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**15 - 18 May 2001**

**301/1311-2**

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# *"Colloidal Routes to Super-Hydrophobic Surfaces"*

**F. LANGE**
**Materials Department**
**UCSB**
**USA**

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***Please note: These are preliminary notes intended for internal distribution only.***

# Colloidal Routes to Super-Hydrophobic Surfaces

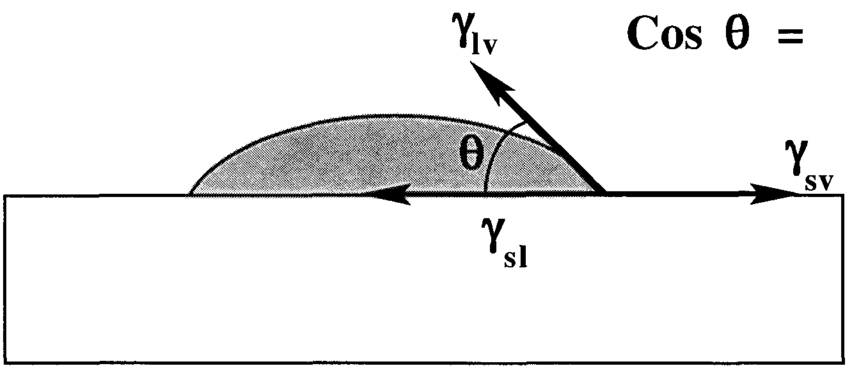

Fred F. Lange

U C S B
MATERIALS

Materials Department
University of California at Santa Barbara

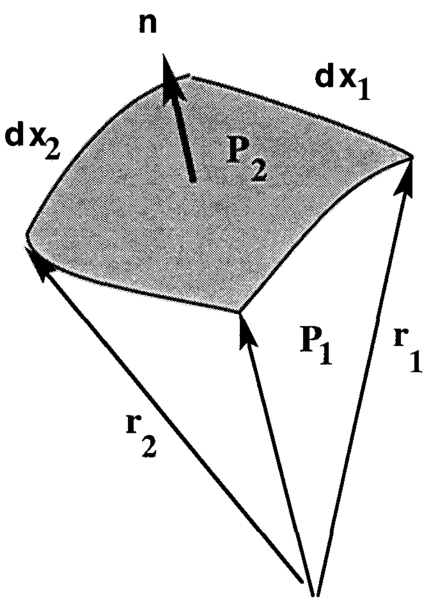
# Classical Wetting and Capillarity

## • Young Equation




$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

## • Laplace Equation



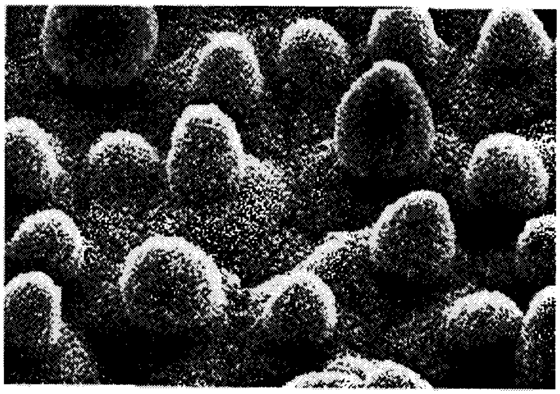

$$\Delta P = P_2 - P_1 = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

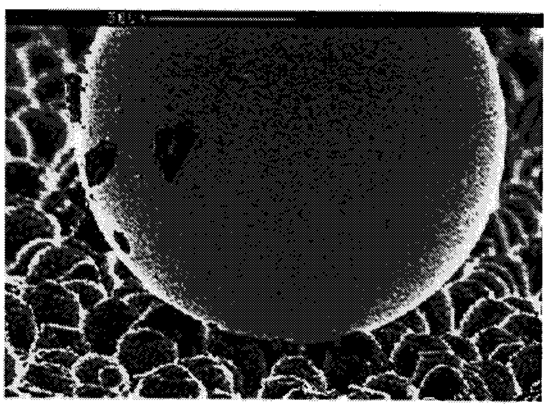
# Outline

- the purity of the Lotus Leaf
- Properties of Super-Hydrophobic Surfaces
- Colloidal Texturing and Properties
- Predictions for Nano-Textured Surfaces

# The Lotus Effect

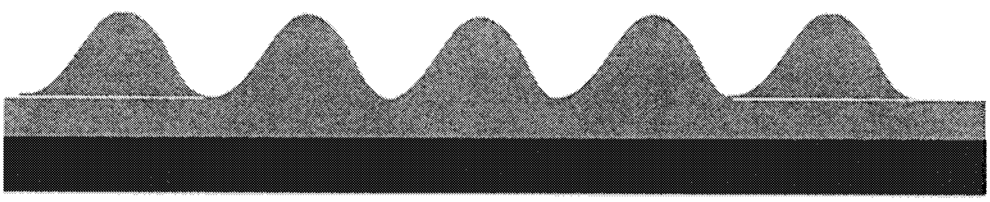
W. Barthlott und C. Neinhuis "Purity of the sacred lotus or escape from contamination in biological surfaces", PLANTA 202: 1-8.(1997)
(University of Bonn, Department of Botany and Botanic Garden)



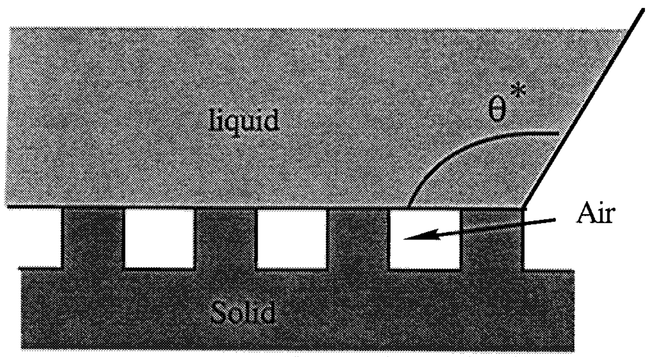


# Model to Explain Super-Hydrophobic Effect

K. Tadanaga, N. Katata, and T. Minami, Super-Water-Repellent $Al_2O_3$ Coating Films with High Transparency, J. Am. Ceram. Soc. 80 1040-1042 (1997).



**Textured, thin film produced by spin coating $Al_2O_3$ precursor**
treated with monolayer of fluoroalkyltrichlorosilane molecules

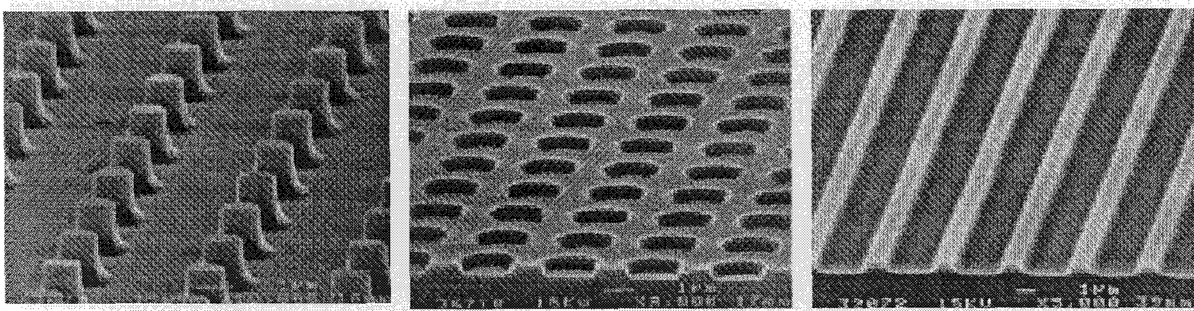



$$\cos\theta^* = -1 + \phi(1 + \cos\theta)$$

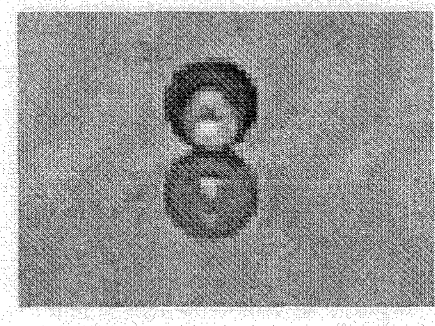
$$\phi = \text{area fraction of wetted 'hills'}$$

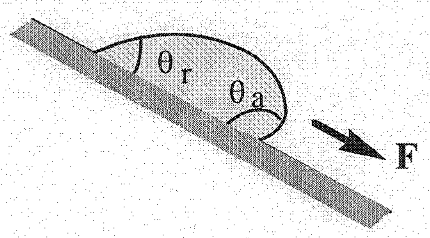
# Relation between Wetting Angle and Wetted Area Fraction

J. Bico, C. Marzolin and D. Quéré, "Pearl Drops", Europhys. Lett., 47 (2), pp. 220 (1999)



Silica Patterned Surfaces, treated with monolayer of fluoroalkyltrichlorosilane molecules



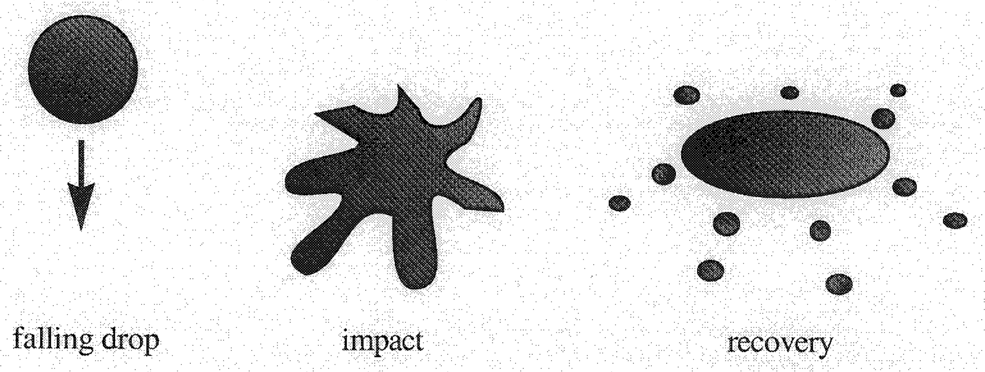



| Pattern | $\phi_s$ | $\theta_a$ | $\theta_r$ | $\theta^*$ |
|---|---|---|---|---|
| Plane | 1 | 118 | 100 | |
| Holes | 0.64 | 138 | 75 | 131 |
| Stripes | 0.25 | 165 (⊥) | 132 | 151 |
| | 0.25 | 143 (//) | 125 | 151 |
| Spikes | 0.05 | 170 | 155 | 167 |

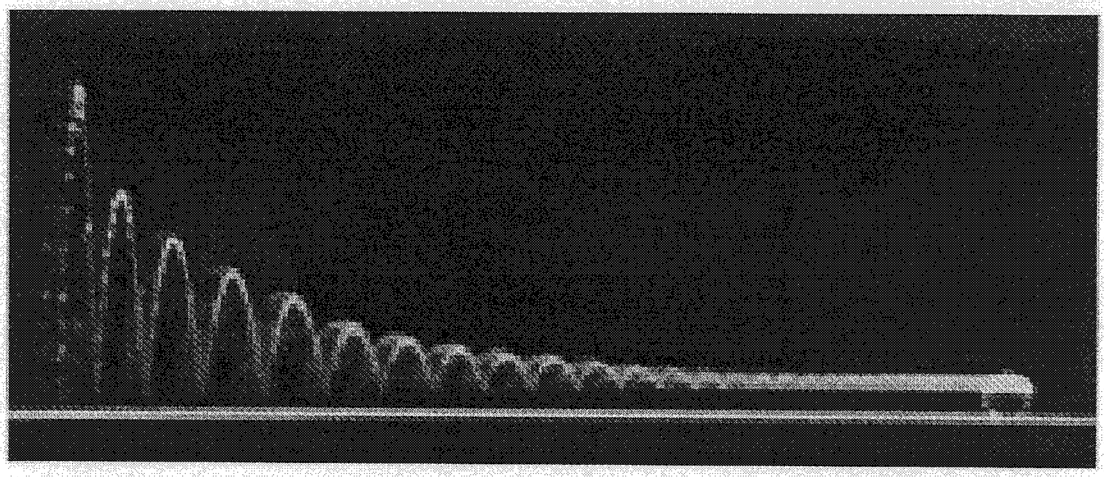
# Bouncing Water Drops

D. Richard and D. Quéré, Europhys.Lett.50 (6) 769 –775 (2000)

## • Normal Surfaces




## • Super-Hydrophobic Surfaces (some cases)

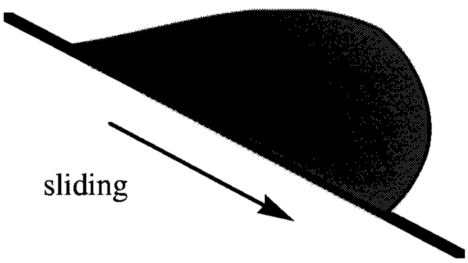


Water drop falling on a super-hydrophobic surface ($\theta$ =170 °) of very small contact angle hysteresis ($\theta_a - \theta_r < 5$ °).

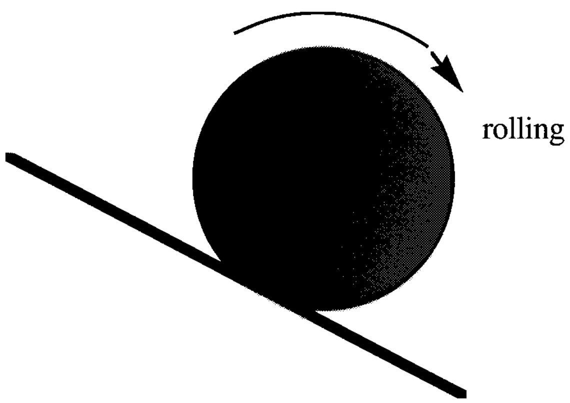
# Rolling Drops

D. Richard and D. Quéré, Europhys. Lett., 48 (3), pp. 286-291 (1999)

• **Normal Surfaces**




• **Super-Hydrophobic Surfaces (some cases)**



# Super-Hydrophobic Surfaces via Texturing with Silica Particles

- Colloidal Chemistry for Texturing

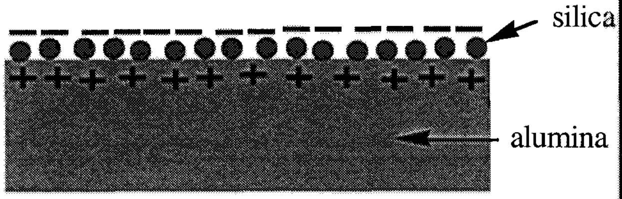
- Wetting Angle vs Wetted Surface Area

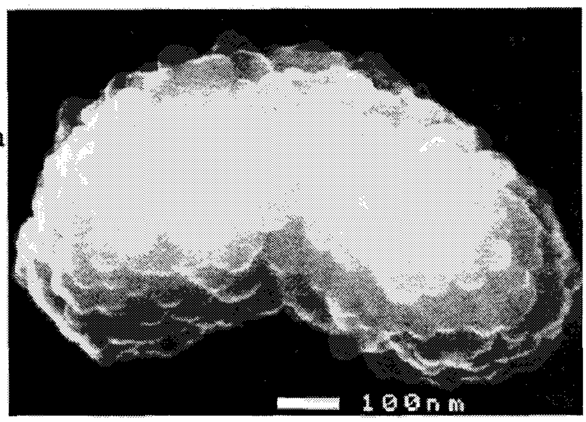
- Conditions for Spontaneous Wetting

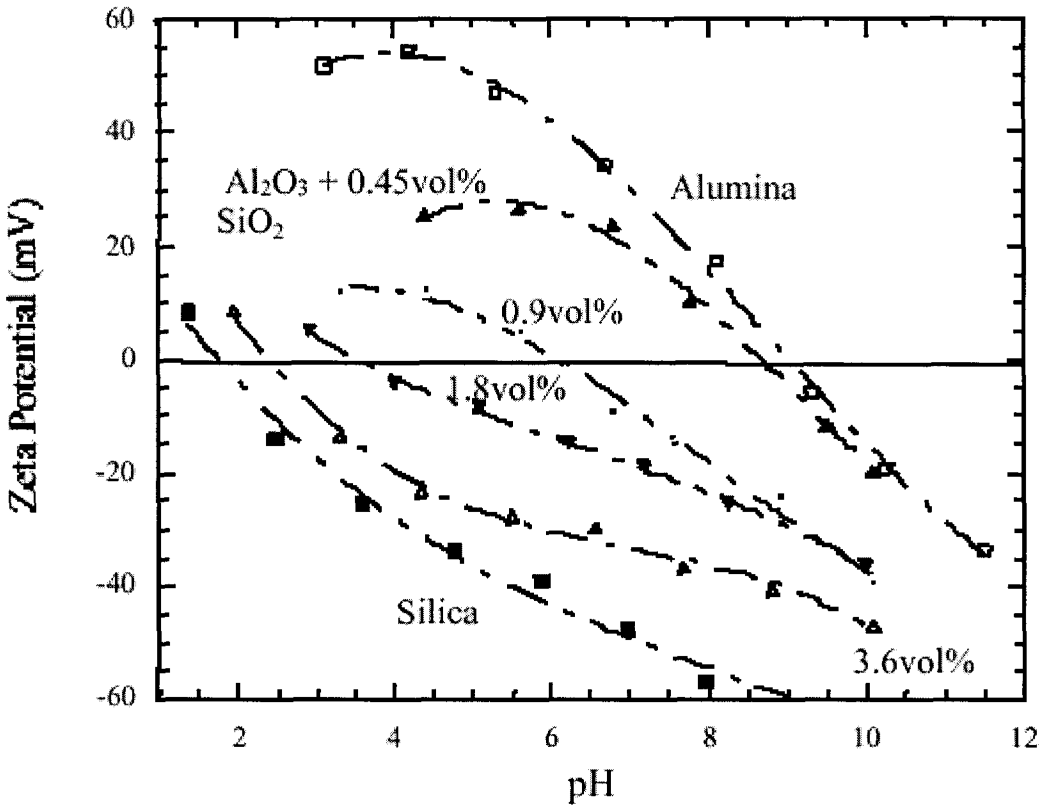
- Conditions for Adherence

# Colloidal Chemistry for Texturing

M.L. Fisher, M. Colic, M.P. Rao, and F.F. Lange "Effect of Silica Nanoparticle Size on the Stability of Alumina/Silica Suspensions," J. Am. Ceram. Soc. 84 (4): 713-718 APR 2001

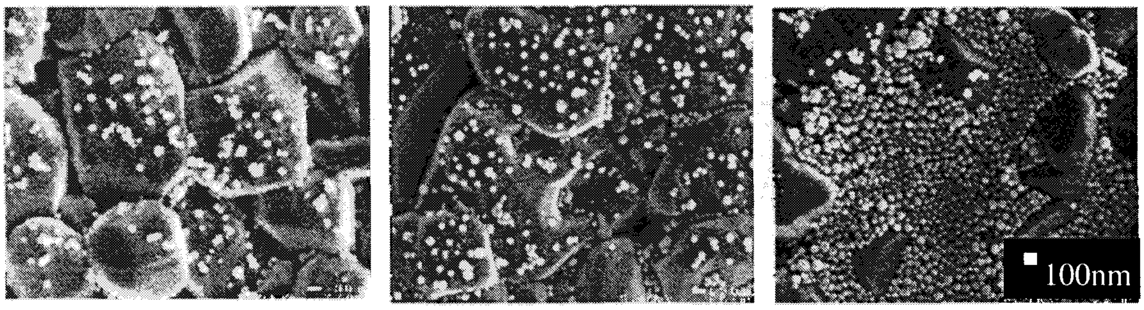


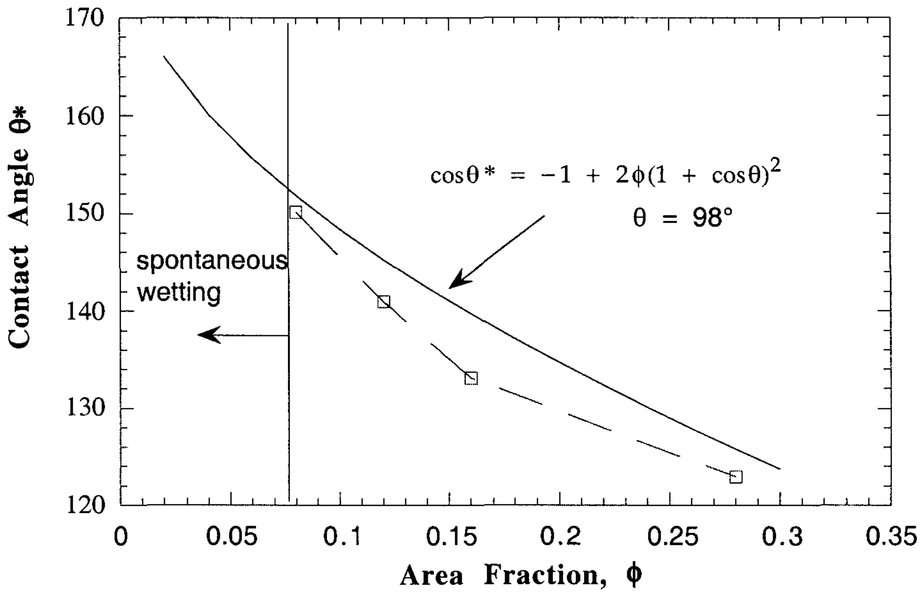



# Textured Surface via Colloidal Interaction

Rob J. Klein*, P. Maarten Biesheuvel, Ben C. Yu, Carl D. Meinhart, and Fred F. Lange, "Producing Super-Hydrophobic Surfaces with Nano-Silica Spheres" to be published

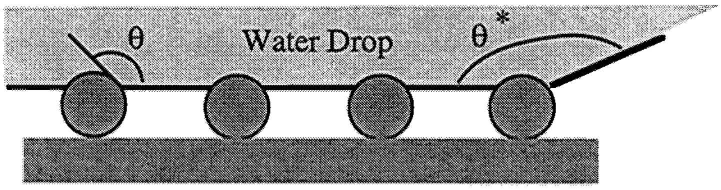



Silica particles (≈ 45 nm in diameter) adsorbed onto the surface of polycrystalline alumina substrates.

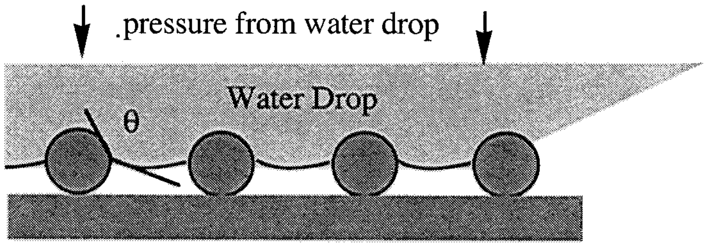


# Conditions for Spontaneous Wetting

a



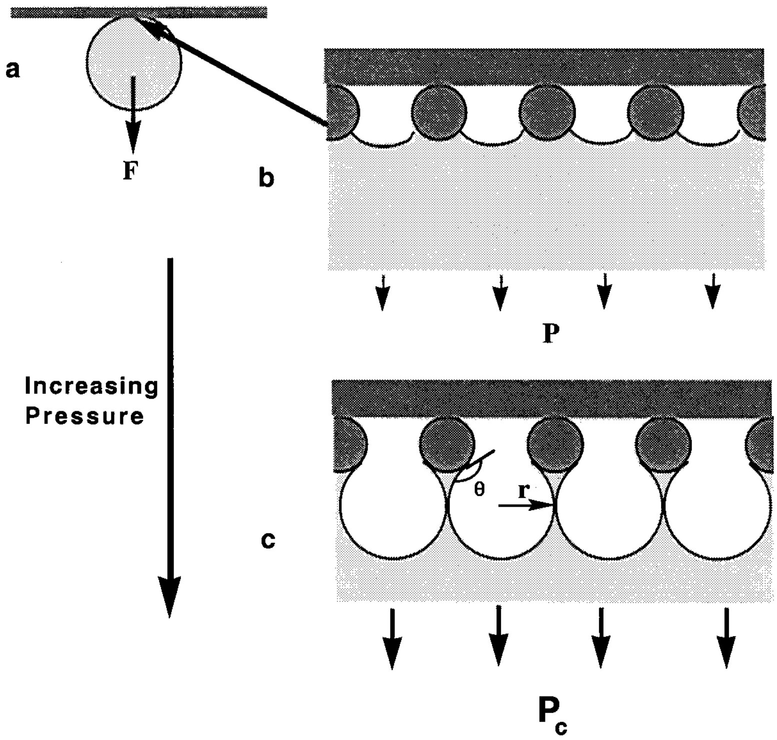

b




$$P_c = \frac{2\phi\gamma\cos\theta}{r(1-\phi)} \approx \frac{2\phi\gamma\cos\theta}{r}, \text{ when } \phi < 0.1$$

# Conditions for Adherence

FF Lange and Ben Yu, unpublished




$$P_d = \frac{2(\phi)^{1/2}}{\pi} \frac{\gamma \cos\theta}{r}$$

# Rheology of Ceramic powders with Chemically Modified Surfaces


## F. F. Lange

UCSB
MATERIALS

Materials Department
University of California at Santa Barbara

# Coworkers-Colloidal Processing

## Former Students

| | |
|---|---|
| **Jeanne Chang, PhD** | Rhone-Poulenc, Princeton, NJ |
| **Erik Luther, PhD** | TPL, Inc., Albuquerque, |
| **Joe Yanez, PhD** | Sanwik, Stockholm |
| **George Franks, PhD** | University of Melbourne |
| **Marion Volpert** | Mechanical Eng., UCSB |
| **Begona Ferrari, PhD** | Instituto de Ceramica y vidrio, Spain |
| **Anja Haug** | Universität Karlsruhe, Germany |

## Current Students

| | |
|---|---|
| **Matt Fisher** | Slurry Proc., Interpenetrating Networks |
| **Ben Yu** | Colloidal Iso-Pressing & Body Mechanics |
| **Sascha Klien** | Processing of Photoionic Band-Gap Materials |
| **Kais Hbaieb** | Plastic Forming via Experiments and FEM |
| **Ryan Bock** | Die Cavities for Colloidal Iso-Pressing |
| **Reto Joray** | Colloial Iso-Pressing |

## Former Postdocs

| | |
|---|---|
| **Tom Kramer** | 3M |
| **Bhashar Velamakanni** | 3M |
| **Microslav Colic** | Santa Barbara |

## Current Postdocs

| | |
|---|---|
| **Lisa Palmquist** | Di-block Co-polymers |

## Colleagues

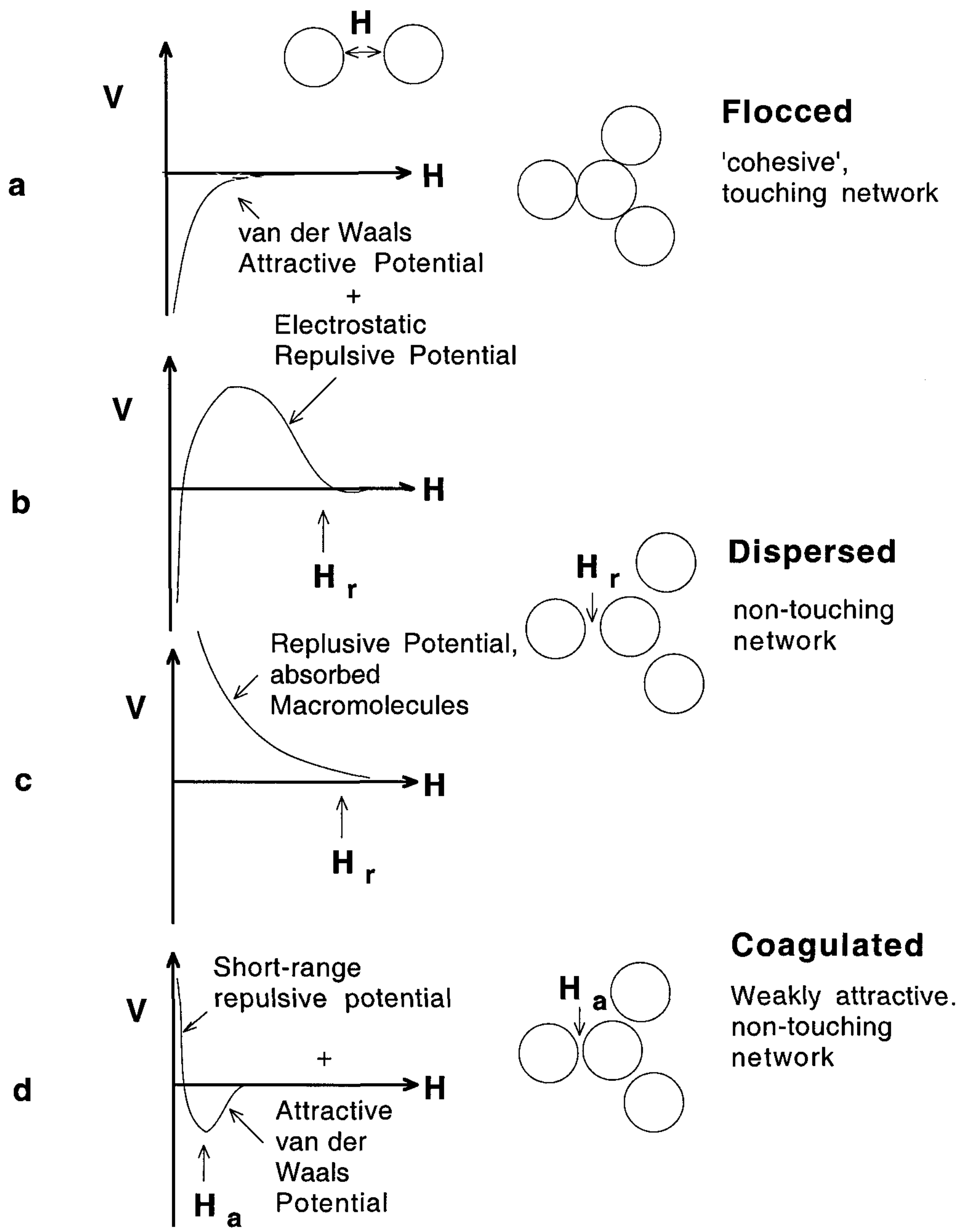
| | |
|---|---|
| Wolfgang Sigmund | Univ. Flordia |
| David Pine | Chemical Eng./Materials |

# Outline

- Interparticle Potentials in Ceramic Processing
- Interparticle Pair Potentials and Rheology
- Specifically Adsorbing Species, Small → Large
    - Counterions
    - Charged Clusters and Marcomolecules
    - Particles
- Growth of Particles and Coating via Adsorption

# Three General Particle Networks

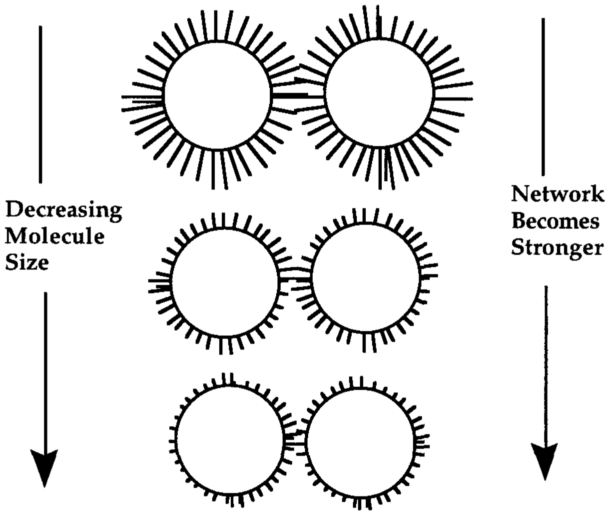
$(0.01 < \phi < \phi_m)$



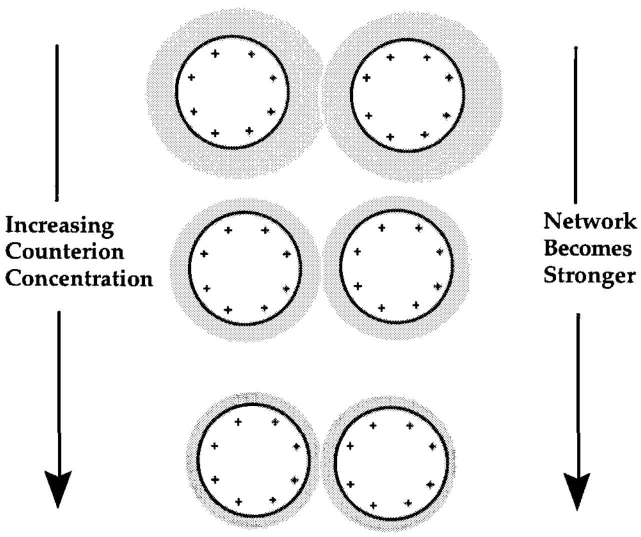
# Two Ways of Producing Short-Range Repulsive Potentials

## (Different Types of Barrier Layers)

- **Chem-Adsorb Molecules**

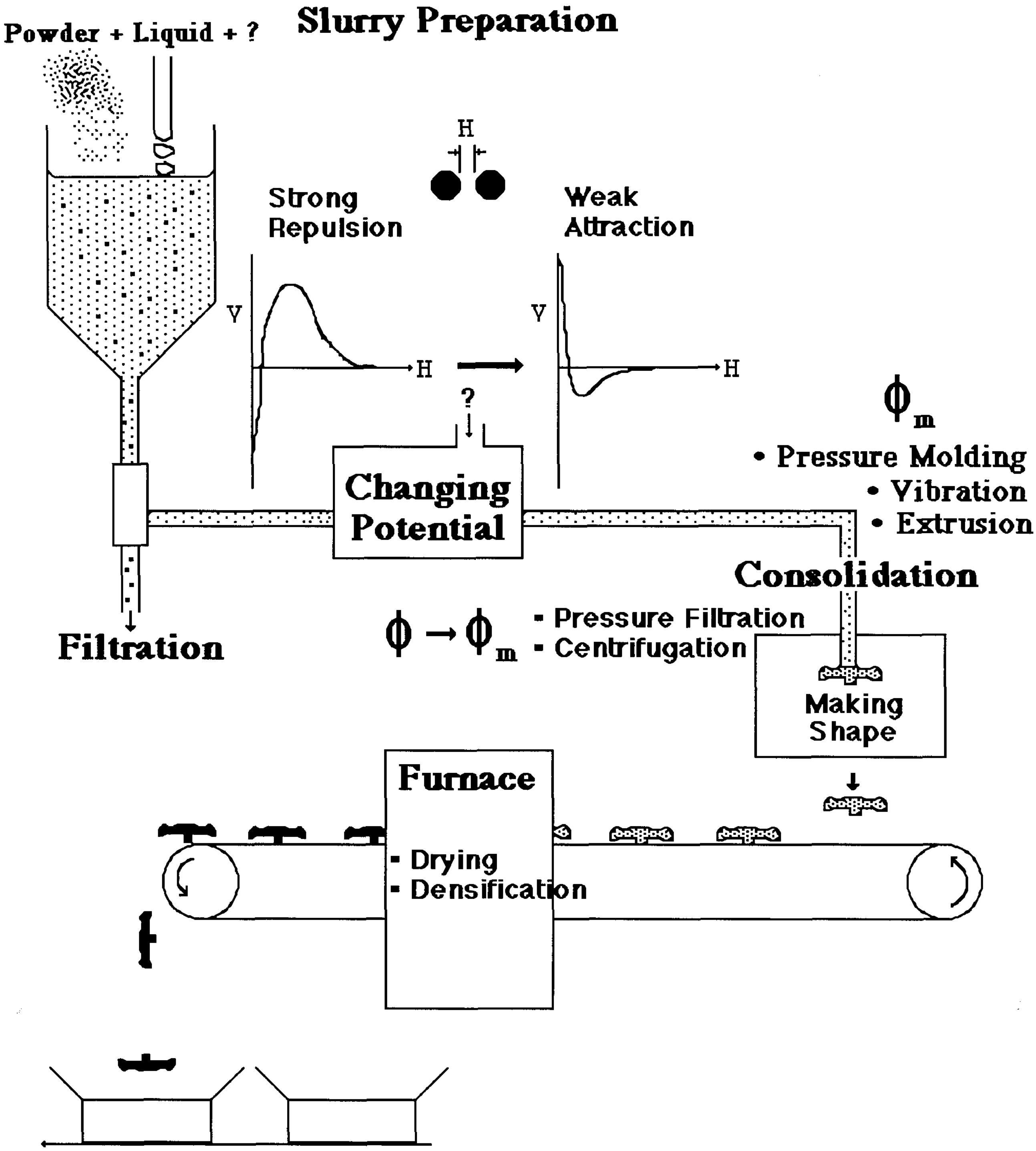



- **Electrostatic Double Layer**



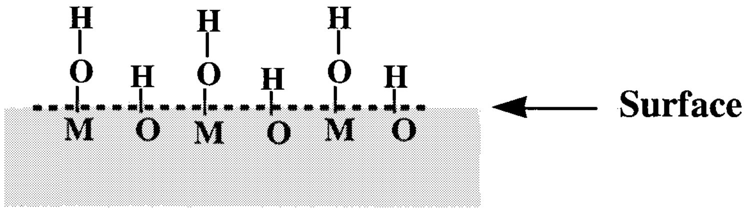
# Colloidal Processing of Powder for Reliable Ceramics

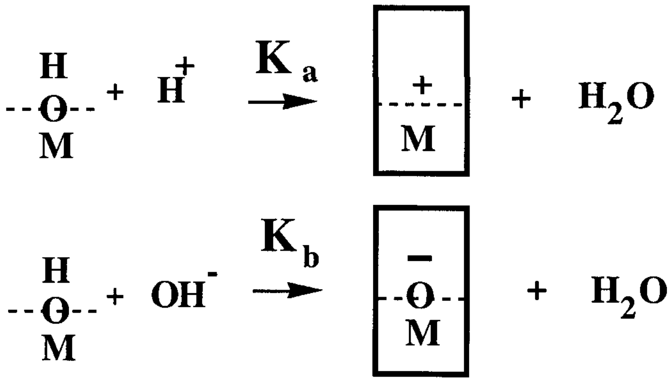
Current Opinion in Solid State & Material Science, 3 [5] 496-500, 1998

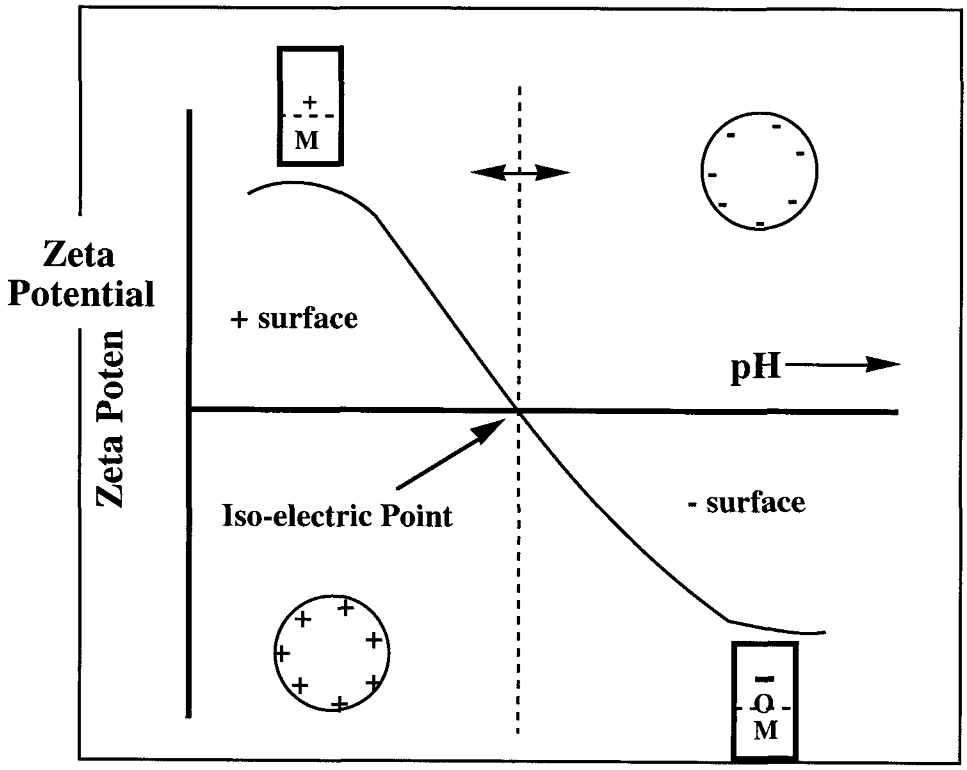


# Repulsion via Counterion Clouds

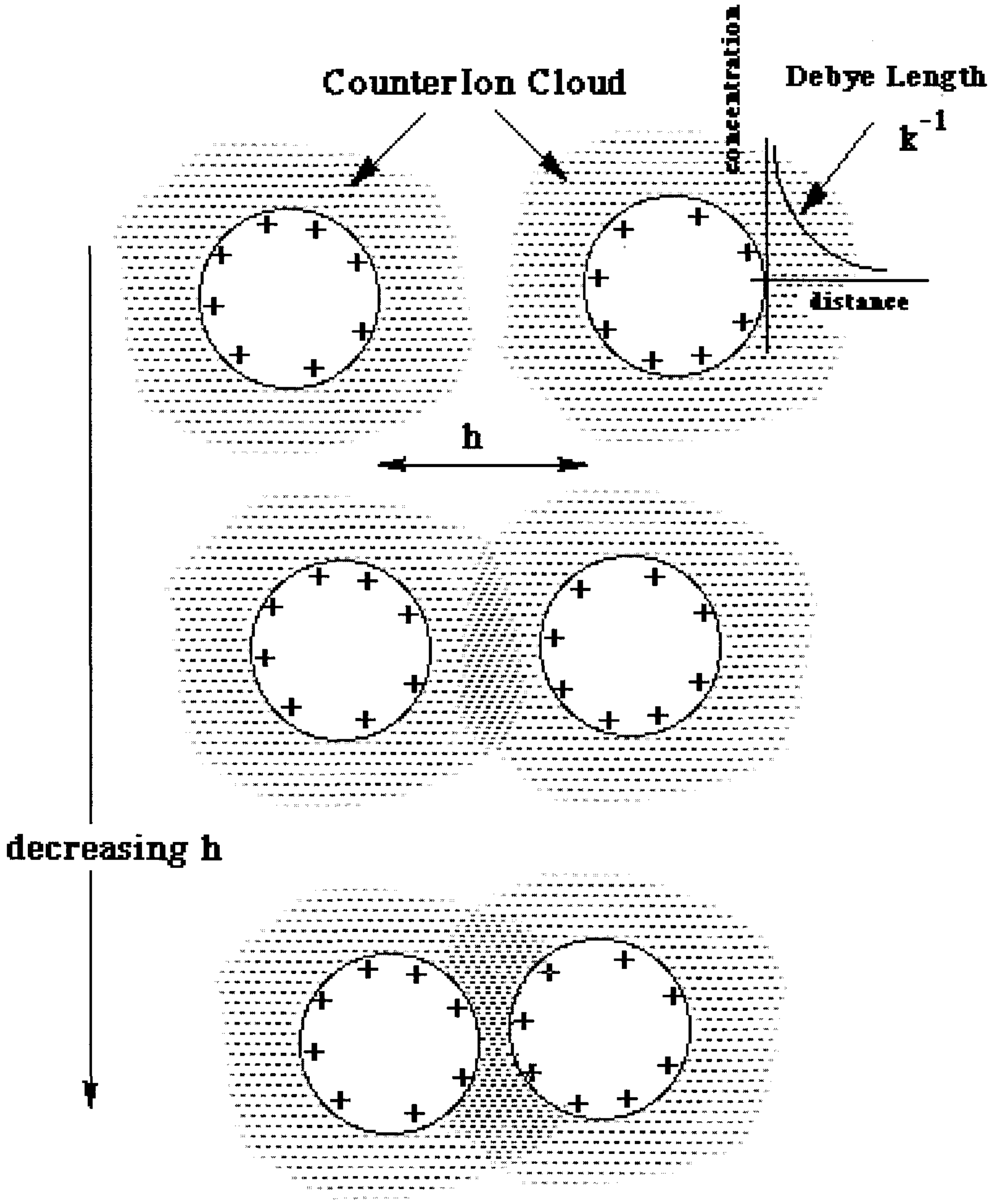
## (Diffusion Double Layer, DLVO)



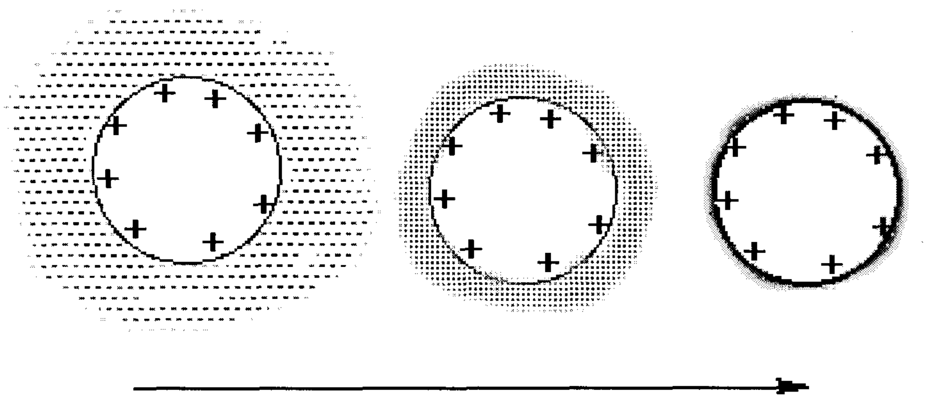



# Penetration of Counterion Clouds origin for Repulsion



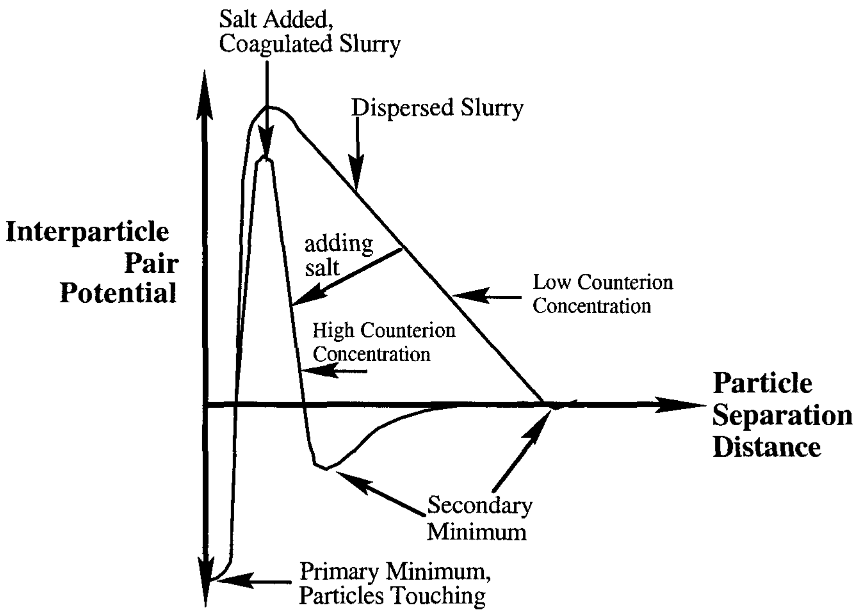

$$V_r = 2\pi \varepsilon \varepsilon_o a \psi^2 \exp\left(-\frac{h}{\kappa^{-1}}\right)$$

# Modified DLVO

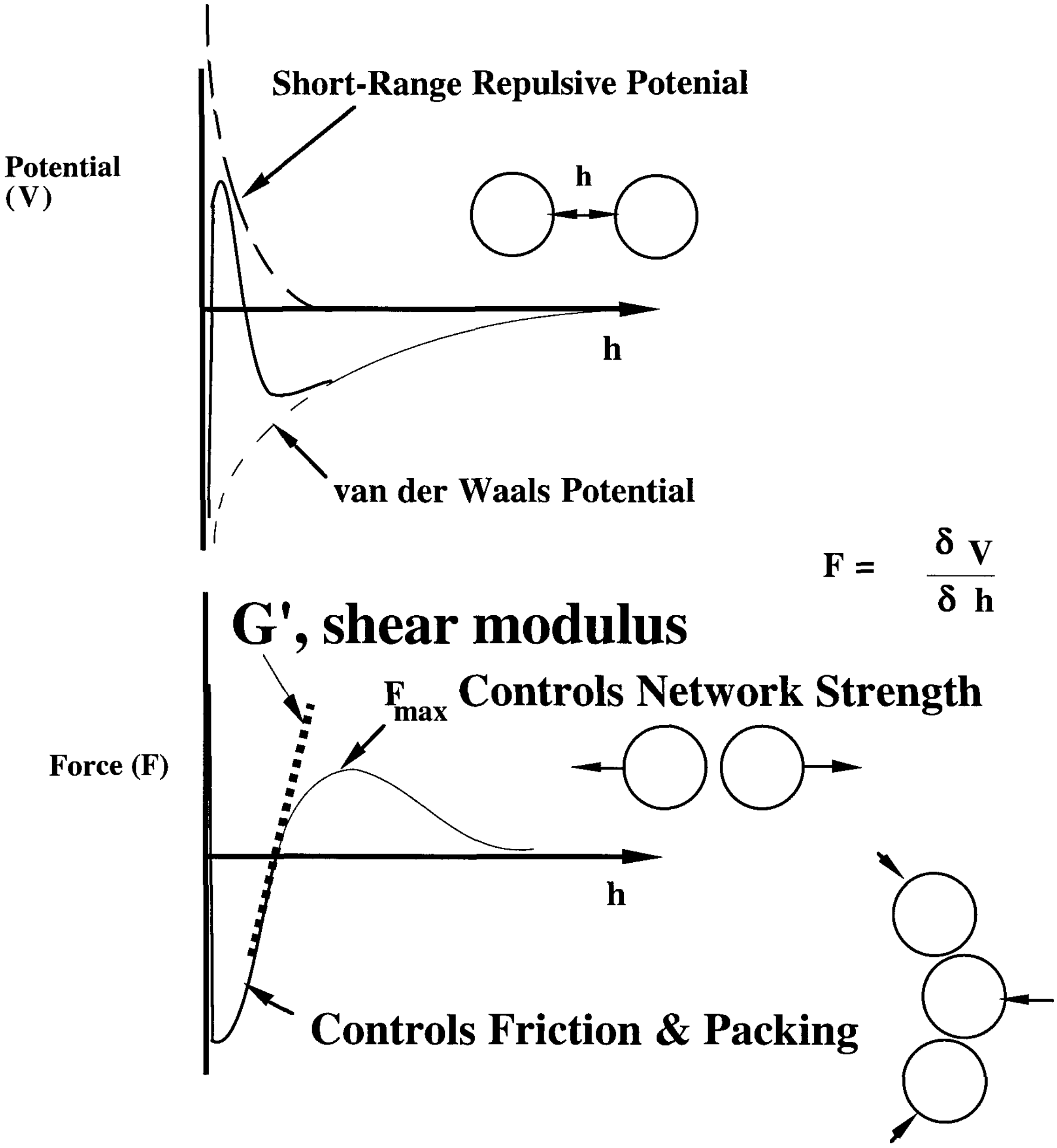


**Adding Salt (Counterions) decreases cloud thickness to a finite value**

**(Modified DLVO)**

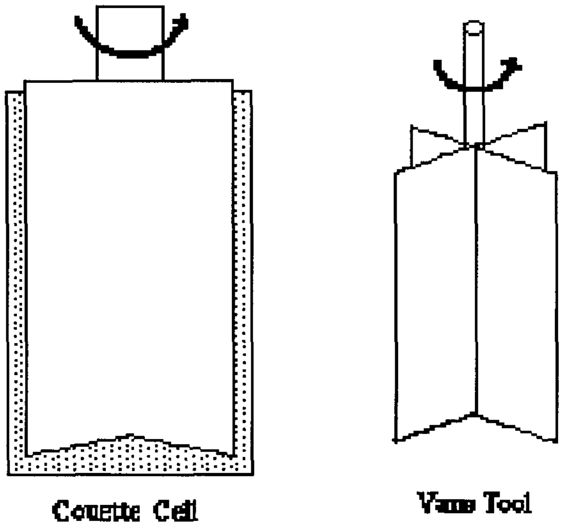


# Network Strength

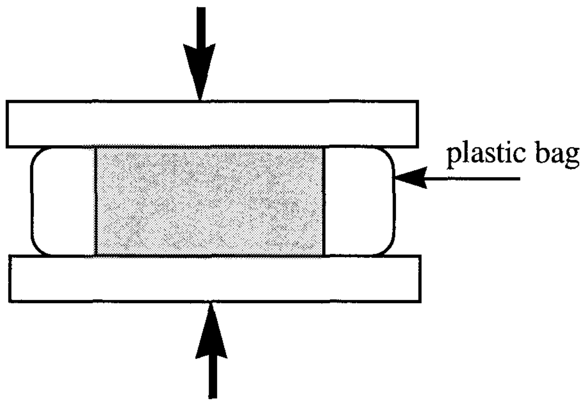


# Measuring Particle Network Properties

- Slurry
    - Viscosity vs Shear Rate
    - Elastic Modulus
    - Yield Stress

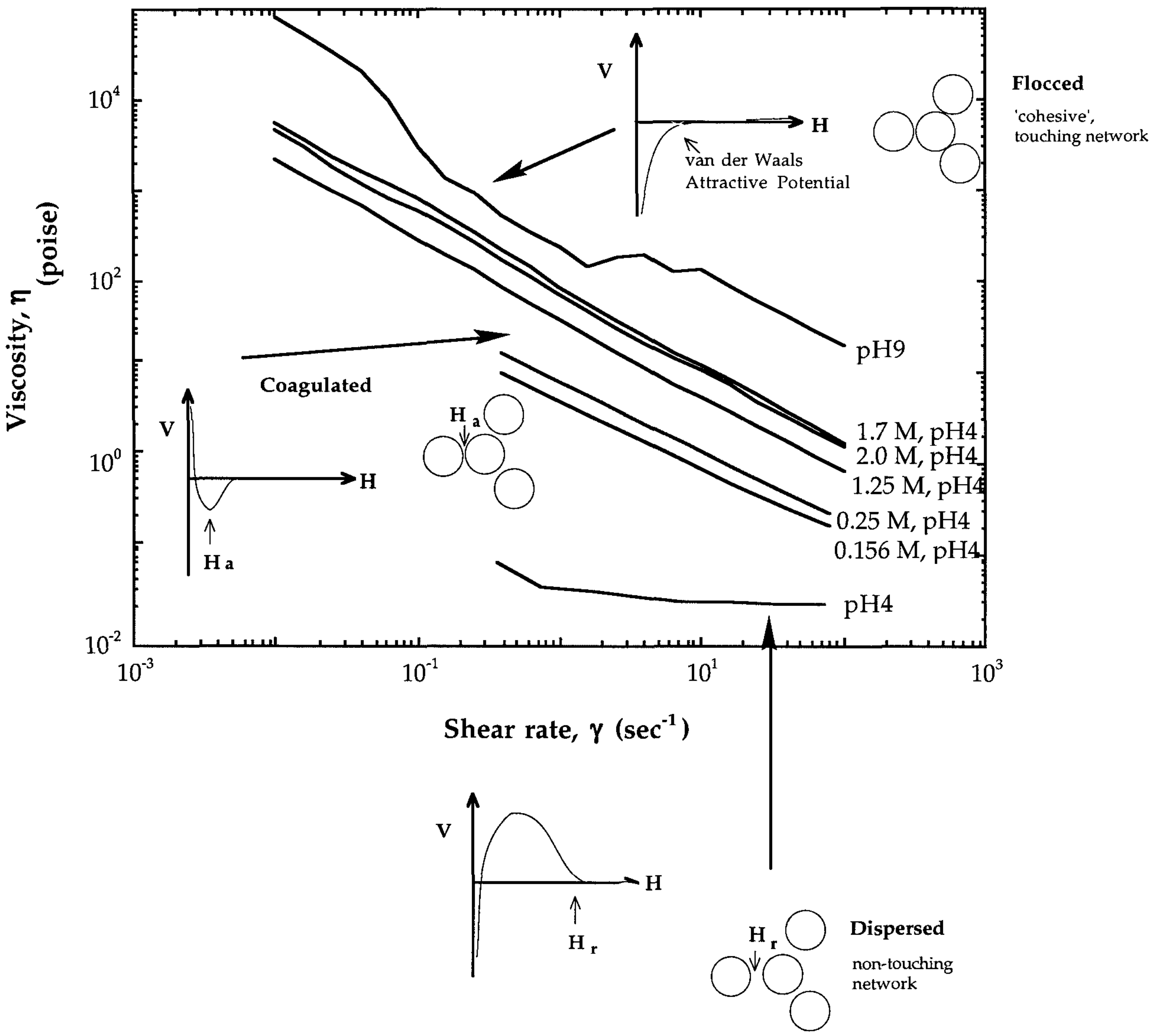



- Consolidated Body
    - Plastic or Brittle Nature
    - Flow Stress



# Viscosity vs Shear Rate

## $Al_2O_3$ (AKP 50), 20 v/o



## Specifically Adsorbing Species, Small → Large

### Adsorption
### ordered or random ???

# Ions

- **$Ba^{+2}$ Cations on (100) $SrTiO_3$**
  L. Zhao, A.T. Chien, F.F. Lange, and J.S. Speck, J. Mat. Res., 111 325-28, 1996

- **Citrate Anions on $Al_2O_3$ Particles**
  Erik P. Luther, George V. Franks, Joseph A. Yanez, F. F. Lange and D. S. Pearson, J. Am. Ceram. Soc. 78 [6] 1495-1500 (1995).

# Clusters/Macromolecules

- **Adsorbtion of $SiW_{12}O_{40}^{-4}$ Anions on Ag(111)**
  Zhong, Klemperer and Gewirth, J.Am. Chem Soc. 118, 5812 (1998)

- **Adsorbtion of Di-Block Copolymers on $Al_2O_3$ Particles**
  Lisa Palmquist, Fred Lange, W. Sigmund and J. Sindel

# Particles

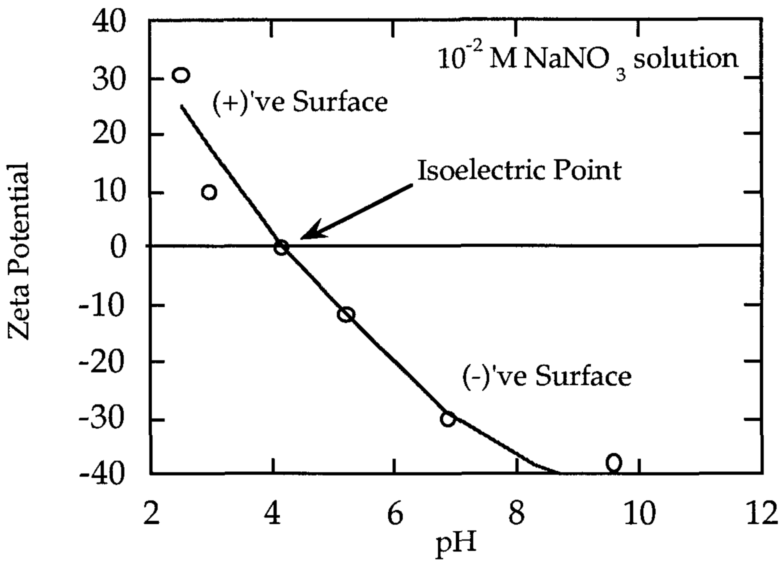
- **Adsorbtion of Silica Spheres on Alumina Particle**
  M. L. Fisher, M. Colic, M. Rau, and F. F. Lange (to be published)

- **Coating Silicon Nitride Particles with 'Alumina'**
  E. P. Luther, F. F. Lange and Dale S. Pearson, J. Am. Cer. Soc. 78 2009-14 (1995).

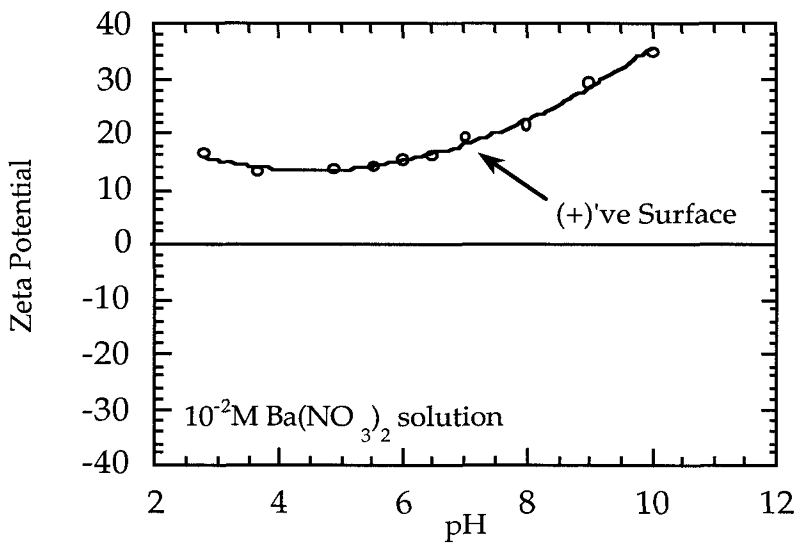
# $Ba^{+2}$ can be a Specifically Adsorbing Counterion

## Electrophoretic Mobility vs. pH for SrTiO3 powder

### $SrTiO_3$ Powder without Barium




### $SrTiO_3$ Powder with Ba Addition

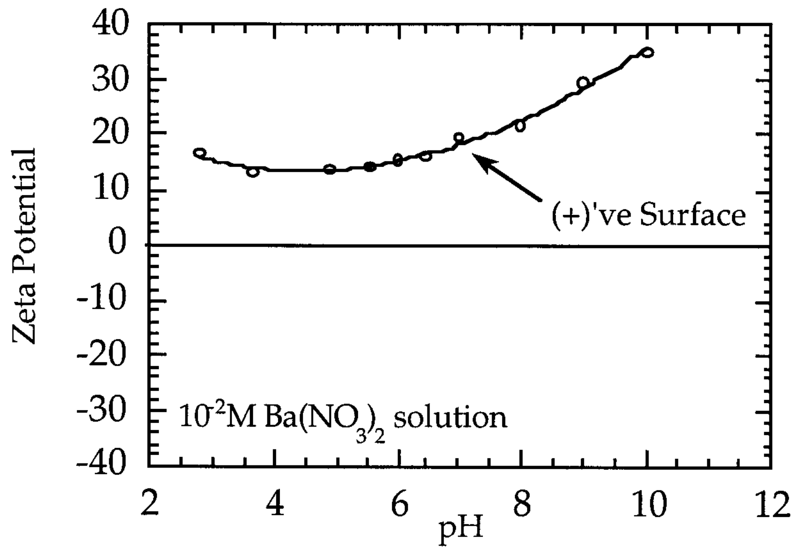


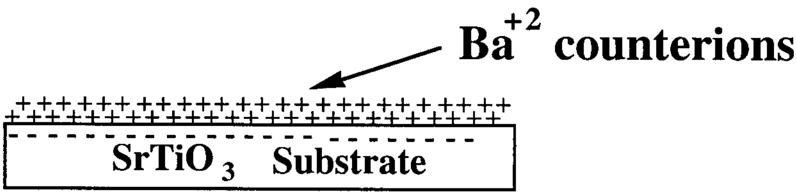
# $Ba^{+2}$ can be a Specifically Adsorbing Counterion

L. Zhao, A.T. Chien, F.F. Lange, and J.S. Speck, J. Mat. Research, 111 325-28, 1996.

- **With $Ba^{+2}$ Additions**

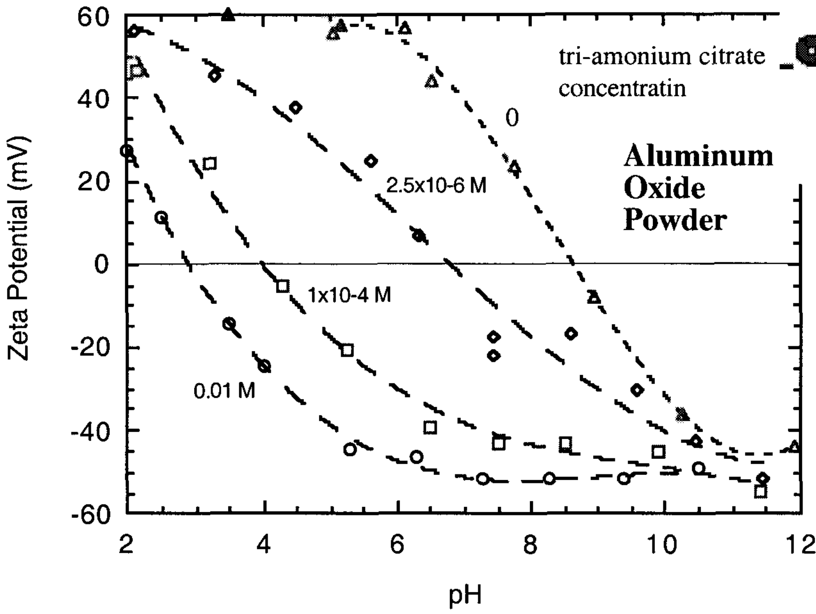
  **($Ba^{+2}$ is a potential determining Counterion)**

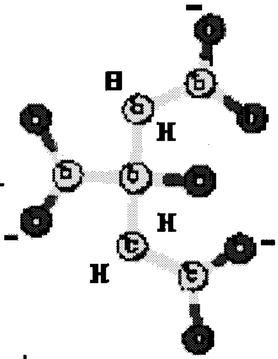


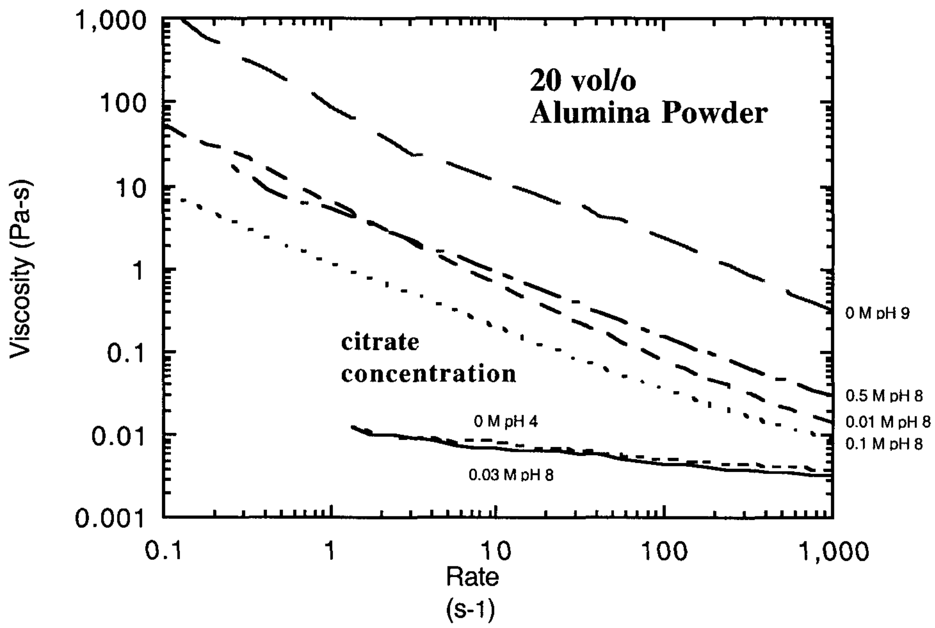

# Specifically Adsorbing Citrate Ion

- Zeta Potential



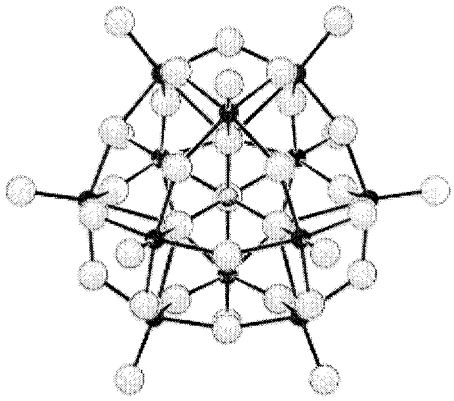
- Viscosity vs Shear rate



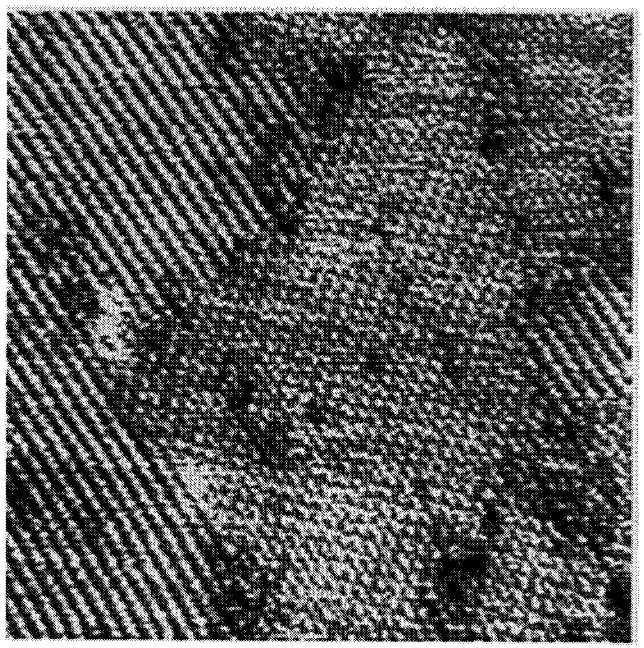
# Adsorbtion of $SiW_{12}O_{40}^{-4}$ Anions on Ag(111)

**Zhong, Klemperer and Gewirth, J.Am. Chem Soc. 118, 5812 (1998)**

- **The Anion** (10.2 Å diameter)

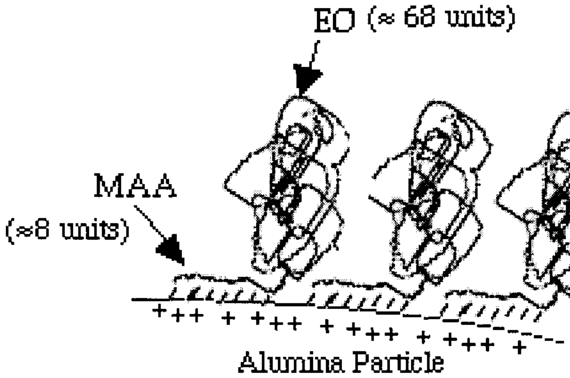


- **AFM of Ordered Arrangment**

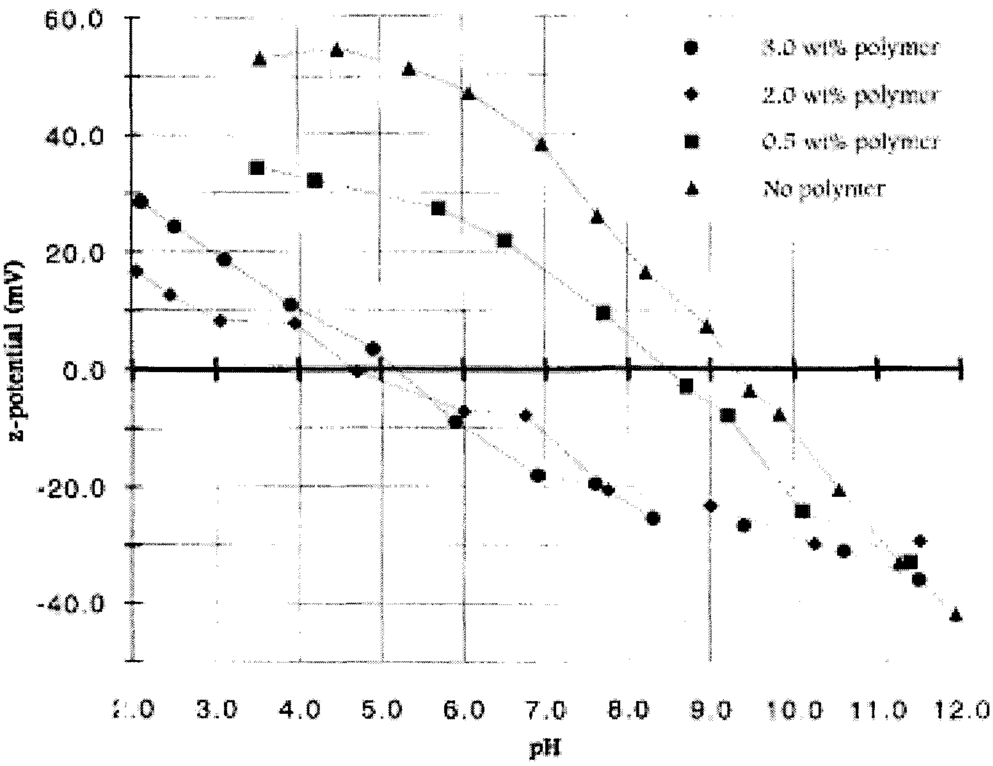


# Di-Block Copolymer/ $Al_2O_3$

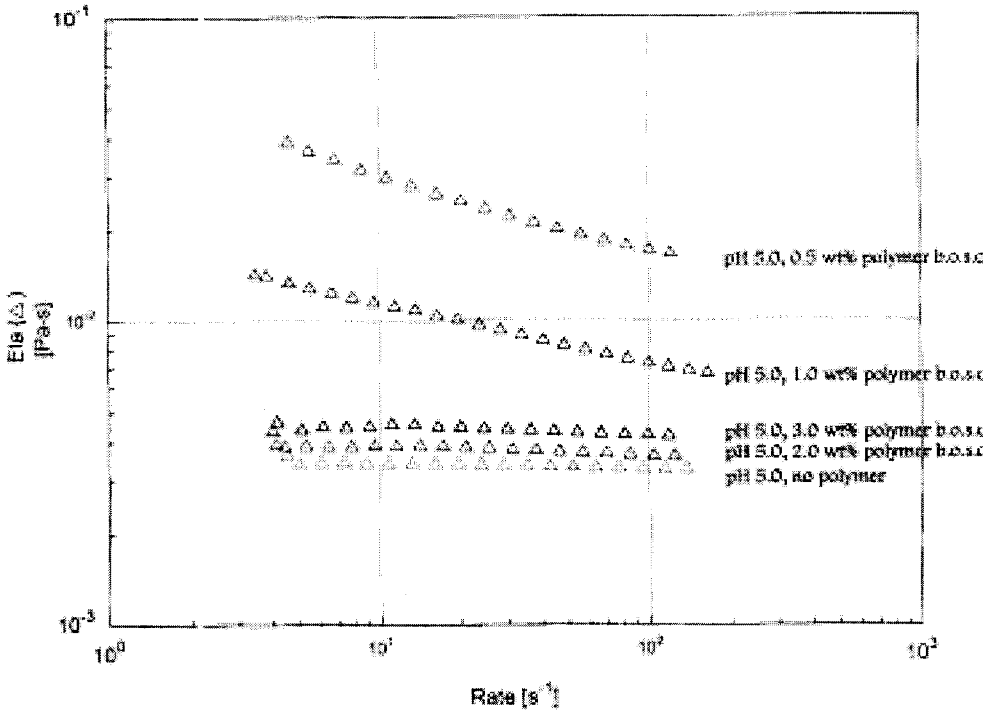
poly(methacrylic acid)-b-(ethylene oxide)




- **Zeta Potential of Coated and Uncoated Powders**

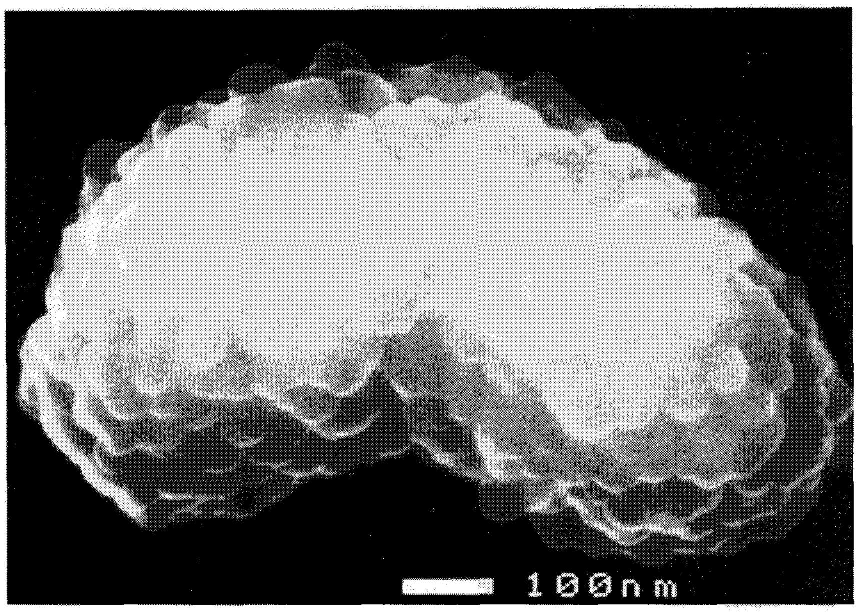


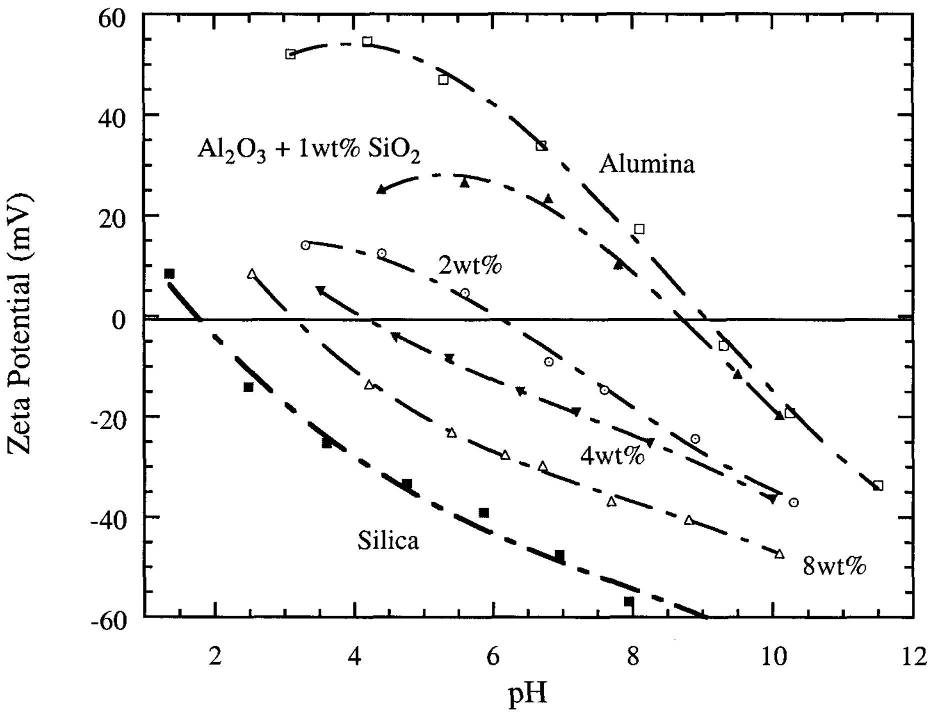
# Viscosity vs Shear Rate at pH 5



# Adsorbtion of Silica Spheres on Alumina Particle

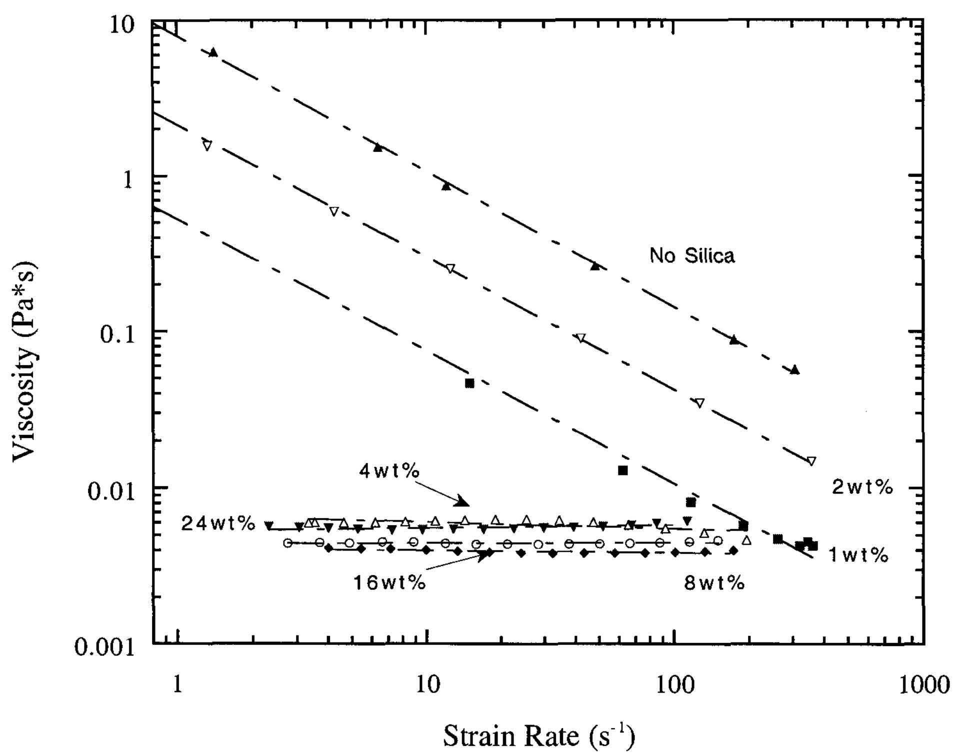
- 25 nm Silica Particles on 250 nm Al2O3 particle



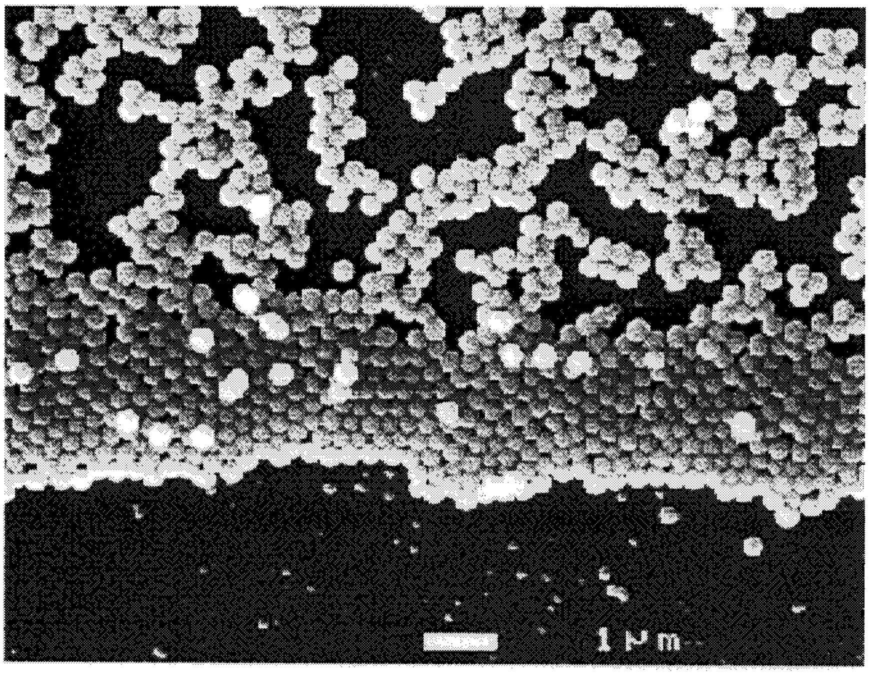
# Adsorbtion of Silica Spheres on Alumina Particle

- 25 nm Silica Particles on 250 nm Al2O3 particle

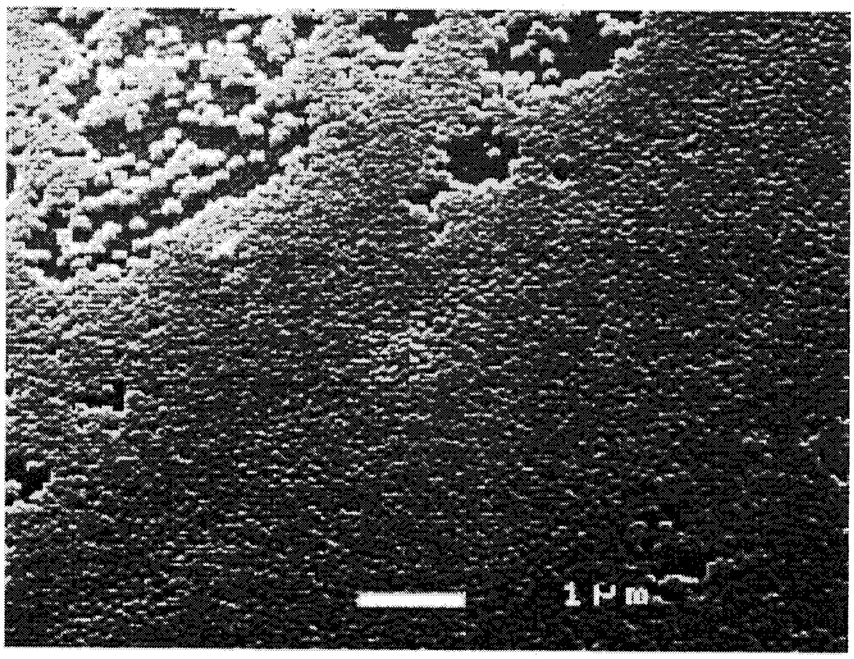


# Adsorbtion of Silica Spheres on Alumina Fiber

- 300 nm Silica Spheres on $Al_2O_3$ Fiber

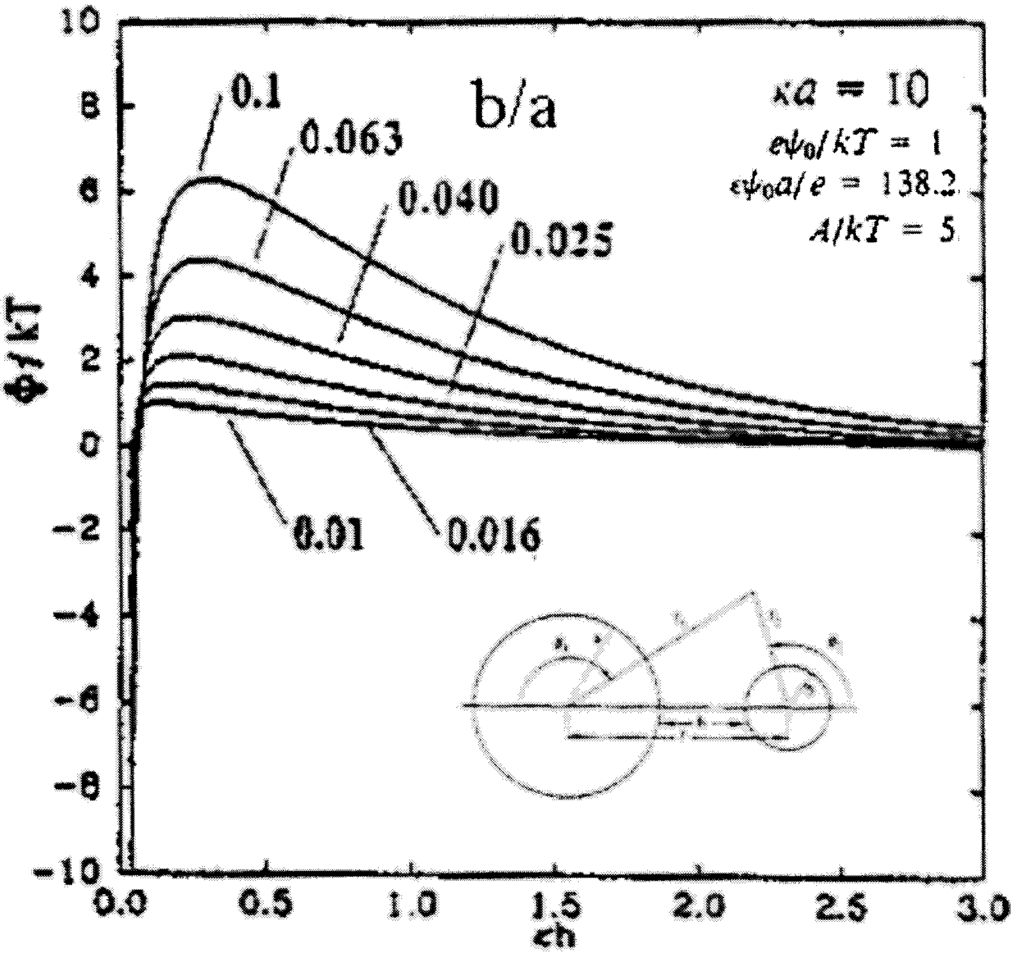



- 85 nm Silica Spheres on $Al_2O_3$ Fiber



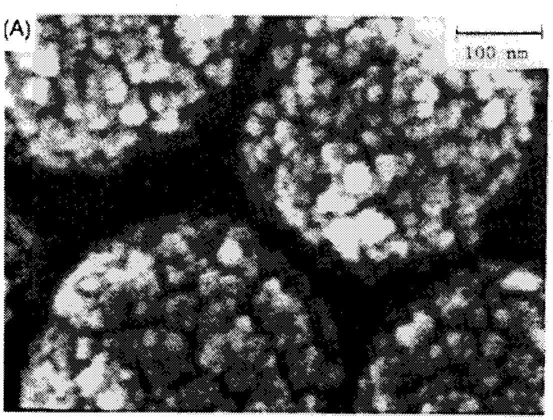
# Small Particles Attracted to Large Particles

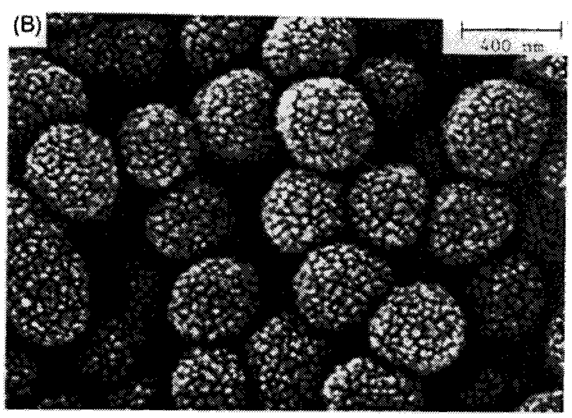
## DLVO derivation




**Edelson and Glaeser, J. Am. Ceram. Soc. 71 (1988)**

**$TiO_2$ particles formed in Solution**

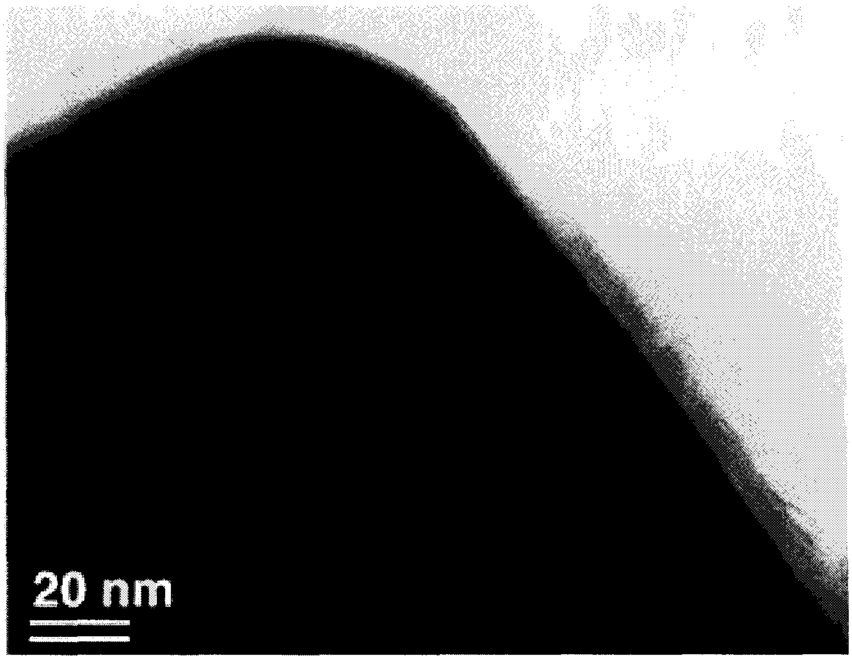


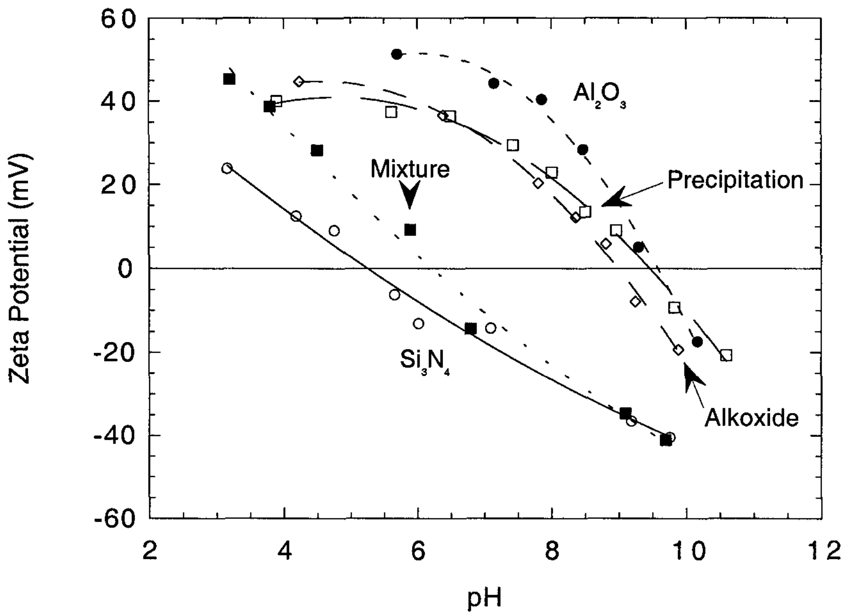



# Coating $Si_3N_4$ Particles with $Al_2O_3$

## Al(NO3)3 + $(H_2N)_2CO$ (urea) + Water

$$(H_2N)_2CO + H_2O + 2H_3O^+ \xrightarrow{\Delta} CO_2\uparrow + 2H_2O + 2NH_4^+$$



# Coating $Si_3N_4$ Particles with $Al_2O_3$

## 20 vol/o Si3N4 Coated Powder