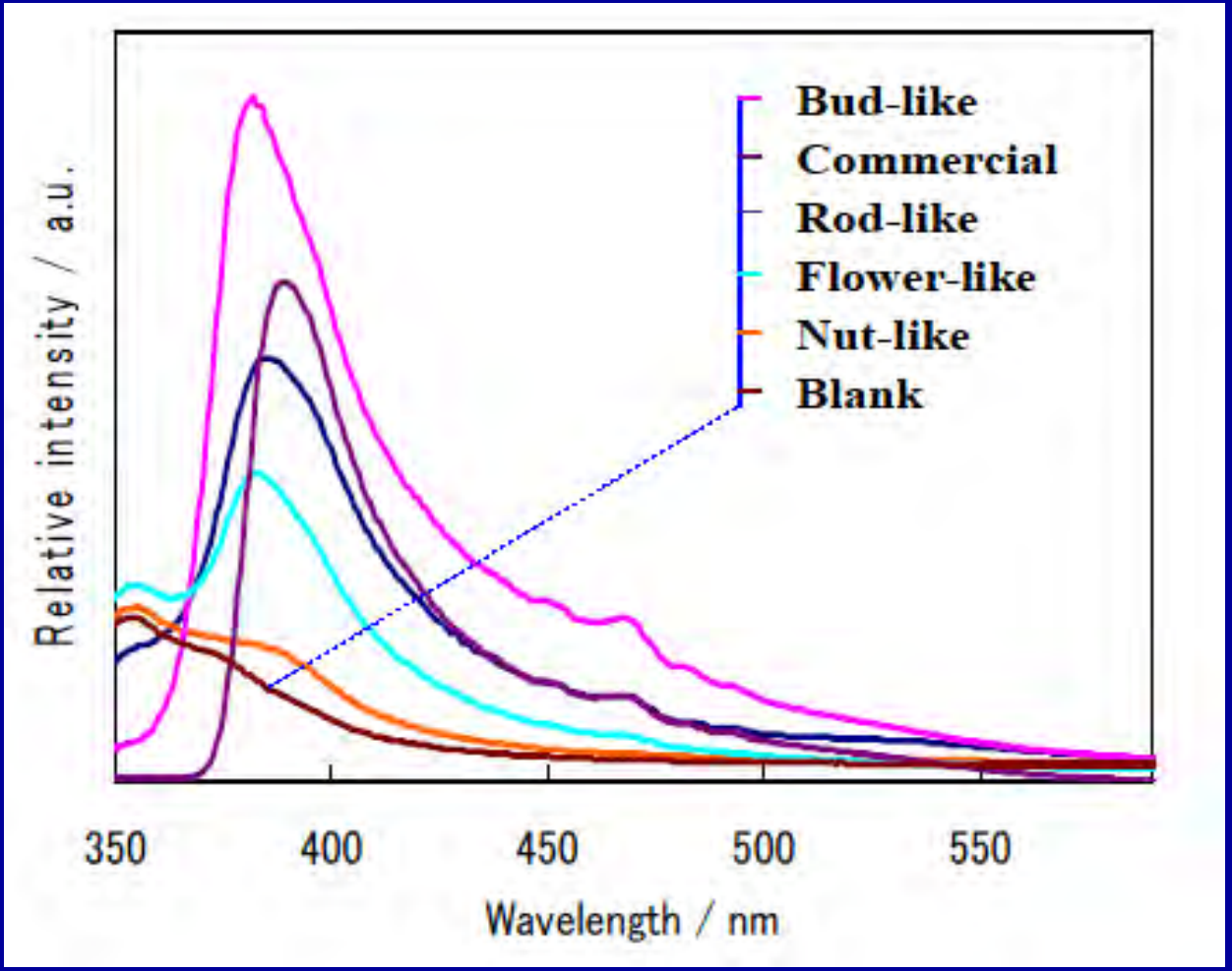
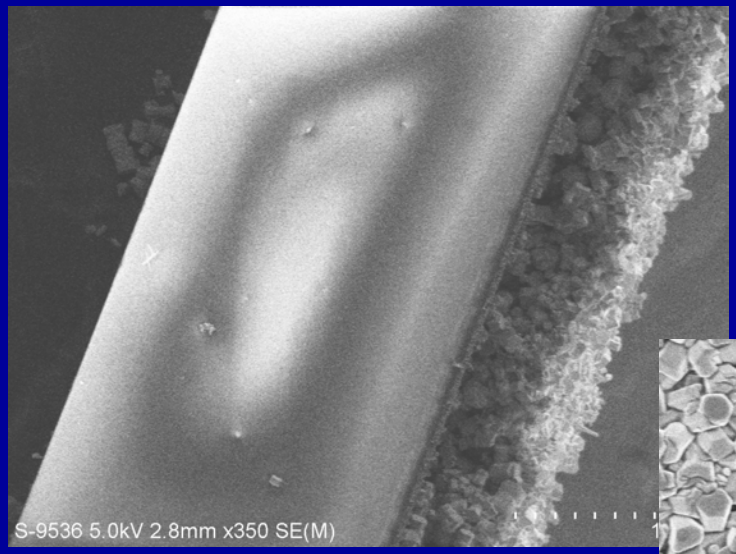
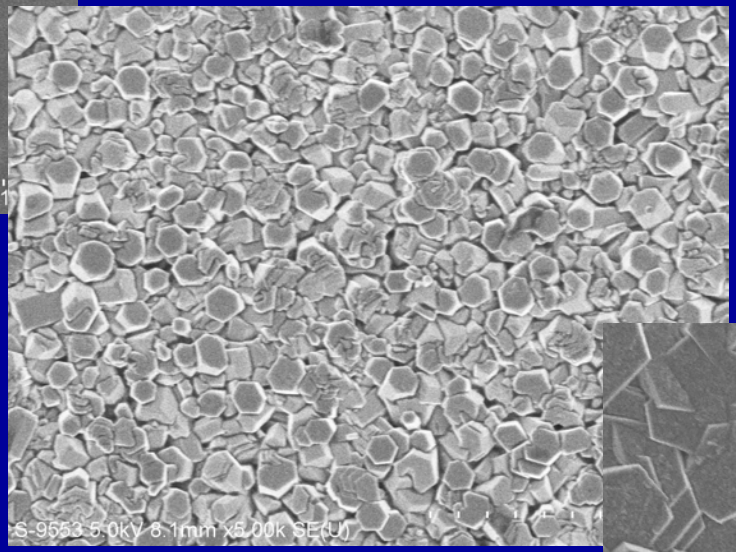
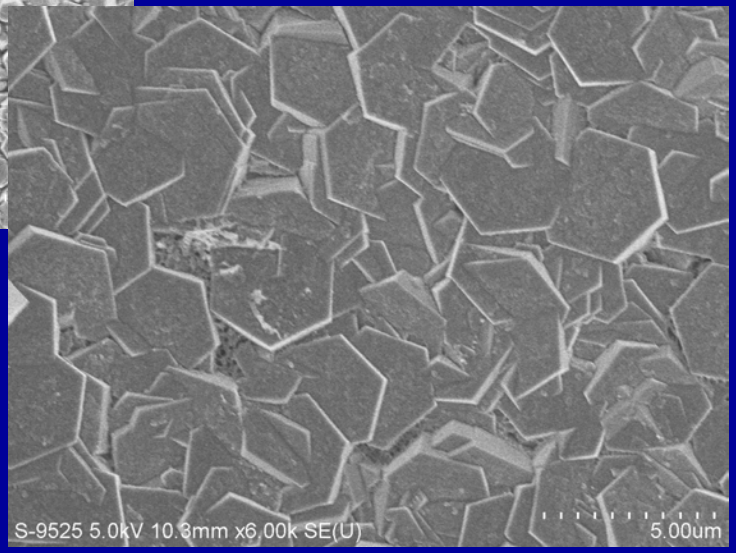


Fig. Photoluminescence spectrum of ZnO crystals with different morphologies.

Morphologies of ZnO Film







Orientated ZnO film with high transparency and conductivity

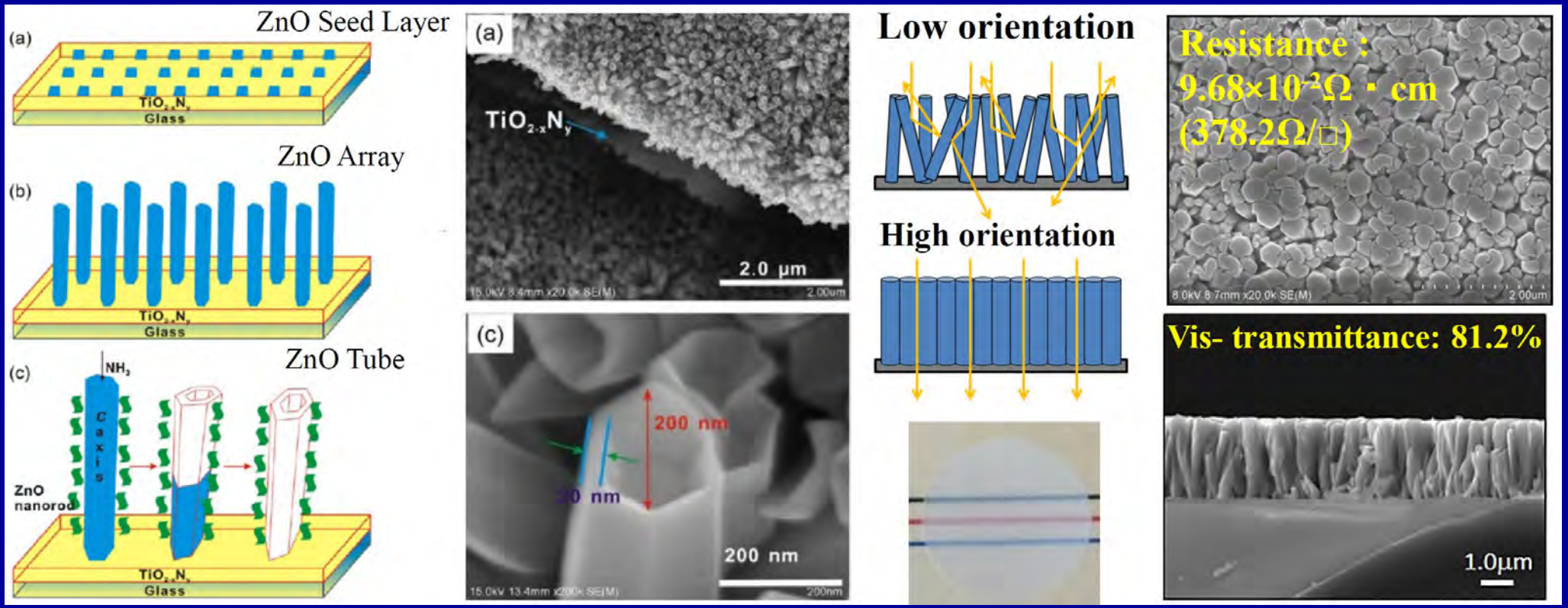


Fig. (Left) Formation process and SEM image of $TiO_{2-x}N_y$ / ZnO oriented tube structure composite thin film; (Right) Excellent transparency and conductivity of ZnO film consisting of hexagonal nanorods oriented on the substrate.

Conclusions

Morphological Control of Zinc Oxide powders and Films could be realized by a Simple Solution Route at Low Temperature :

1) ZnO nano rods and nanoscrews superstructures were successfully synthesized by a low temperature heating process in solution at 95°C. Low concentration and long aging time preferred to form a developed nanoscrews, nanodisks and other superstructures.

2) The films with different superstructures showed quite different physical-chemical properties such as superhydrophobicity / superhydrophilicity, and photoluminescence properties.

3) The ZnO-nanoscrews / $TiO_{2-x}N_y$ composite film showed excellent photocatalytic deNO_x ability, indicating the light utilize efficiency could be improved by panoscopic assembled superstructure.

4) Orientated ZnO films with high transparency and conductivity were successfully synthesized by solution process.

5) Solution processing is one of the important methods in the synthesis of functional materials.


Thank you for your attention !
100 nm