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208

## **Nanotechnology in Materials**

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Princeton Materials Institute  
Princeton University

# NANOTECHNOLOGY IN MATERIALS

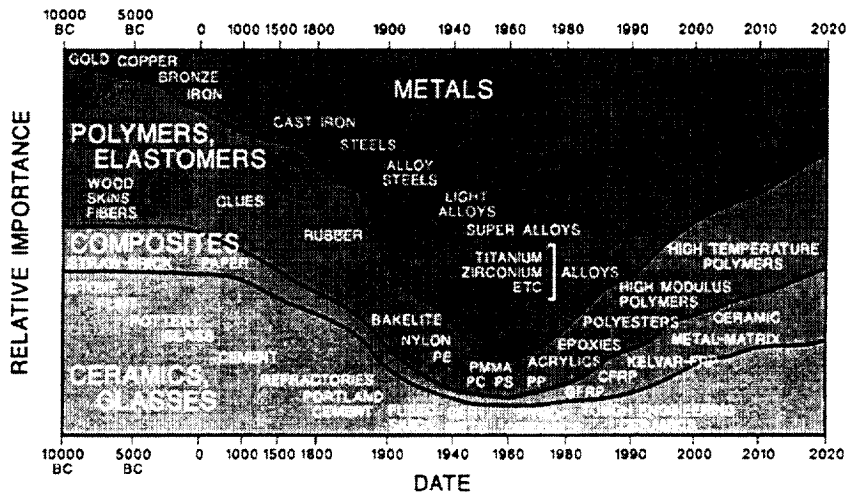
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Princeton University, Princeton, New Jersey



Princeton University

## Evolution of Engineering Materials





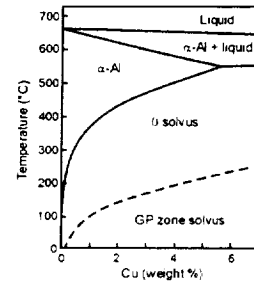
Princeton University

## What is Nanotechnology?

### Precipitation Hardening in the First Aerospace Aluminum Alloy: The Wright *Flyer* Crankcase

Frank W. Gayle and Martha Goodway

SCIENCE • VOL. 266 • 11 NOVEMBER 1994



*"An aluminum copper alloy (with a copper composition of 8 percent by weight) was used in the engine that powered the historic first flight of the Wright brothers in 1903. Examination of this alloy shows that it is precipitation-hardened by Guinier-Preston zones in a bimodal distribution, with larger zones (10-22 nanometers) originating in the casting practice and finer ones (3 nanometers) resulting from ambient aging over the last 90 years."*



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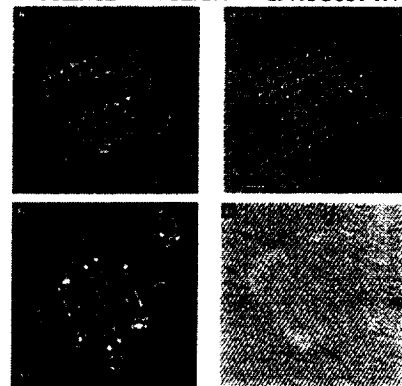
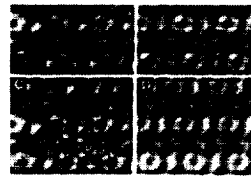
ARTICLES

### Structure Determination of $Mg_5Si_6$ Particles in Al by Dynamic Electron Diffraction Studies

H. W. Zandbergen,\* S. J. Andersen, J. Jansen

SCIENCE • VOL. 277 • 29 AUGUST 1997

Precipitation hardening, in which small particles inhibit the movement of dislocations to strengthen a metal, has long been used to improve mechanical strength, especially of aluminum alloys. The small size of precipitates and the many possible variants of the orientation relation have made their structural determination difficult. Small precipitates in commercial aluminum-magnesium-silicon alloys play a crucial role in increasing the mechanical strength of these alloys. The composition and structure of the  $\beta'$  phase in an aluminum-magnesium-silicon alloy, which occur as precipitates typically 4 nanometers by 4 nanometers by 50 nanometers and are associated with a particularly strong increase in mechanical strength, were determined. Element analysis indicates that the composition is  $Mg_5Si_6$ . A rough structure model was obtained from *ab initio* reconstruction from high-resolution electron microscopy images. The structure was refined with electron diffraction data (overall *R* value of 3.1 percent) with the use of a recently developed least squares refinement procedure in which dynamic diffraction is fully taken into account.



*"Precipitation hardening, in which small particles inhibit the movement of dislocations to strengthen a metal, has long been used to improve mechanical strength, especially of aluminum alloys."*

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## Hierarchy in Bone

The hierarchy is shown in seven levels:

- Level 1: Major components** (100 nm scale bar)
- Level 2: Mineralized collagen fibril** (200 nm scale bar)
- Level 3: Fibril array** (200 nm scale bar)
- Level 4: Fibril array patterns** (Schematic diagram showing various fibril arrangements)
- Level 5: Cylindrical motifs: osteons** (10 μm scale bar)
- Level 6: Spongy vs compact bone** (Micrographs of different bone types)
- Level 7: Whole bone** (Image of a whole bone)

S. Weiner and H. D. Wagner, *Ann. Rev. Mater. Sci.* **28**, 271-98 (1998).

Princeton University

**Three Key Lessons:**

- Discrete levels and/or scales with organization starting at 1-100 nm.
- Levels of structural organization are held together by specific interactions.
- Hierarchical composite systems designed to meet a wide range of functional requirements.

The collage includes various images: a layered biological structure, a porous lattice, a 3D cube, a rectangular block with internal structure, a circular porous structure, a 3D cube with a tree-like structure on top, a rectangular block with a tree-like structure on top, a porous lattice with a 500 nm scale bar, and a porous lattice with a 0.15 nm scale bar.



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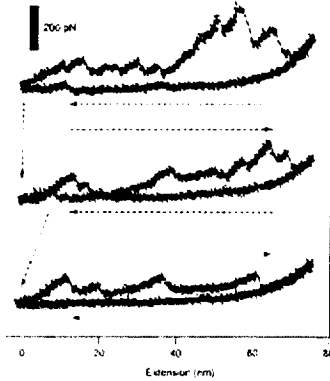
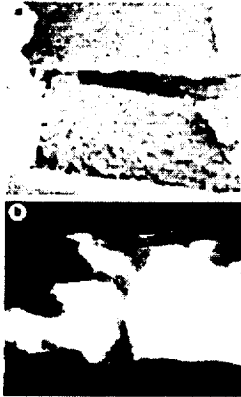
## letters to nature

### Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites

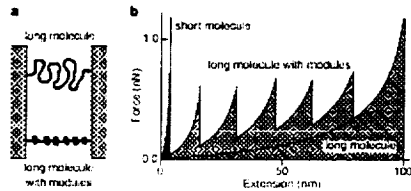
Bettye L. Smith<sup>1</sup>, Timon E. Schiller<sup>2</sup>, Marco Viani<sup>3</sup>, James B. Thompson<sup>4</sup>, Neil A. Frederick<sup>5</sup>, Johannes Kindt<sup>6</sup>, Angela Beldner, Galen D. Stucky, Daniel E. Morse<sup>7</sup> & Paul K. Hansma<sup>1</sup>

<sup>1</sup>Department of Physics, <sup>2</sup>Department of Chemistry and Materials, and <sup>3</sup>Department of Molecular, Cellular and Developmental Biology, University of California at Santa Barbara, California 93106, USA; <sup>4</sup>Department of Molecular Biology, Swiss Federal Institute for Research in Aquatic Science and Technology, Dübendorf, Switzerland; <sup>5</sup>Department of Chemistry, The University of Texas at Austin, Texas 78712, USA; <sup>6</sup>These authors contributed equally to this work

NATURE 413, 802-805 (2005) | DOI: 10.1038/432802a

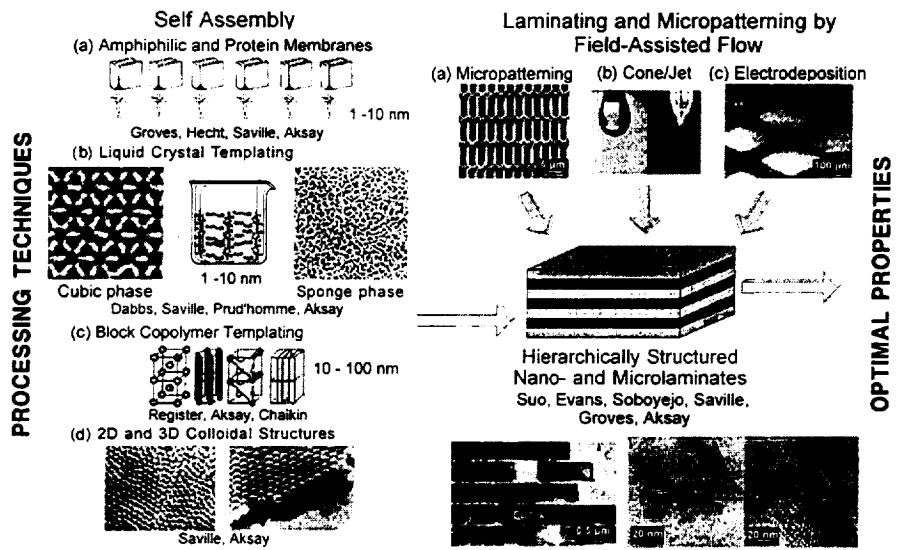


*"Thus the break strength of each adhesive molecule would be the force required to break a strong bond: of the order of one nano-newton (estimate by dividing one electron volt by an extension of one ångström). For a material with many strongly bound molecules in parallel, the macroscopic tensile strength is expected to be of the order of several giga-pascals."*



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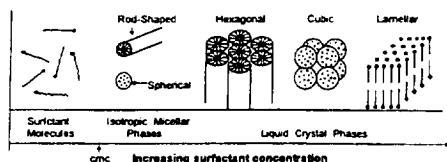
## Goals and Organization





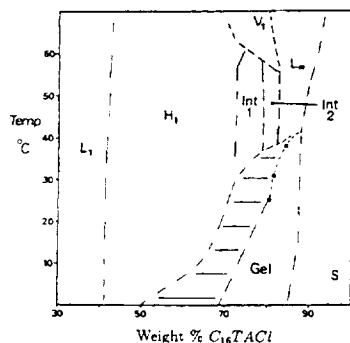
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## CTAC (Cetyltrimethyl Ammonium Chloride)



### Phase sequence of surfactant-water binary system

D. Myers, *Surfactant Science and Technology*, VCH: New York (1992)



### Partial phase diagram for the CTAC-water system

- L<sub>1</sub>: micellar solution;
- H<sub>1</sub>: hexagonal phase;
- L<sub>α</sub>: Lamellar phase;
- Gel: Monolayer interdigitated gel phase;
- V<sub>1</sub>: bicontinuous cubic phase;
- S: Solid phase; Int-1 and Int-2, intermediate phases.

Gel phase is separated from the H<sub>1</sub> phase by a two-phase region

U. Henriksson *et al.*, *J. Phys. Chem.* **96** 3894-902 (1992)

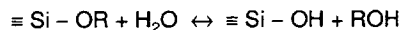


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## TEOS (Tetraethoxysilane)

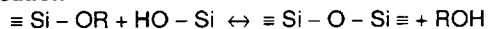
### Hydrolysis and Condensation

#### 1) Hydrolysis



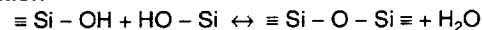
The R represents an alkyl group. In this reaction, the alkoxide groups (OR) are replaced by hydroxyl (OH) groups.

#### 2) Alcohol Condensation



Siloxane bonds (Si - O - Si) and Alcohol (ROH) are produced.

#### 3) Water Condensation



Siloxane bonds and water (H<sub>2</sub>O) are produced.

**At low pH and high water concentration:** The hydrolysis finishes in a very short period of time; therefore, the hydrolysis and condensation reactions are well separated.

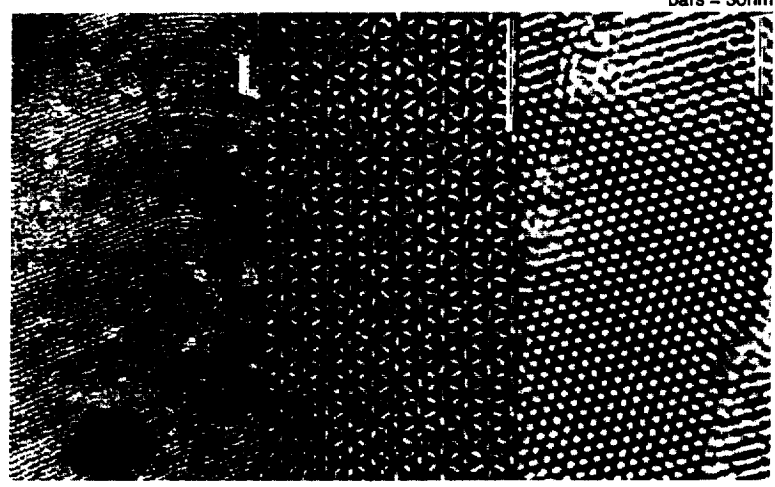
C. Jeffrey Brinker *et al.*, *Sol-gel Science* (Academic Press, San Diego, 1986)



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# Lamellar, Cubic and Hexagonal Mesoporous Structures

bars = 30nm



M. D. McGehee, S. M. Gruner, N. Yao, C. M. Chun, A. Navrotsky, and I. A. Aksay, *Proc. 52nd Ann. Mtg. MSA* 448-9 (1994)



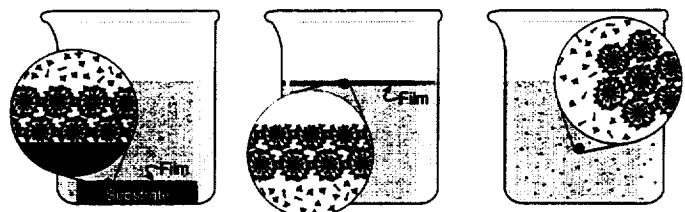
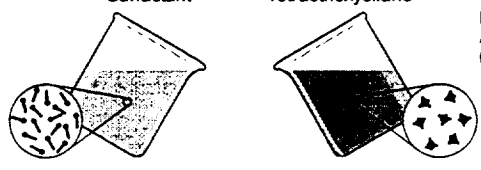
Princeton University

# Templating Self-Assembled Surfactants

Surfactant

Tetraethoxysilane

D.M. Dabbs and I.A. Aksay,  
*Ann. Rev. Phys. Chem.*  
(in press, 2000)




Solid/Liquid Interface

Air/Liquid Interface

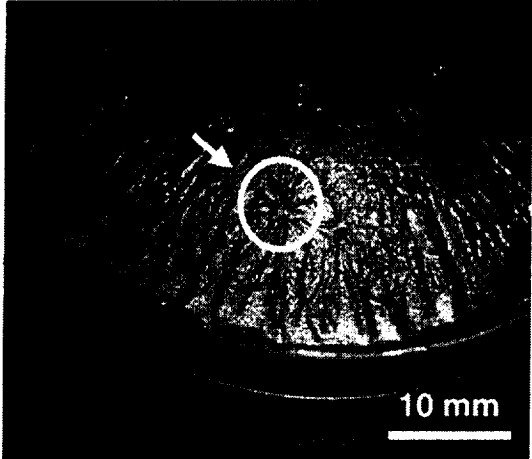
Homogeneous Nucleation

Heterogeneous nucleation




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### Self Healing Inorganic/Organic Films

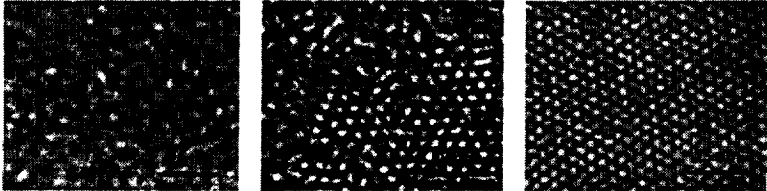


A circular defect in a film is highlighted by a white circle, with a white arrow pointing to the edge of the defect. A scale bar in the bottom right corner indicates 10 mm.

N. Yao, A. Y. Ku, N. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, *Chem. Mater.* 12 [6] 1536-548 (2000)

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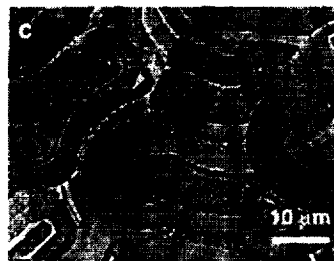
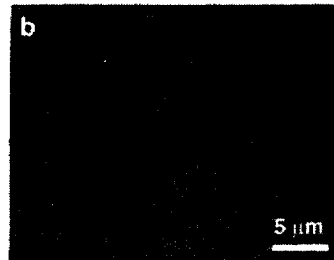
### Film Growth: Mesoscopic Crystallization



Three panels showing the evolution of mesoscopic crystallization over time: 30 minutes, 5 hours, and 2 days. The crystallization process is shown as a transition from a dark, featureless surface to a surface covered with a dense network of bright, interconnected crystalline structures.

30 minutes      5 hours      2 days

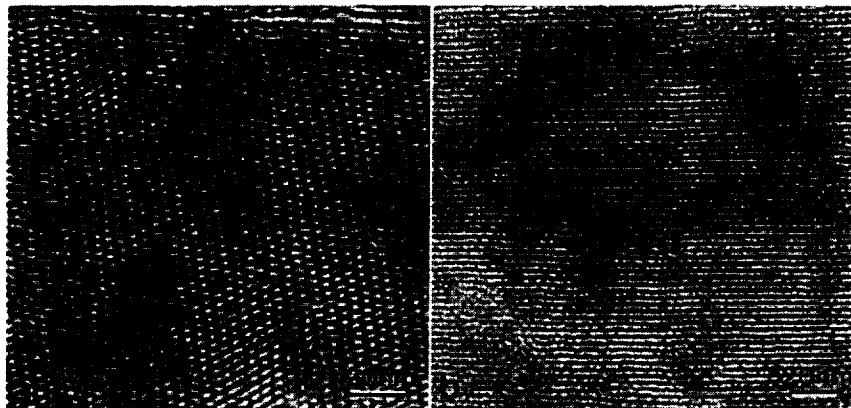
N. Yao, A. Y. Ku, N. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, *Chem. Mater.* 12 [6] 1536-548 (2000)



N. Yao, A. Y. Ku, N. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, *Chem. Mater.* 12 [6] 1536-548 (2000)

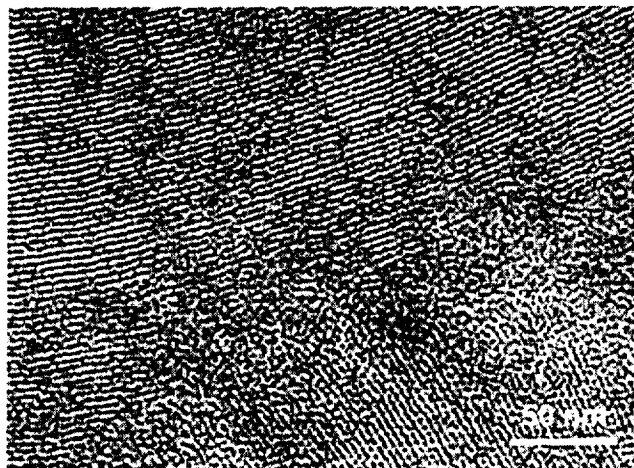


### Mesostructured Silica Film on Mica





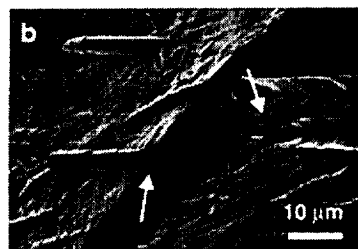
### Cross-Sectional TEM: Film at the Air-Water Interface



N. Yao, A. Y. Ku, N. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, *Chem. Mater.* 12 [6] 1536-548 (2000)



### Film Grown at the Air/Water Interface

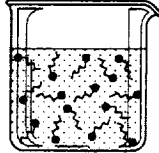


N. Yao, A. Y. Ku, N. Nakagawa, T. Lee, D. A. Saville, and I. A. Aksay, *Chem. Mater.* 12 [6] 1536-548 (2000)

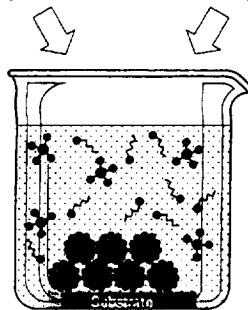
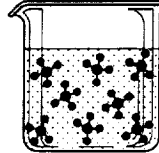


## Synthesis of Mesostructured Silica Films

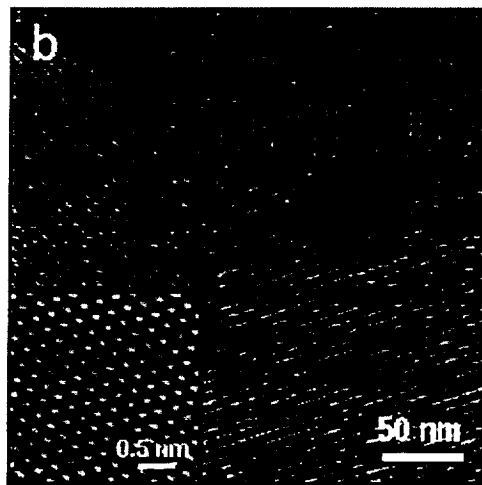
Cetyltrimethyl ammonium chloride (CTAC)



Tetraethoxysilane



## Mesostructured Silica on Graphite-AFM



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## Mesostructured Inorganics Through Liquid Crystal Templating

- **Surfactant-based procedure yields mesostructured inorganic materials**  
 C. T. Kresge et al., *Nature* 359 (1992); and, J. S. Beck et al., *J. Am. Chem. Soc.* 114 [27] (1992).

I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, S. M. Gruner *Science* 273 892-98 (1996).

Mica      Graphite      Silica

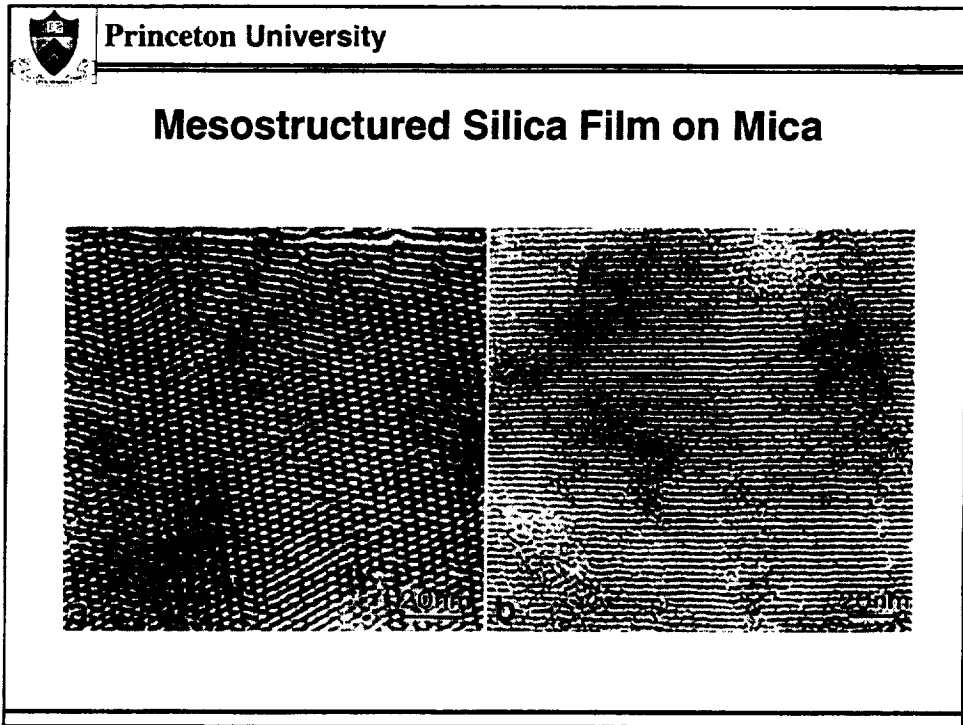
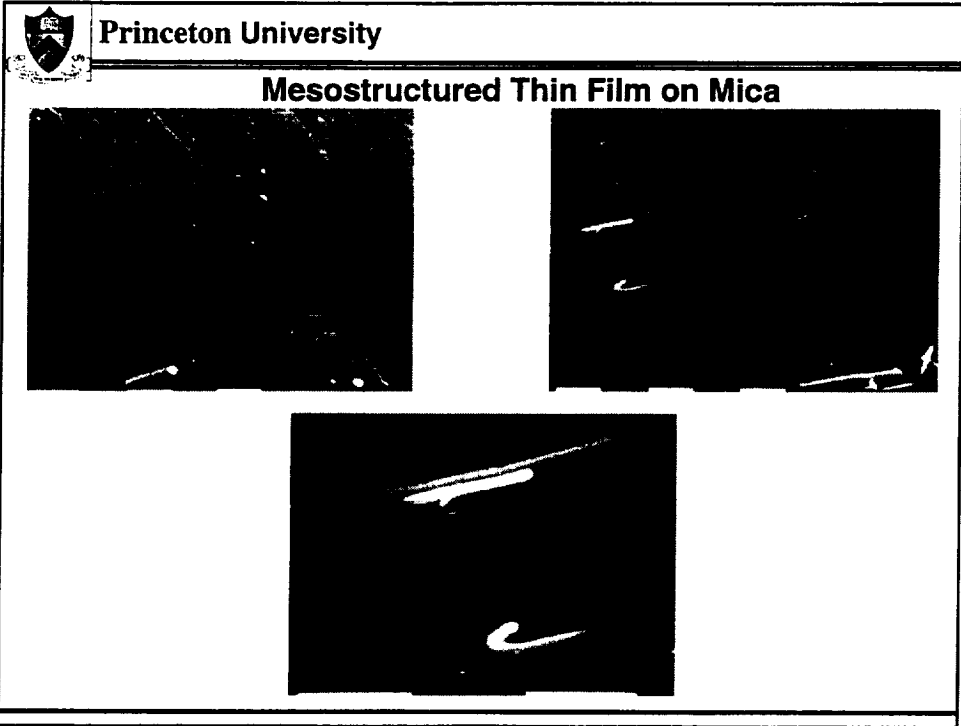
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## In-plane Orientational Alignment: On Mica

A 2-D azimuthal scan of the (101) Bragg peak for the film grown on mica for 24 hours. Note that peaks are observed at  $\phi = \pm 30^\circ$ , corresponding to the tubules along N1 and N2 ( $\phi = \pm 60^\circ$ ), but no peak is observed at  $\phi = \pm 90^\circ$ , which would correspond to tubules laying along the b-axis direction.

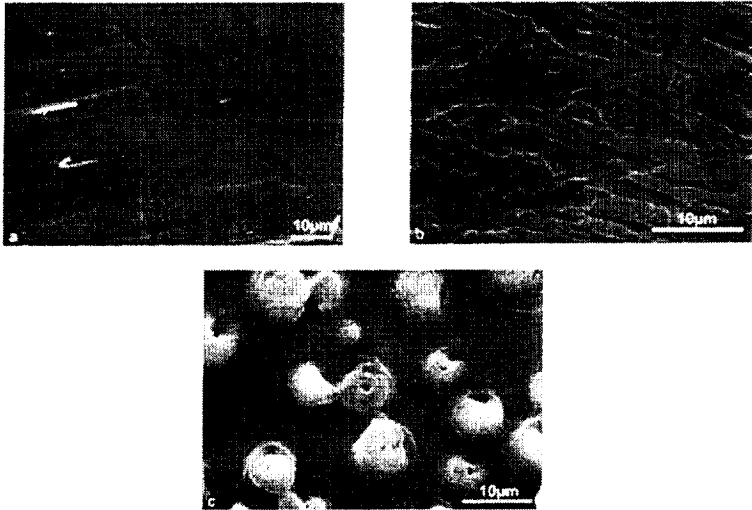
Schematic of the lattice structure of the mica surface. The tubules of the film are aligned along the two next-nearest-neighbor directions N1 and N2 of the pseudo-hexagonal structure.

• Silicon    ○ Oxygen




 Princeton University

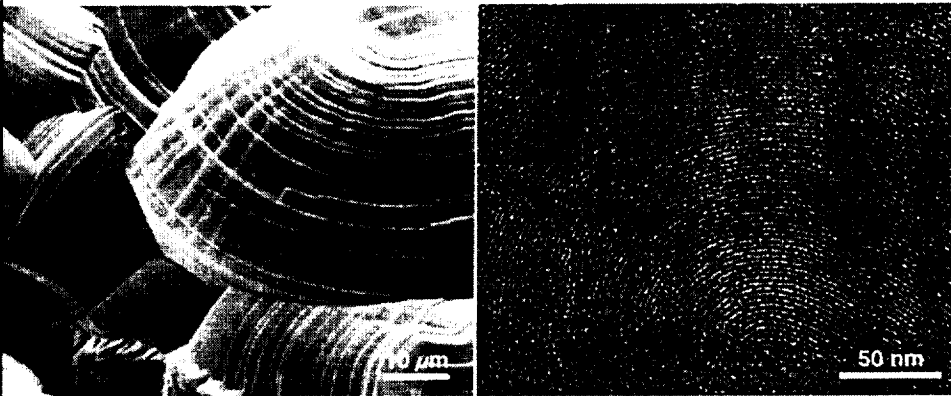
### Mesostructured Thin Films



a  $10\mu\text{m}$  b  $10\mu\text{m}$  c  $10\mu\text{m}$

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### Hierarchically Structured Mesoscopic Silica Film



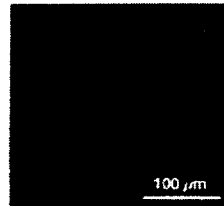
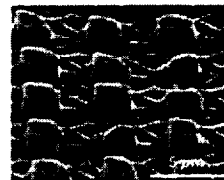
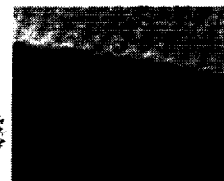
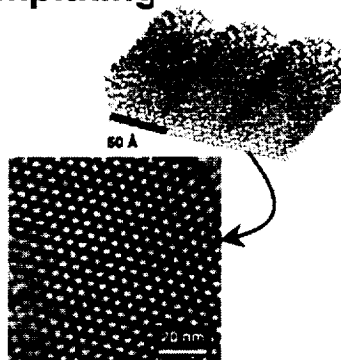
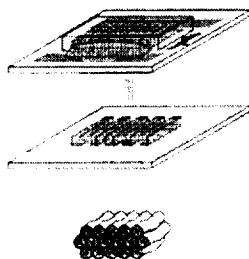
$10\mu\text{m}$   $50\text{ nm}$

On silica substrate



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## Liquid Crystal Templating



I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, S. M. Gruner, *Science* 273 892-98 (1996);

M. Trau, N. Yao, E. Kim, Y. Xia, G. M. Whitesides, I. A. Aksay, *Nature* 390 [6661] 674-76 (1997)

A. Y. Ku, D. A. Saville, I. A. Aksay, unpublished research (2000)



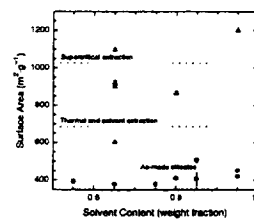
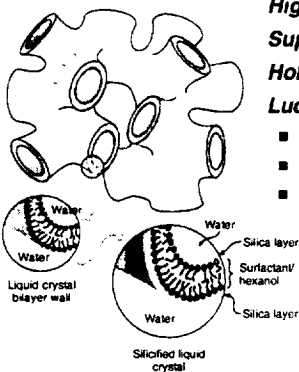
Princeton University

## L<sub>3</sub>-Templated Silicates

*High surface area with contiguous, uniform pore structure*  
*Supercritically extracted to remove template (N. Mulders)*  
*Holographic storage medium (H. Katz,*

*Lucent Technologies):*

- High permeability for precursors
- *In-situ* reaction and curing
- Two-photon write-and-read



**Cubic Phase:**

M. D. McGehee, S. M. Gruner, N. Yao, C. M. Chun, A. Navrotsky, and I. A. Aksay, *Proc. 52nd Ann. Mtg. MSA* (1994) 448-9.

**L<sub>3</sub> Silicates:**

K. M. McGrath, D. M. Dabbs, N. Yao, I. A. Aksay, and S. M. Gruner, *Science* 277 552-6 (1997).

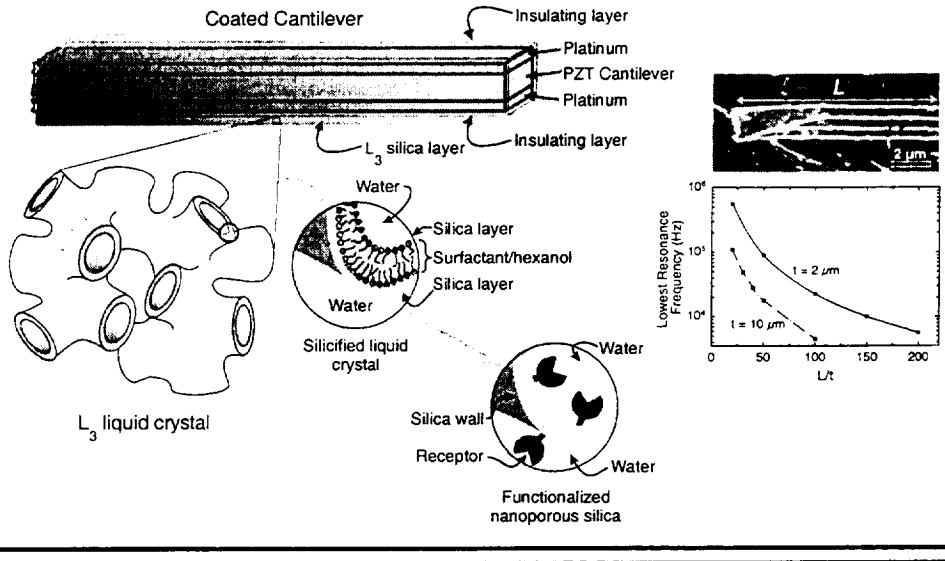
K. M. McGrath, D. M. Dabbs, K. J. Edler, N. Yao, I. A. Aksay, and S. M. Gruner, *Langmuir* 16 398-406 (2000).

D. M. Dabbs, S. M. Gruner, N. Mulders, and I. A. Aksay, unpublished research (2000).

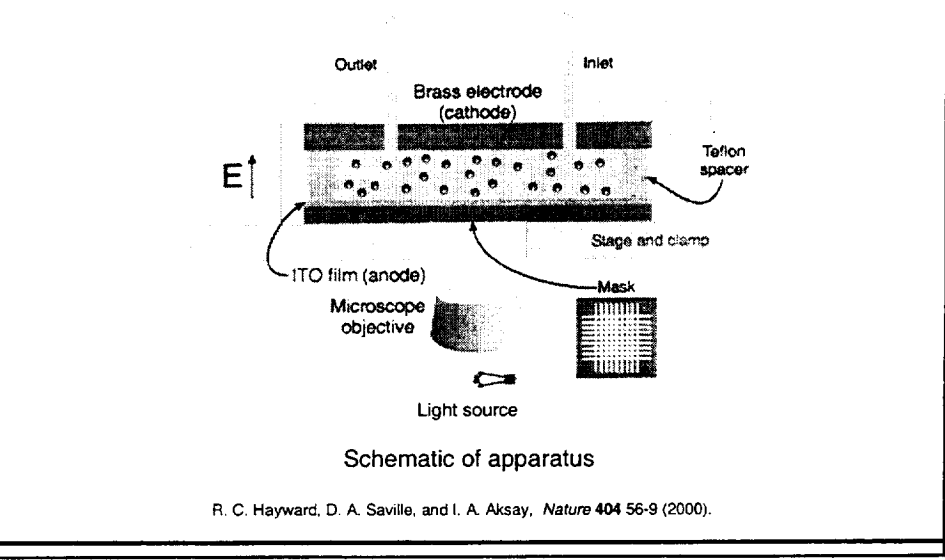




### Mesostructured Coating on PZT Cantilever



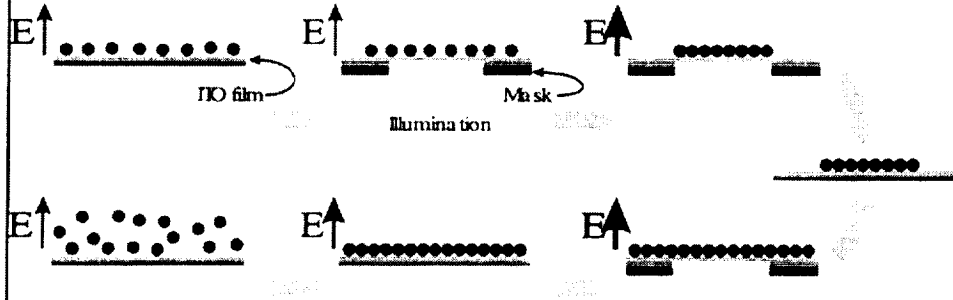
### Light-Modulated Electrophoretic Deposition





## Pattern Formation

Patterned assembly followed by fixing to substrate

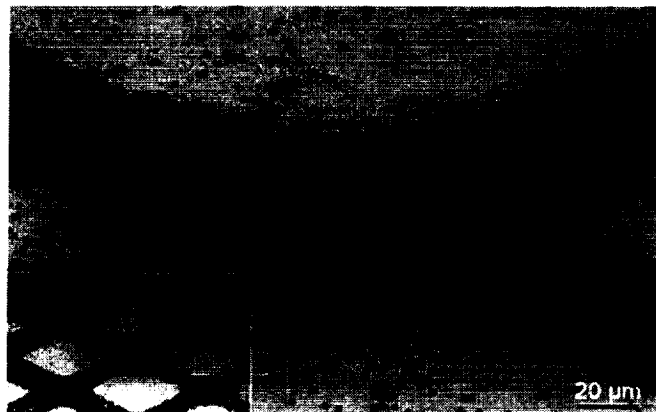


General assembly followed by patterned fixing to substrate

R. C. Hayward, D. A. Saville, and I. A. Aksay, *Nature* 404 56-9 (2000).



## Patterned Colloidal Particles

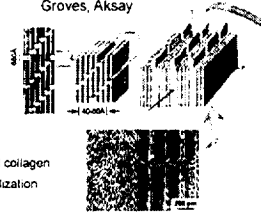


R. C. Hayward, D. A. Saville, and I. A. Aksay, *Nature* 404 56-9 (2000).



# Princeton University

(a) Living Cells  
Schwarzbauer, Carbeck,  
Groves, Aksay

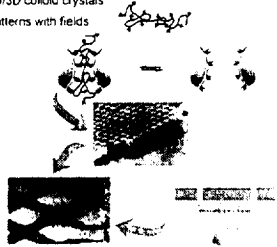


- Templated collagen
- Biomneralization

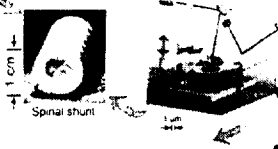
### HYBRID-SYNTHONS

(c) Patterned Colloidal Crystals  
Carbeck, Saville, Aksay

- 2D/3D colloid crystals
- Patterns with fields



(b) Templates through Laser Rastering  
Prud'homme, Aksay



- Stereolithography
- 2-Photon beam scanning
- 2D/3D scaffolds

### NOVEL NANOLITHOGRAPHIES

(d) Nanolithography through Self-Assembly in Templates  
Saville, Aksay

- Soft lithography
- E-beam lithography
- Templates/fields

