

Nanopartículas

Partículas porosas

# Padrão de patenteamento no Brasil

- Dominância de algumas empresas:
  - Procter and Gamble, Dow Chemical, L'Oreal e Rohm & Haas, (acima de 20.000 patentes depositadas no Exterior)
- Em termos de patentes depositadas nos Estados Unidos, observa-se que a Dow Chemical depositou mais patentes do que a Procter & Gamble
- Não participam empresas como a Hewlett-Packard, IBM, Motorola, Siemens
  - inexistência de uma produção industrial brasileira significativa, na área de semicondutores e equipamentos de TI
- Pouca participação de empresas farmacêuticas

# **Maiores depositantes no Brasil em nanotecnologia**

**L'Oreal : 19 patentes (nanopigmentos [9], nanoemulsões [8] e nanocápsulas [2])**

**Procter & Gamble: 11 patentes (nanocristalino [4], nanopartículas [3], nanofiltração [1], nanômetro [1], nanoporoso [1] e tamanho nano [1]).**

**Rhodia Chimie com 9 patentes (nanofibrilas [5], nanopartículas [2], nanométrico [1], nanofibras [1]).**

**Dow Chemical com 7 patentes (nanocompósitos [2], nanofiltração [1], pó nanoescalar [1], nanocompostos [3]).**

**Bayer AG com 6 patentes (nanopartículas [2], nanométricas [1], nanoescala [1], nanoestruturado [1], escala nano [1]).**

**Rohm and Haas com 5 patentes ( nanocompósitos [4] e nanômetros [1]).**

**Eastman Chemical e Solutia com 4 patentes, todas em nanocompósitos.**

# Propriedades especiais

- Muita área, pouco volume
  - Superplasticidade
    - Moldagem à temperatura ambiente?
  - Tensão superficial negativa
  - Confinamento quântico
  - Pouco espalhamento da luz
  - Pouca sedimentação
- Dispersão segue equação de estado termodinâmica
  - Como se fosse solução



# Modificação de superfície de Teflon

- Teflon exposto a  $\text{Fe}(\text{CO})_5$  adquire cor laranja-avermelhada, permanente
- Mecanismo:
  - A)  $\text{Fe}(\text{CO})_5$  é sorvido pelo Teflon
  - B)  $\text{Fe}(\text{CO})_5$  é oxidado pelo ar formando óxido
  - C) o óxido permanece imóvel no interior do Teflon
- Resultado prático: molhabilidade, adesão
- Conceito: síntese em ambiente confinado
  - Síntese em microemulsões

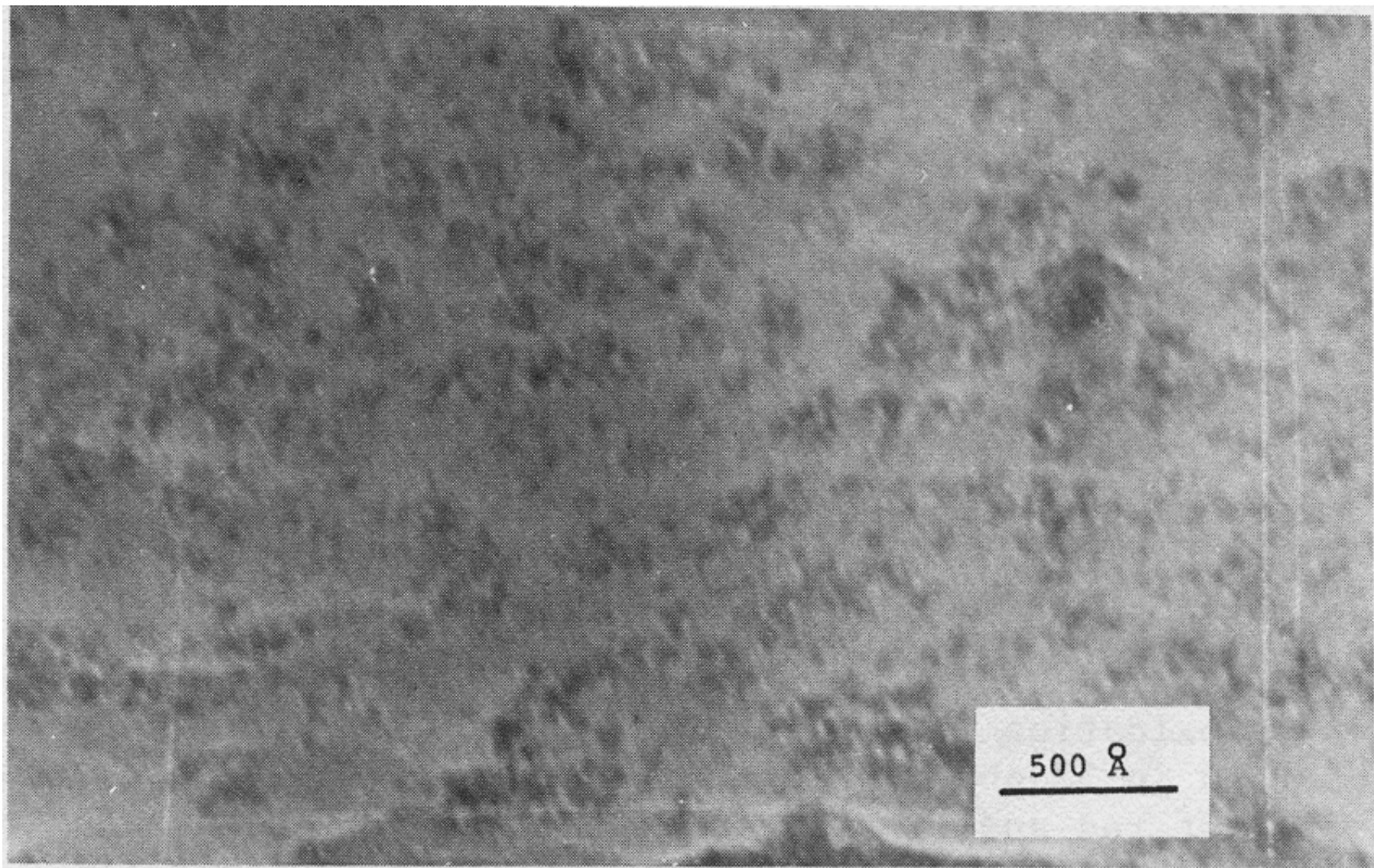


Figure 3. Electron Micrograph of  $\text{Fe}_2\text{O}_3$ -impregnated PTFE.

Surface Contamination, 1979

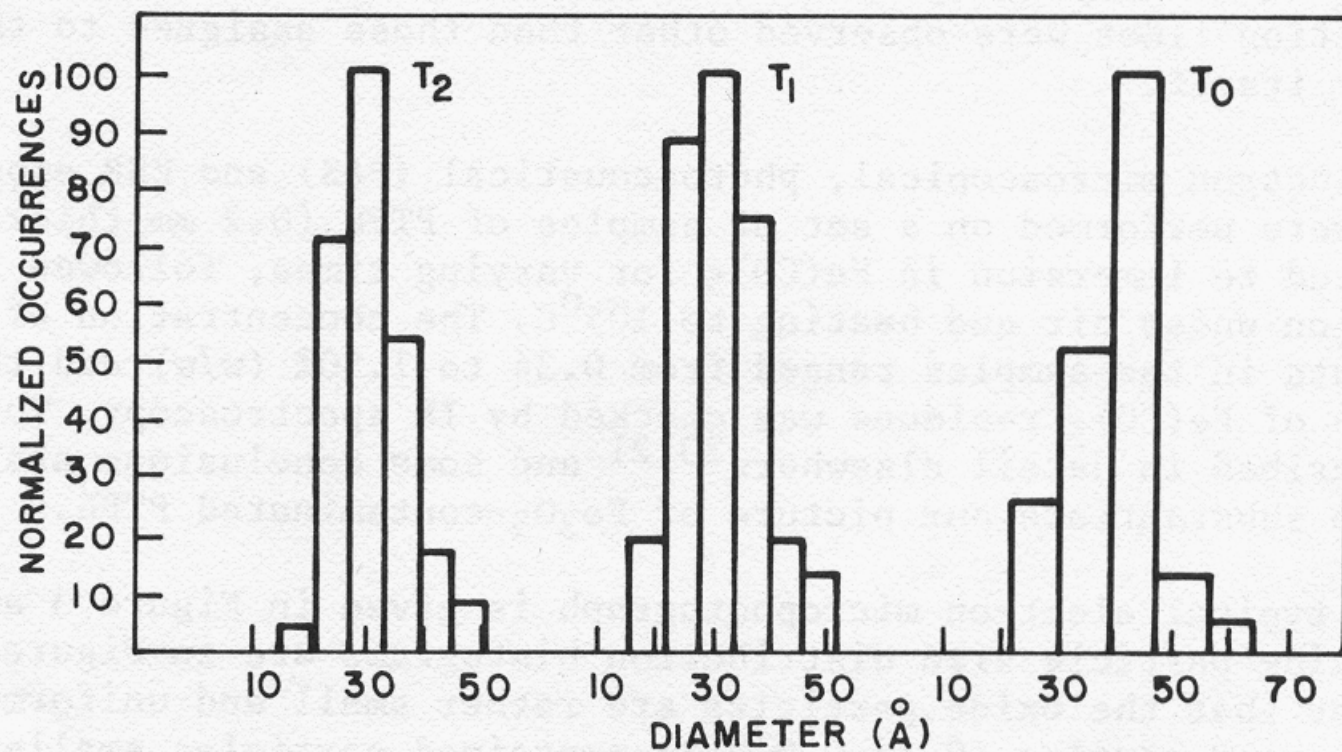
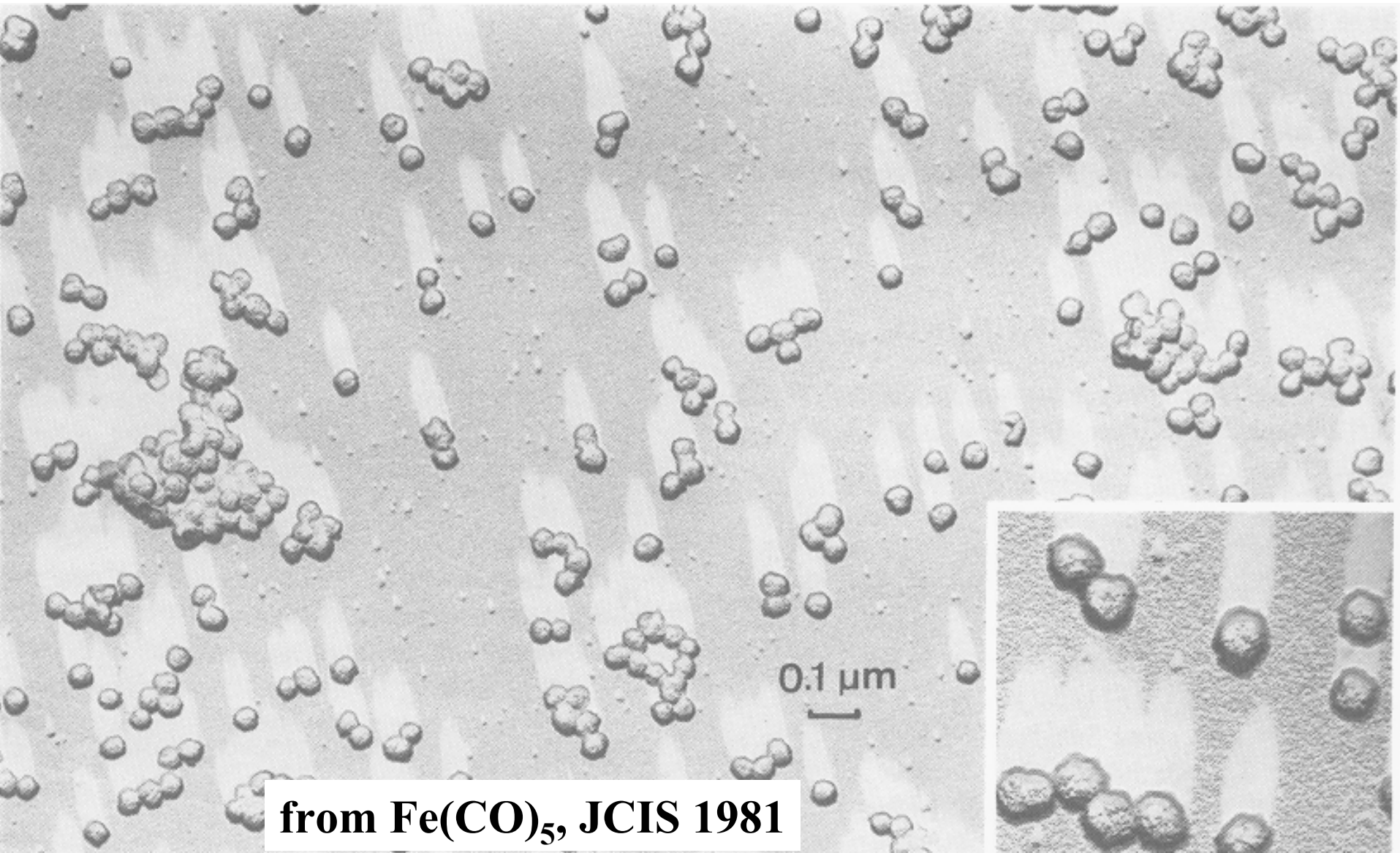


Figure 4. Particle size distribution histograms of Fe<sub>2</sub>O<sub>3</sub> in PTFE. Fe<sub>2</sub>O<sub>3</sub> concentration in the samples: T<sub>0</sub>, 0.34; T<sub>1</sub>, 0.58; T<sub>2</sub>, 0.62%.

# Nanopartículas de hidroxioacetato de ferro (III)



from  $\text{Fe}(\text{CO})_5$ , JCIS 1981

## Nanopartículas em polifosfato de alumínio

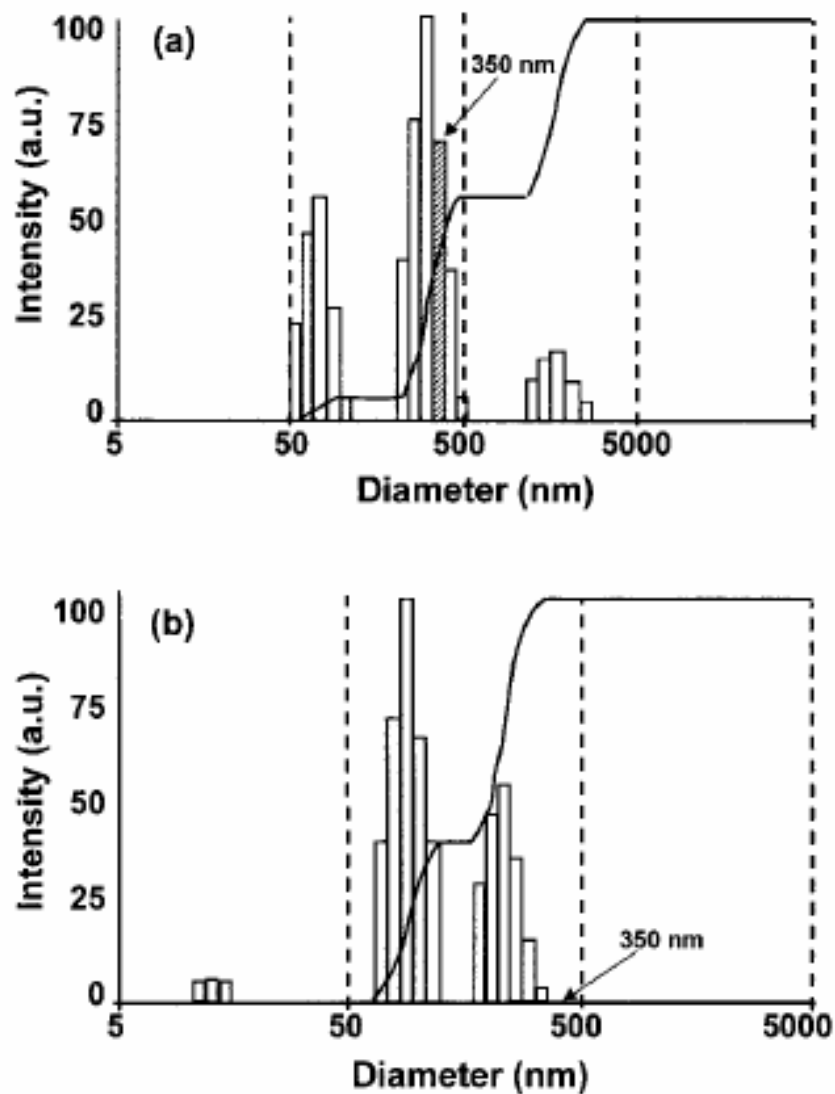


FIG. 1. Multimodal particle diameter distribution of the  $P_3Al_{1.5}N_3$  sample (a) as prepared and (b) after centrifugation (10,800g, 5 min).

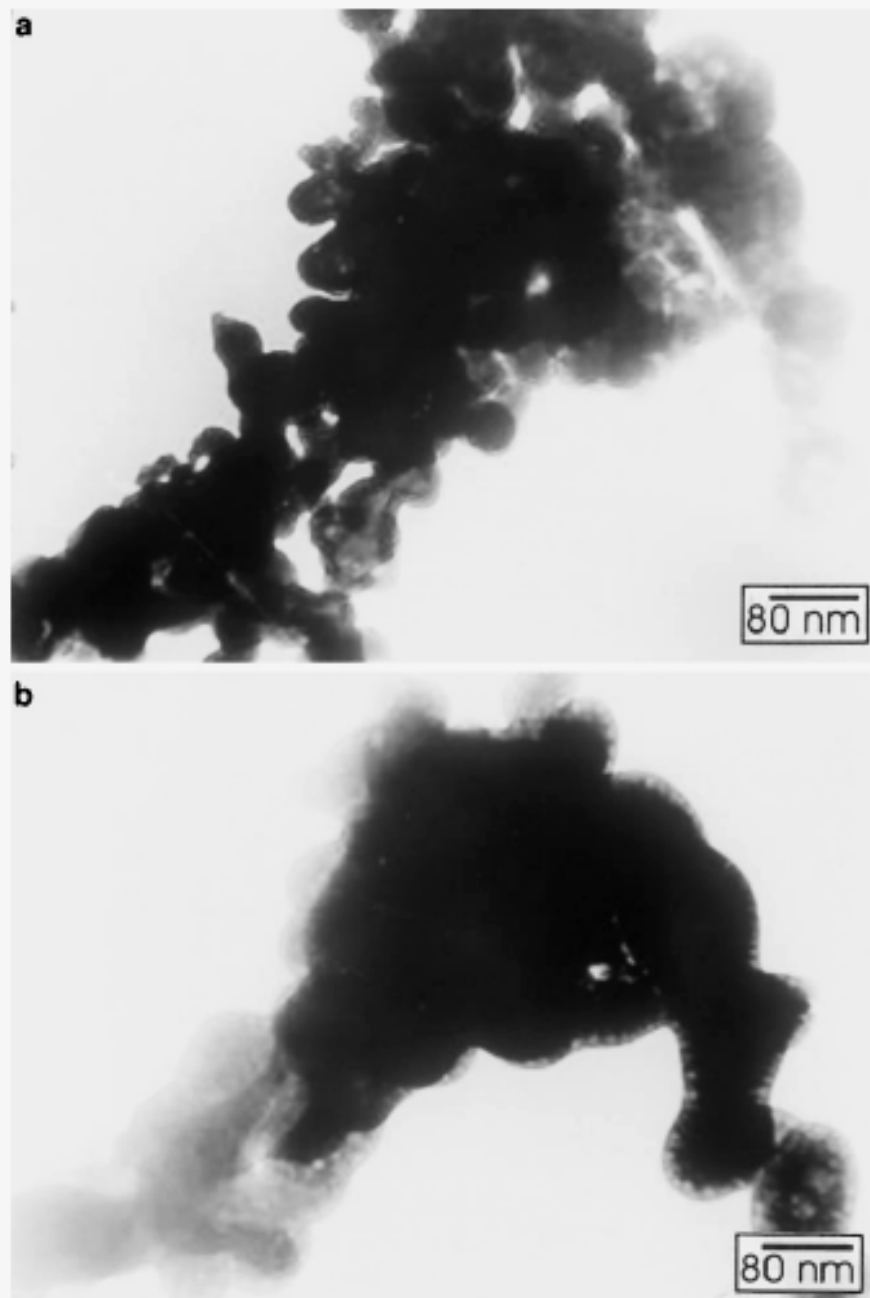


FIG. 2. Bright-field transmission electron micrographs (a) of aggregated particles obtained by lyophilization of the dialyzed middle layer of the  $P_{16}Al_{100}N_{170}$  sample and (b) the same sample, but after 3 min of beam exposure. Note the voids at the particle border.



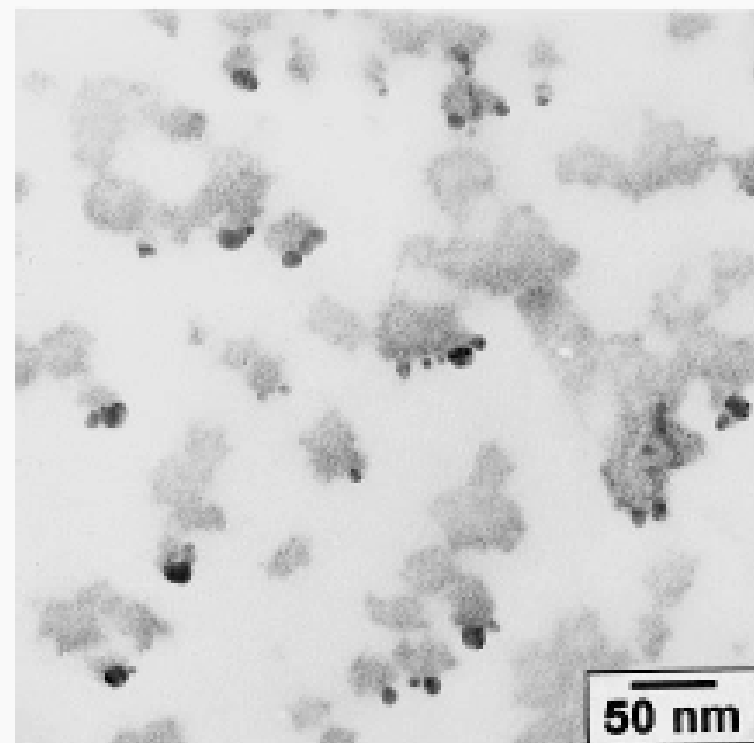
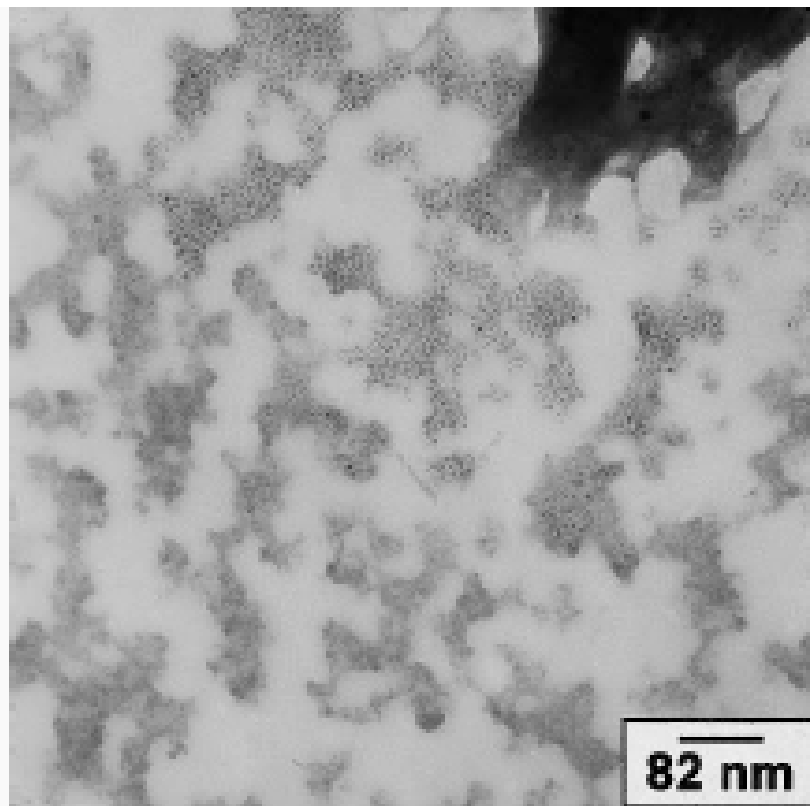


FIG. 3. Bright-field transmission electron micrographs of particles obtained by lyophilization of the dialyzed top layer of the  $P_{60}Al_{100}N_{170}$  sample.

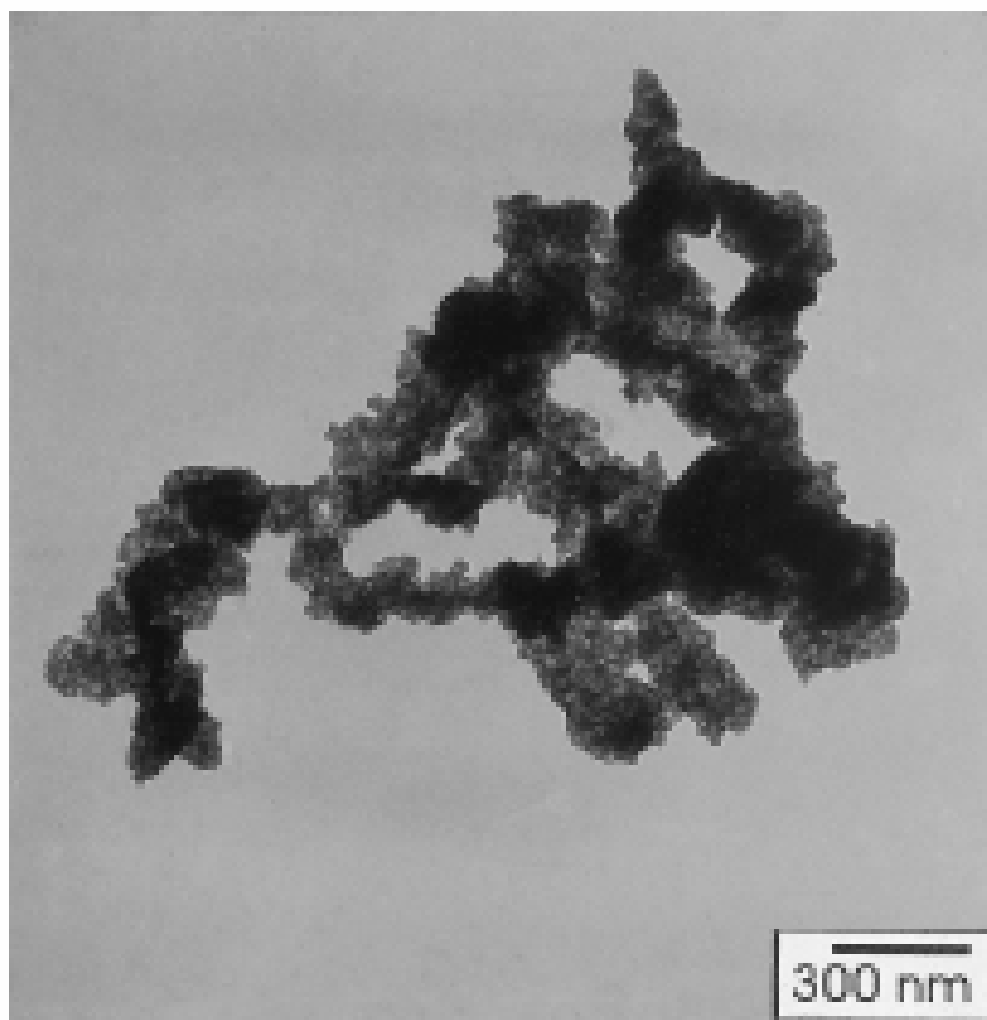


FIG. 4. Bright-field transmission electron micrograph of an aggregate of very small particles from the  $P_{3.8}Al_{1.1}N_{1.1}$  lyophilized sample.



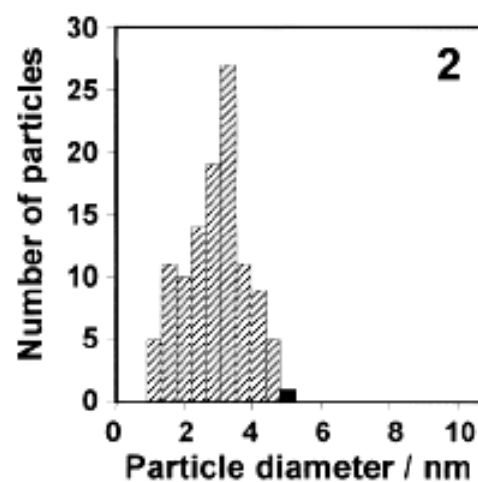
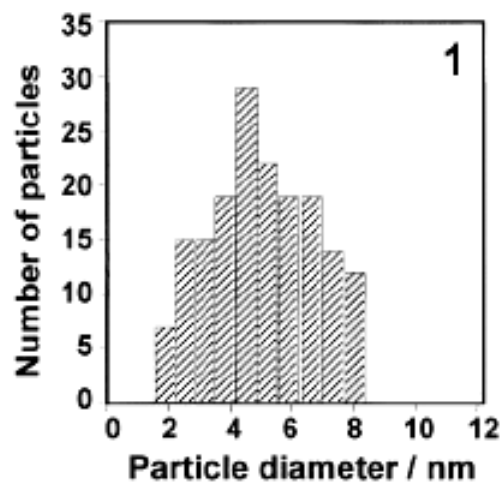
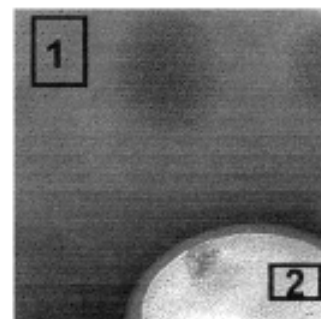
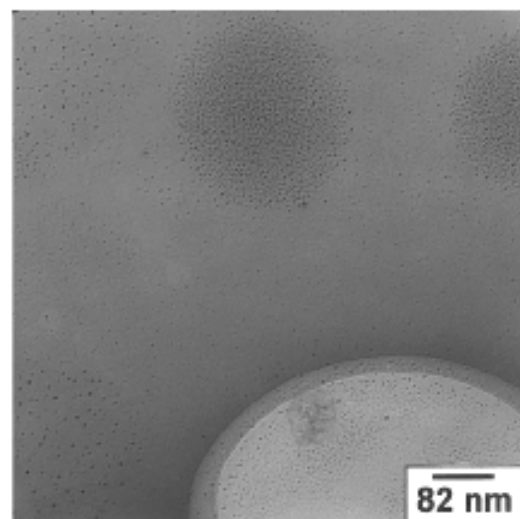


FIG. 5. Bright-field transmission electron micrographs of three different domains of the  $P_{30}Al_{22}N_{12}$  sample and the corresponding particle diameter histograms obtained from the images. The histograms refer to the particles within rectangles drawn in the image replicas, to the right of each picture.

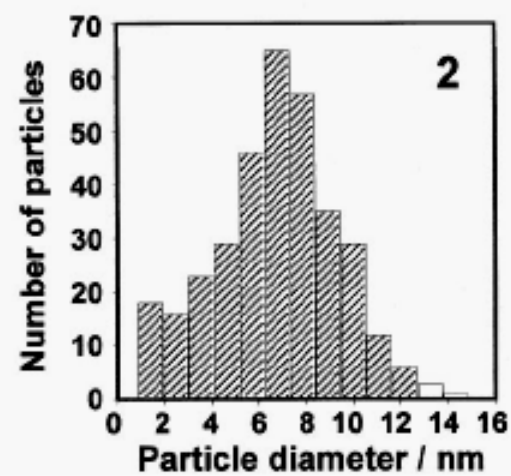
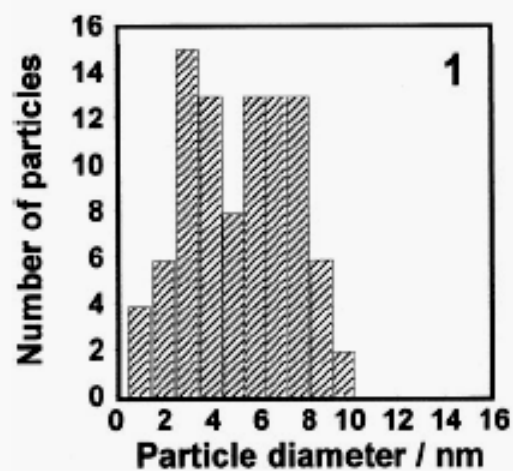
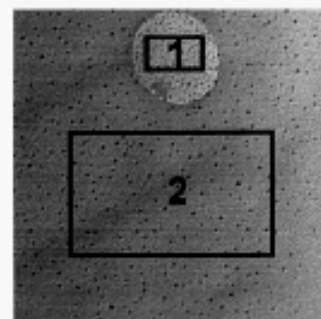
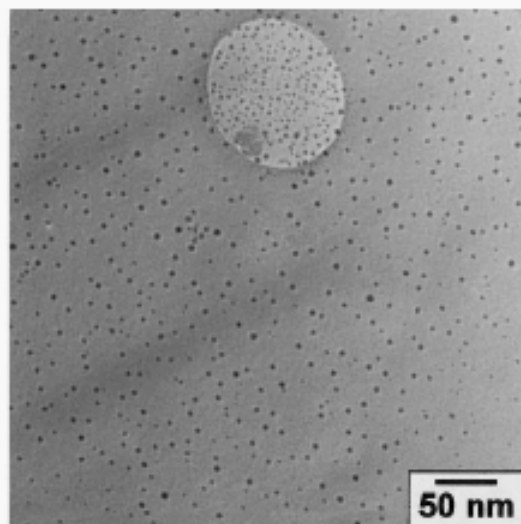


FIG. 5—Continued

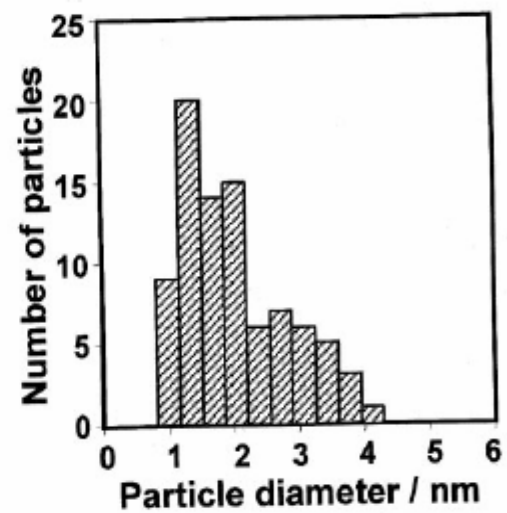
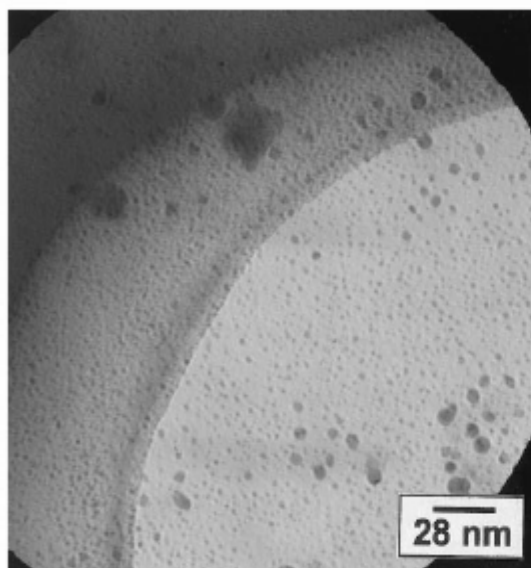
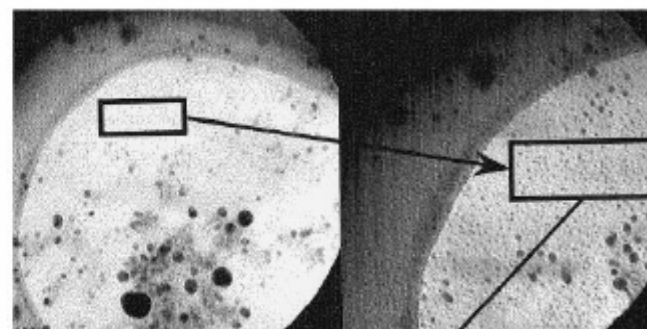
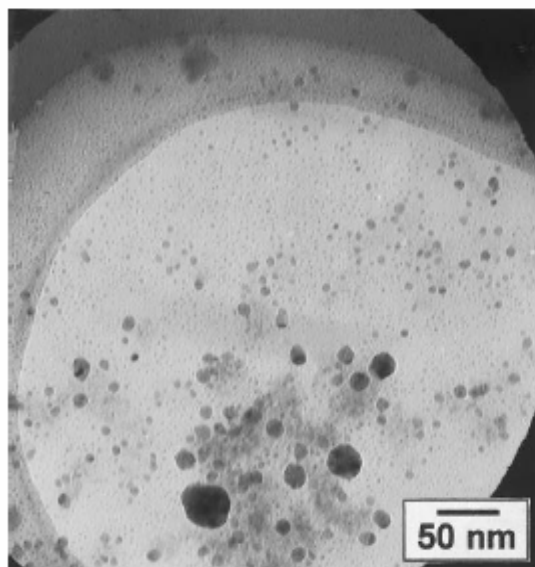


FIG. 5—Continued

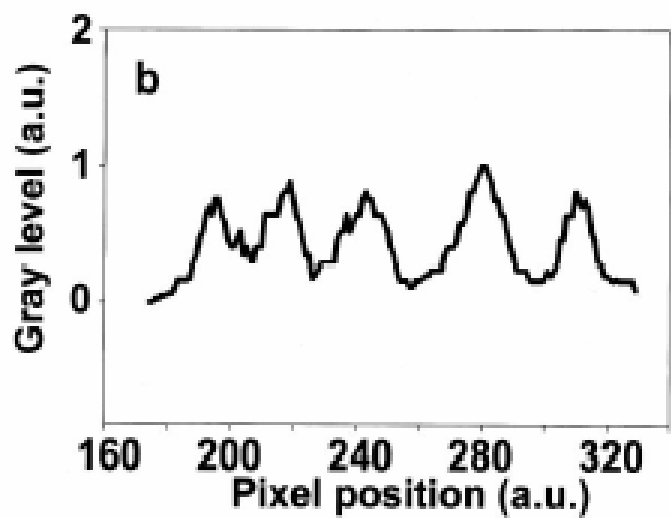
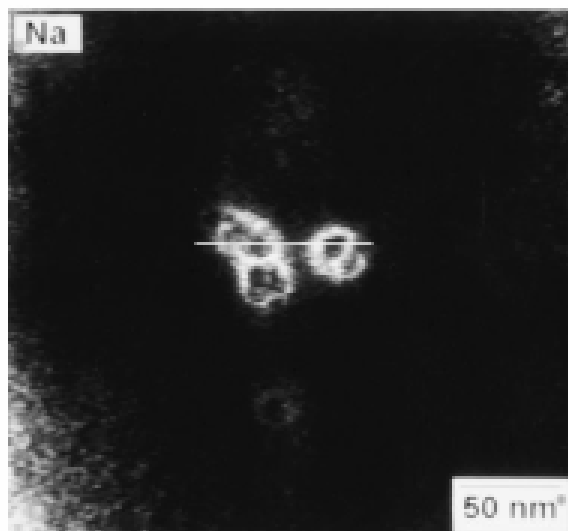
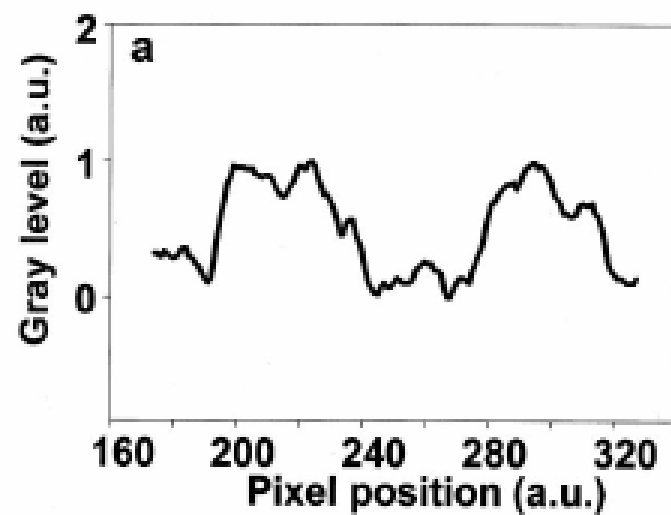
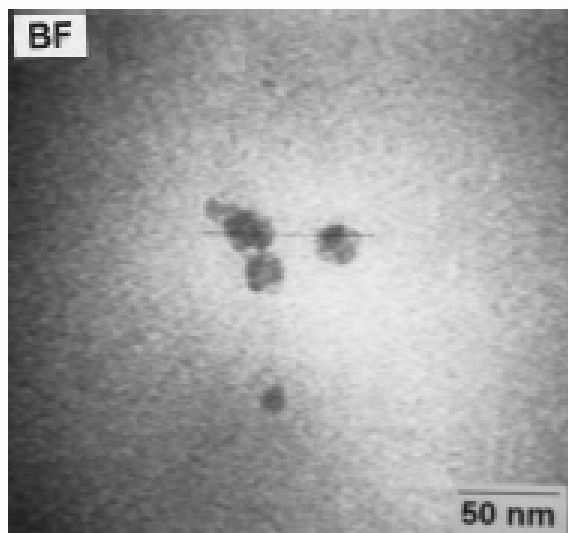


FIGURE 4

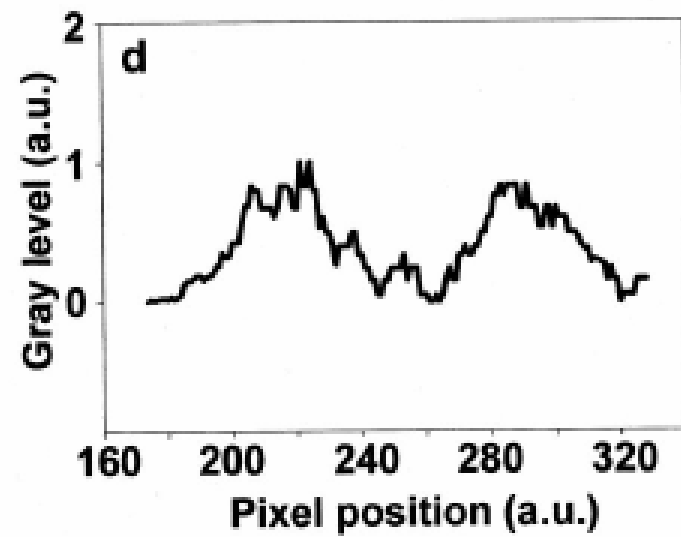
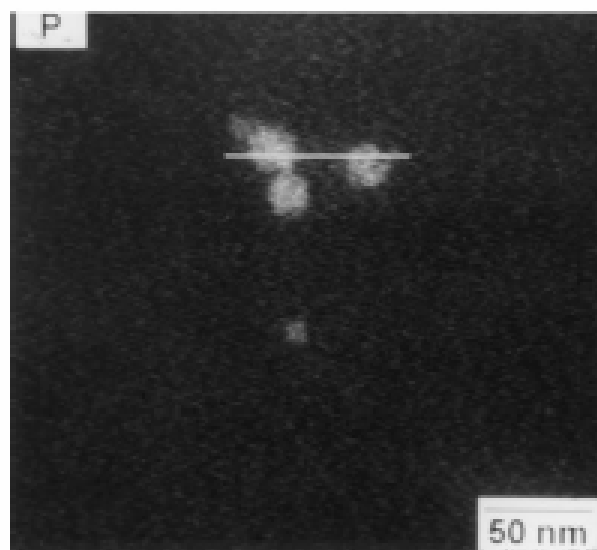
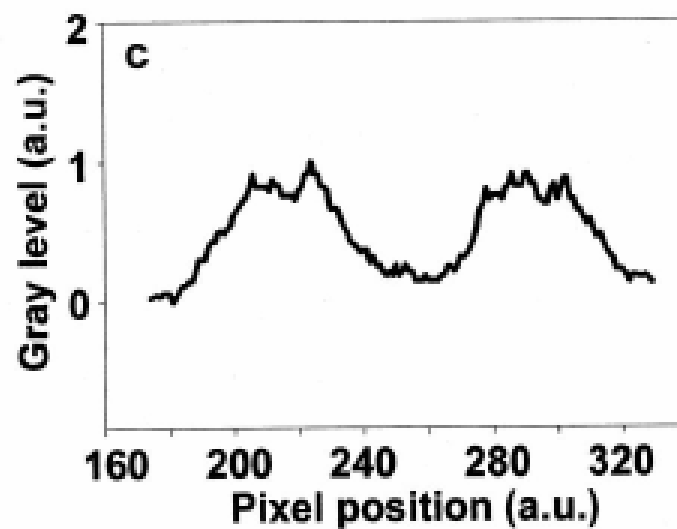
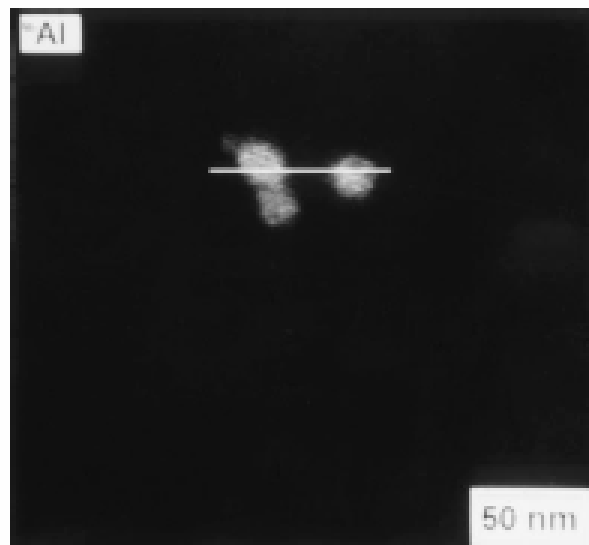


FIG. 6—Continued

Por que há formação de  
partículas?  
Como são as partículas?

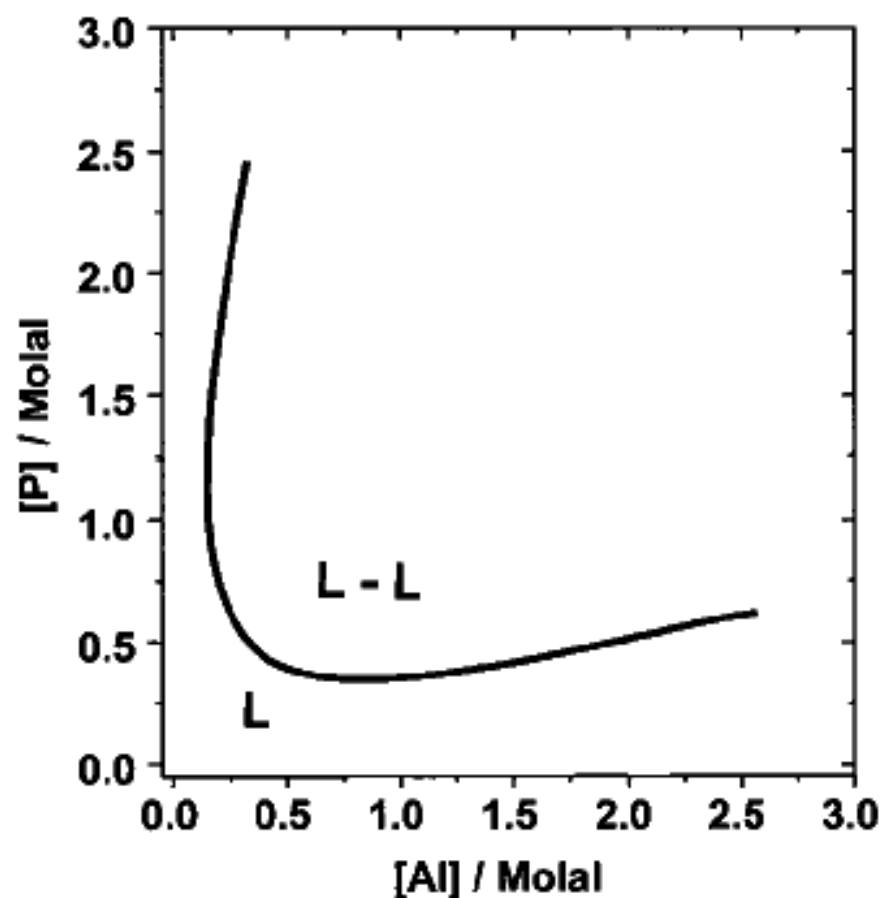


FIG. 7. Phase diagram for the  $(\text{NaPO}_3)_n\text{-Al}(\text{NO}_3)_3\text{-H}_2\text{O}$  system. The solid line gives the pairs of molalities of P and Al limiting single-phase (L) and two-phase (L-L) domains.

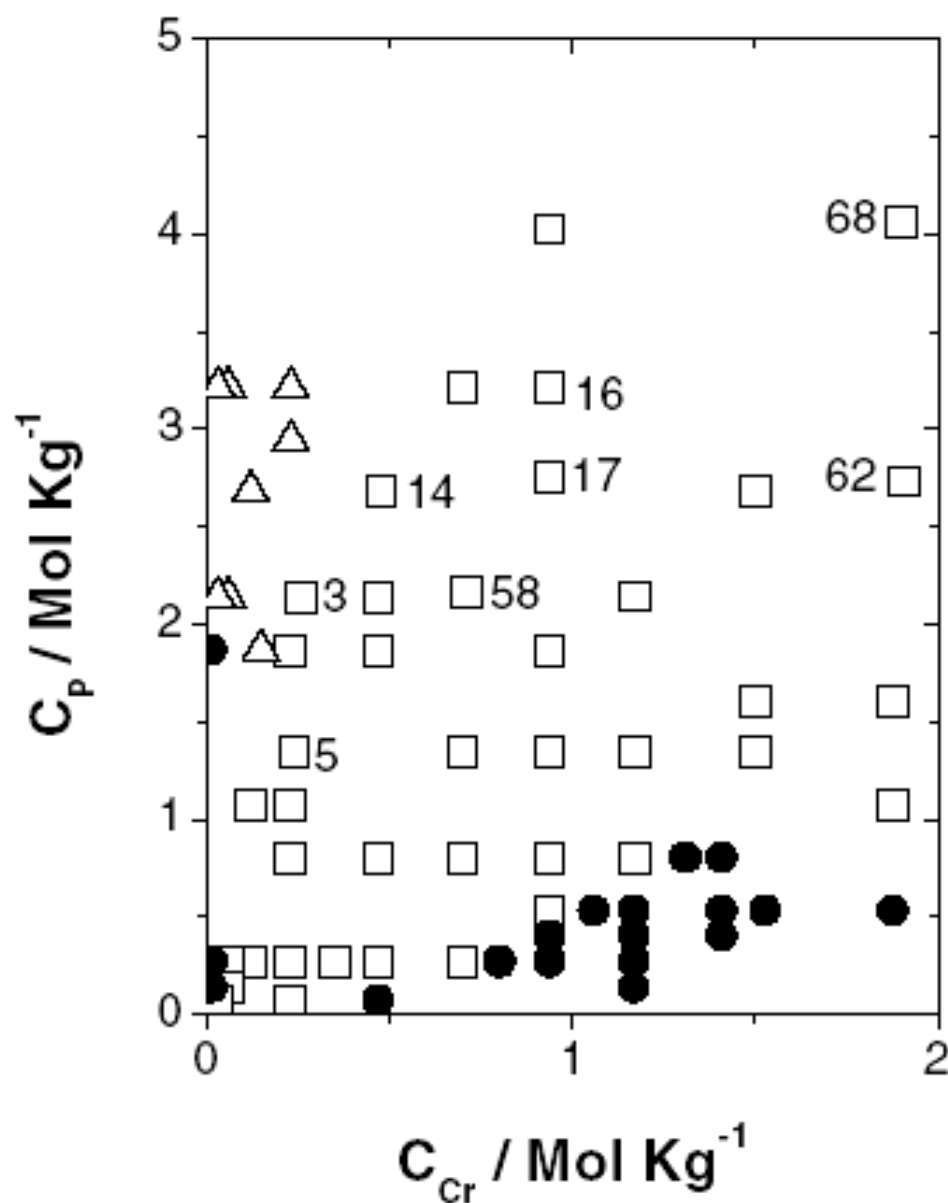
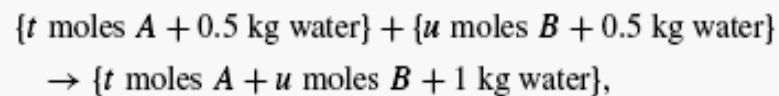


FIG. 1. Experimental phase diagram for the  $(\text{NaPO}_3)_n\text{-Cr}(\text{NO}_3)_3\text{-H}_2\text{O}$  system at 298 K. ( $\square$ ) Two coexisting liquid phases, ( $\bullet$ ) one liquid phase, ( $\triangle$ ) one liquid phase and one solid phase.





$$G_{\text{mix}}^E / n_W M_W = y(1-y)RT I_T \{b_{01}(I_T/m^0) + 1/2 b_{02}(I_T/m^0)^2\},$$

$$\Delta G_{\text{mix}}^{\text{id}} / n_W M_W = RT(m_A Y_A \ln Y_A + m_B Y_B \ln Y_B)$$

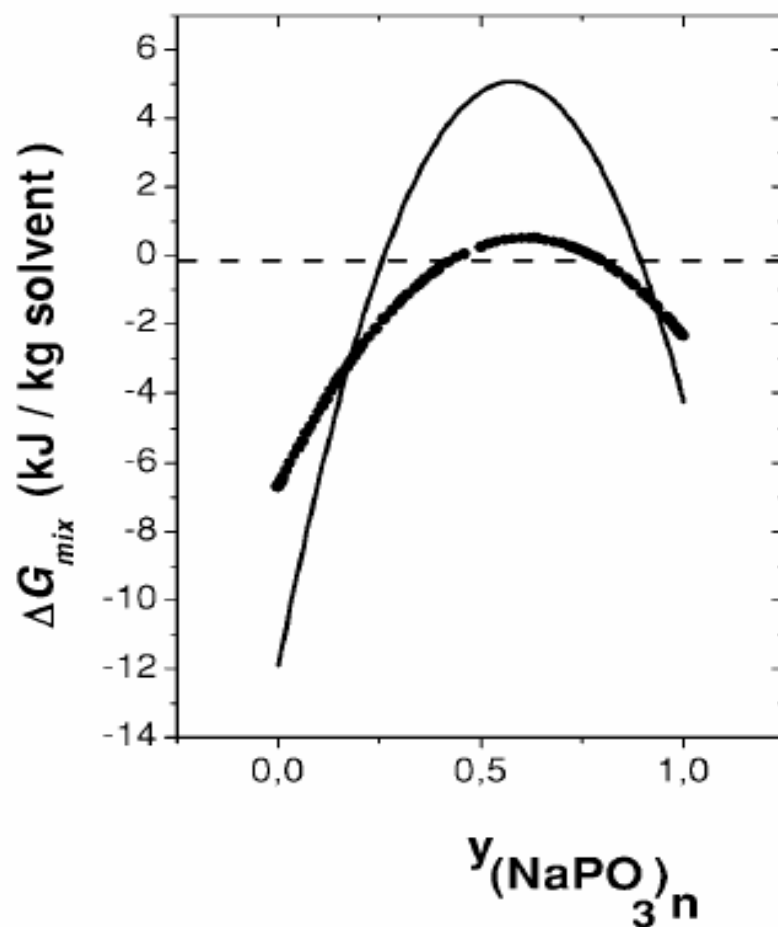


FIG. 8. The real mixing free energies calculated for the system  $(\text{NaPO}_3)_n$ – $\text{Cr}(\text{NO}_3)_3$ – $\text{H}_2\text{O}$  as a function of sodium polyphosphate ionic strength fraction,  $y$ . (—)  $I_T = 10.4 \text{ mol kg}^{-1}$ , ( $\cdots$ )  $I_T = 5.8 \text{ mol kg}^{-1}$ .

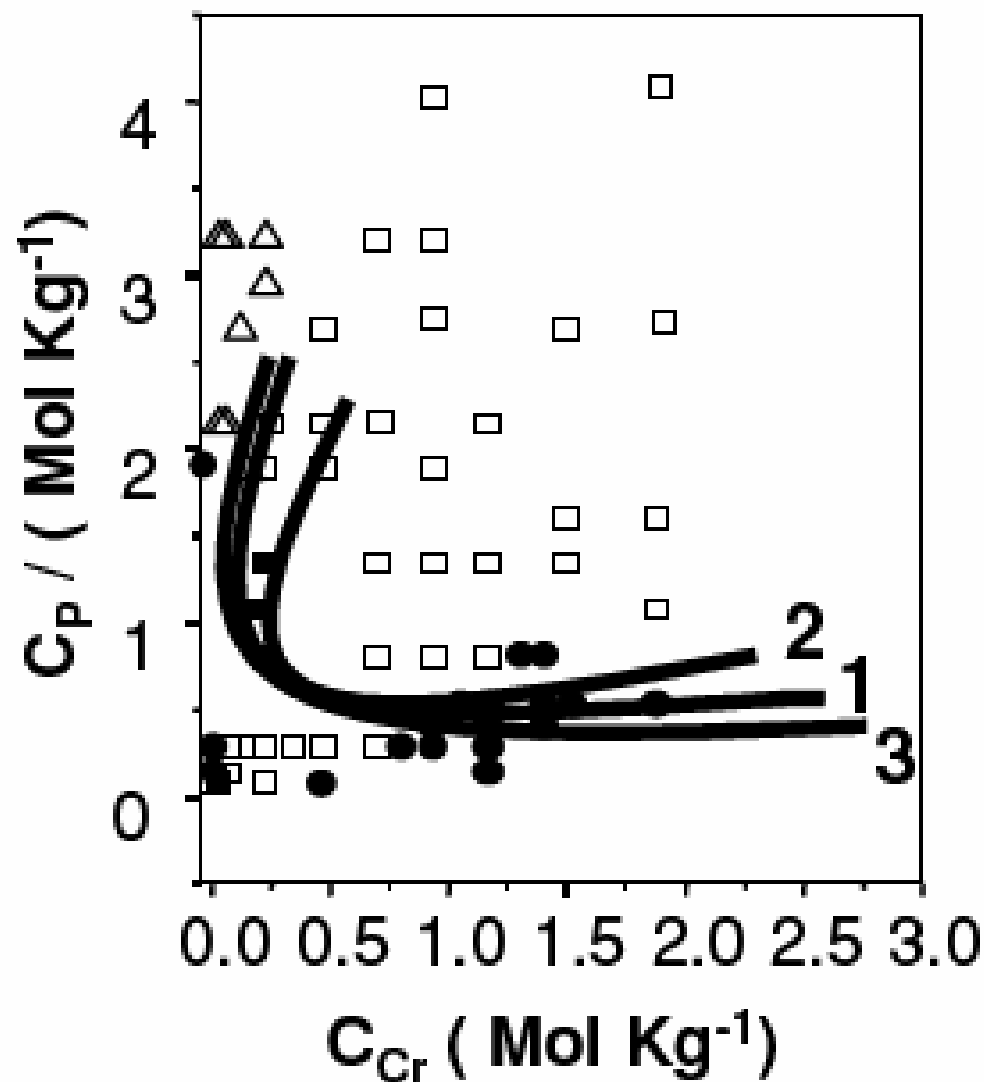


FIG. 9. Calculated phase diagrams. Each line corresponds to  $\Delta G_{\text{mix}} = 0$ , for a pair of  $b_{01}$  and  $b_{02}$  parameters. (1)  $b_{01} = 0.27$ ,  $b_{02} = -0.015$ ; (2)  $b_{01} = 0.23$ ,  $b_{02} = -0.015$ ; (3)  $b_{01} = 0.23$ ,  $b_{02} = -0.010$ . The symbols are as in Fig. 1.

# SILÍCIO NANOPOROSO: luminescência no visível

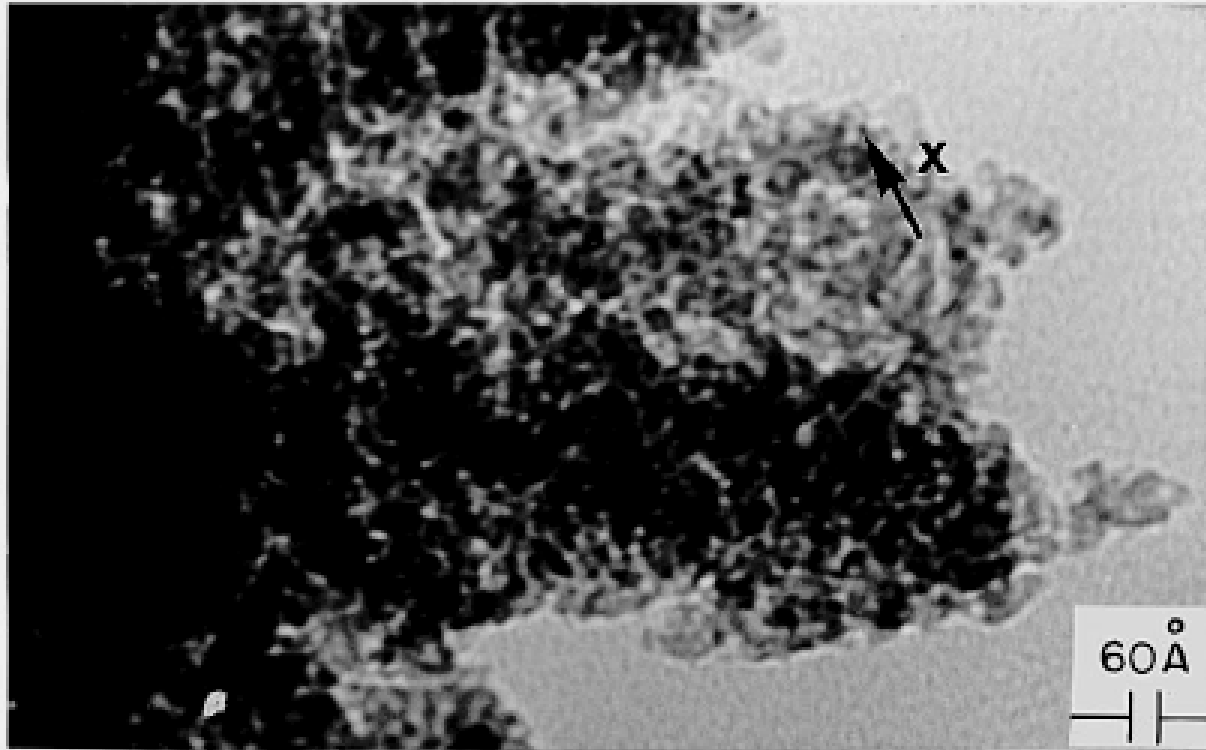


FIG. 1. Transmission electron micrograph of the porous silicon structure formed on *n*-type 0.009  $\Omega$  cm,  $\langle 100 \rangle$ -oriented silicon.  $I = 100$  mA/cm<sup>2</sup>.

Mecanismo: a corrosão do silício é muito mais rápida em algumas faces do que em outras. Provoca a formação de **poros**.

## Determinação da espessura: Espalhamento múltiplo

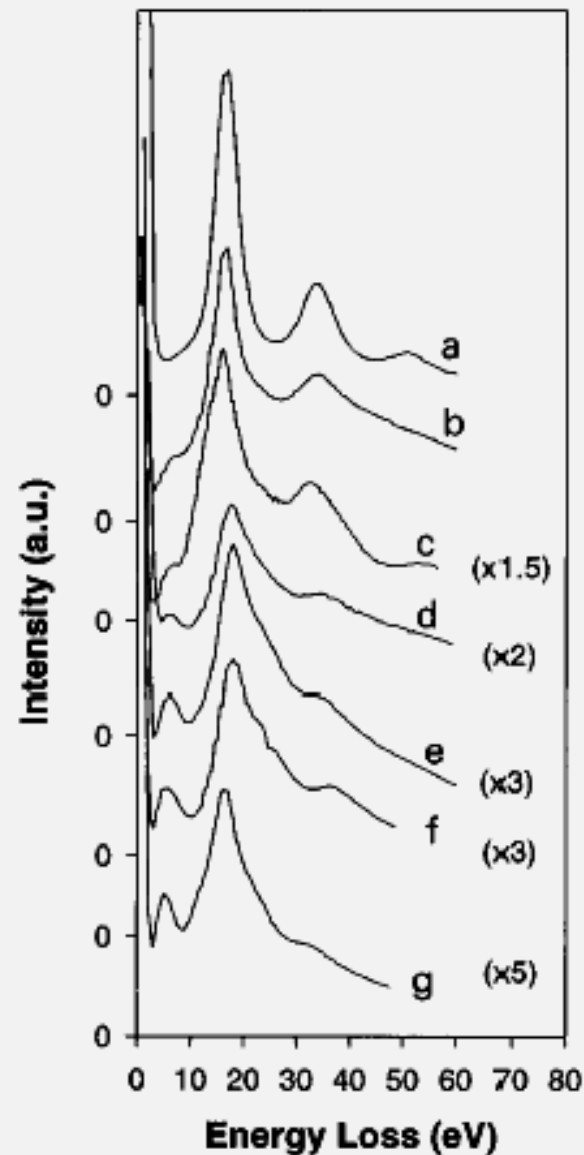


FIG. 2. EELS spectrum as a function of slab thickness. (a) silicon slab, (b) porous silicon; slab thickness  $1.29 \lambda_p$ , where  $\lambda_p$  is the plasmon mean free path,  $1.06\lambda_p$ , (c)  $0.78\lambda_p$ , (d)  $0.74\lambda_p$ , (e)  $0.60\lambda_p$ , (f)  $0.34\lambda_p$ .

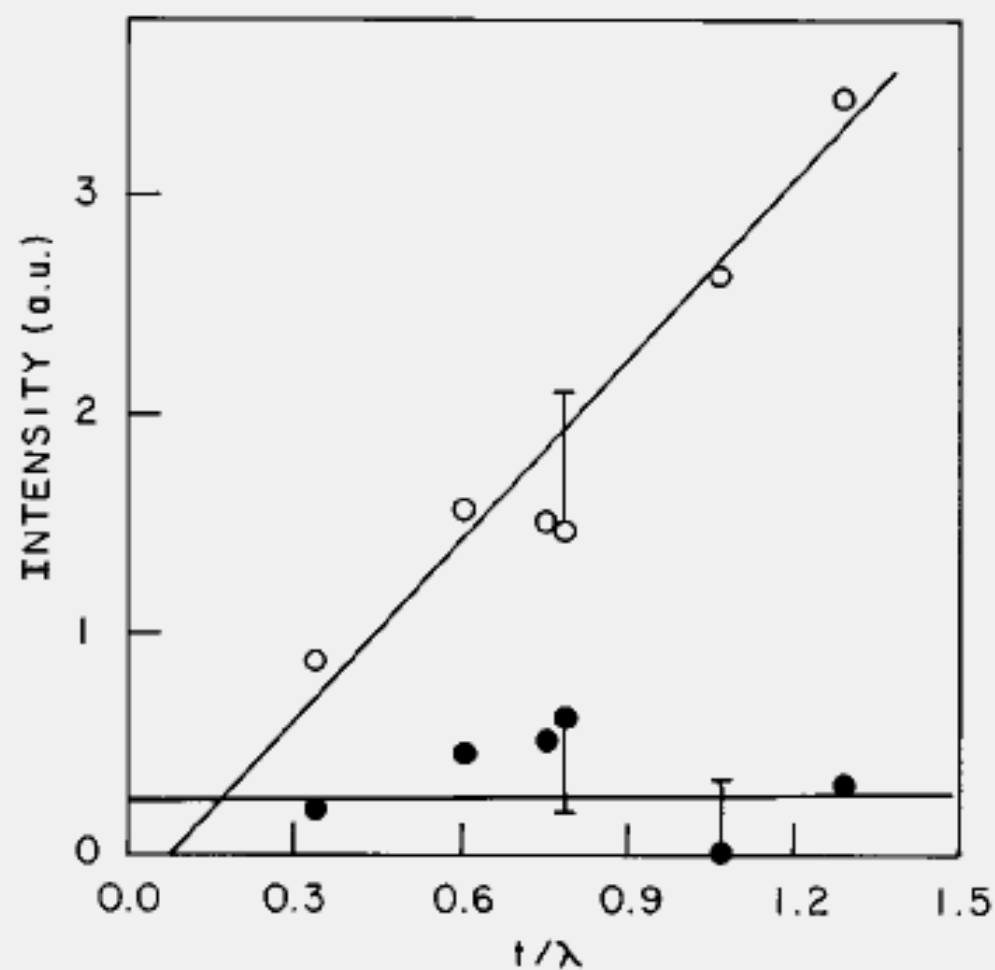
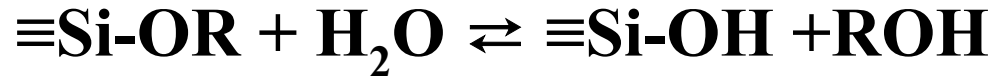


FIG. 3. Plasmon volumetric peak absorption at  $\sim 16.9$  eV (integrated signal) as a function of slab thickness (open circles). Surface plasmon absorption (filled circles).

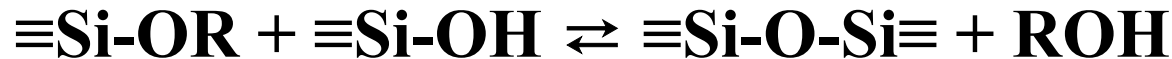
# Formação de partículas, géis e vidros

hidrólise



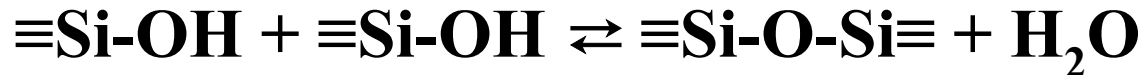
esterificação

condensação com eliminação de álcool



alcoólise

condensação



hidrólise

*Em excesso de água, a reação não ocorre de forma completa gerando uma gama de espécies intermediárias  $[\text{SiO}_x(\text{OH})_y(\text{OR})_z]$  com vários graus de hidrólise e condensação.*

# Polimerização

Monômero



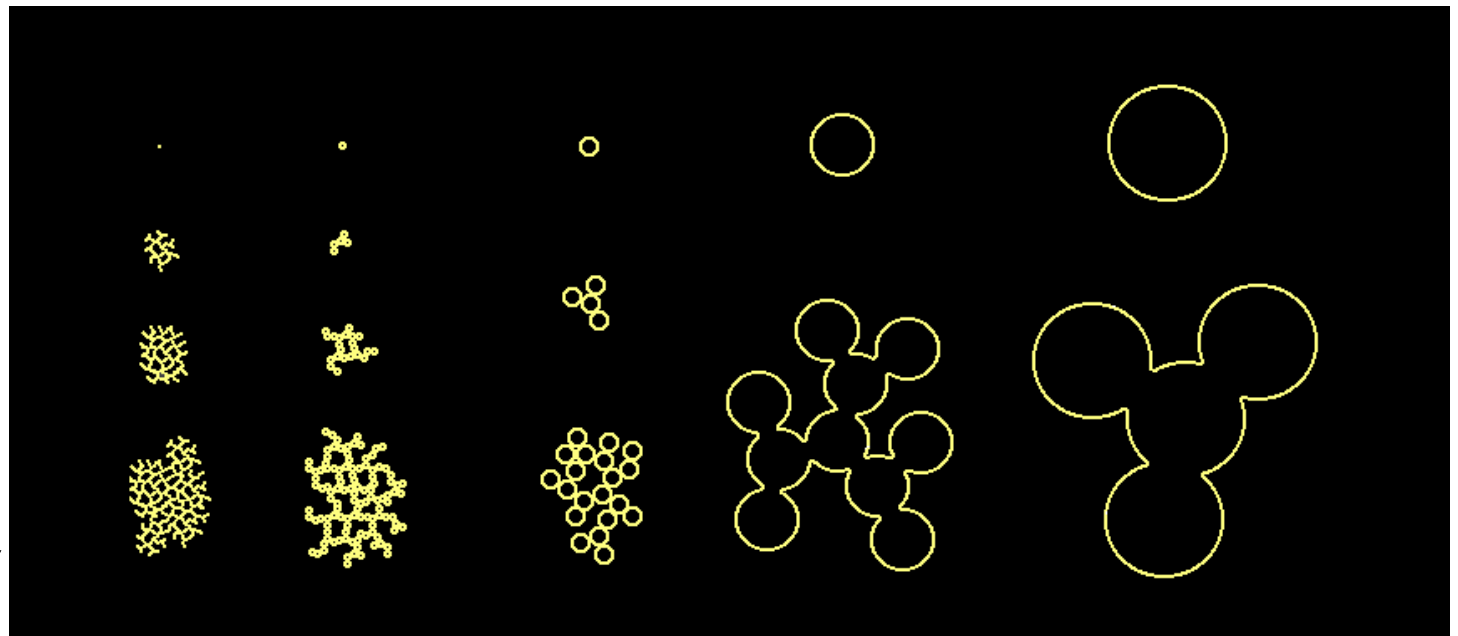
Polímero



Partícula

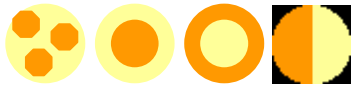

pH 7-10, na ausência de sal

pH <7  
ou  
pH 7-10  
na  
presença  
de sal



*Brinker and Scherrer, 1990*

# Quanto as partículas são uniformes?

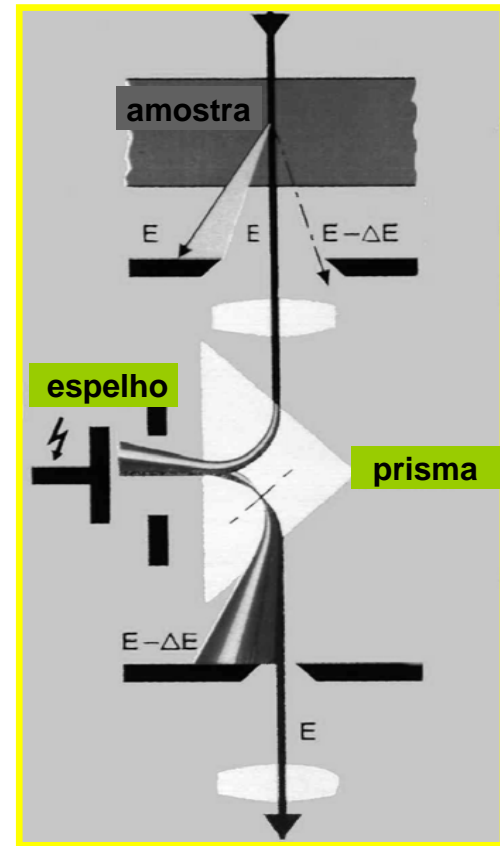
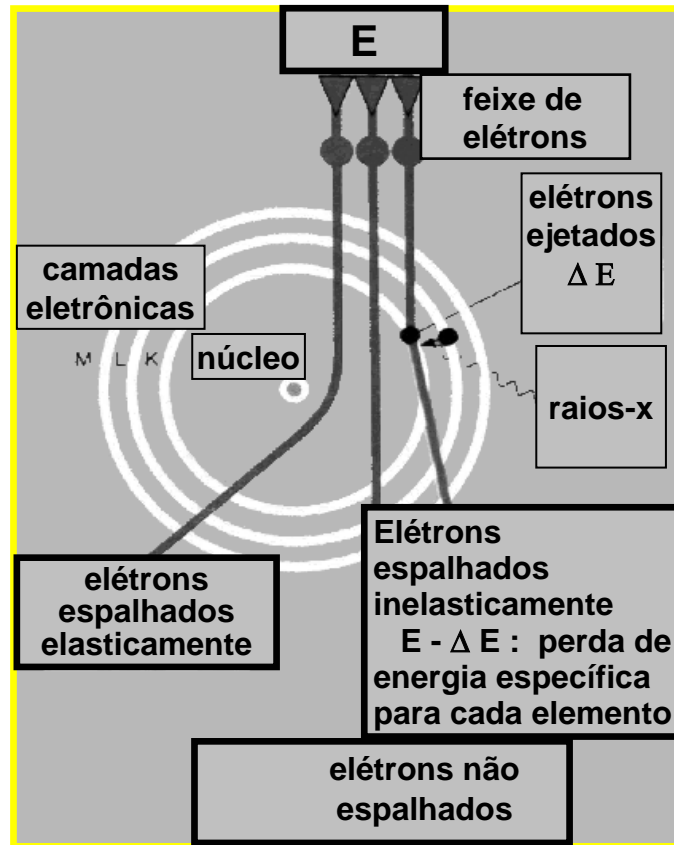
- **Distribuição dos constituintes químicos:**
  - no interior das partículas? 
  - entre diferentes partículas? 
- **Outras questões:**
  - distribuição de cargas elétricas
  - capacidade de formação de filmes
  - localização e distribuição de adsorbatos



# **Métodos**

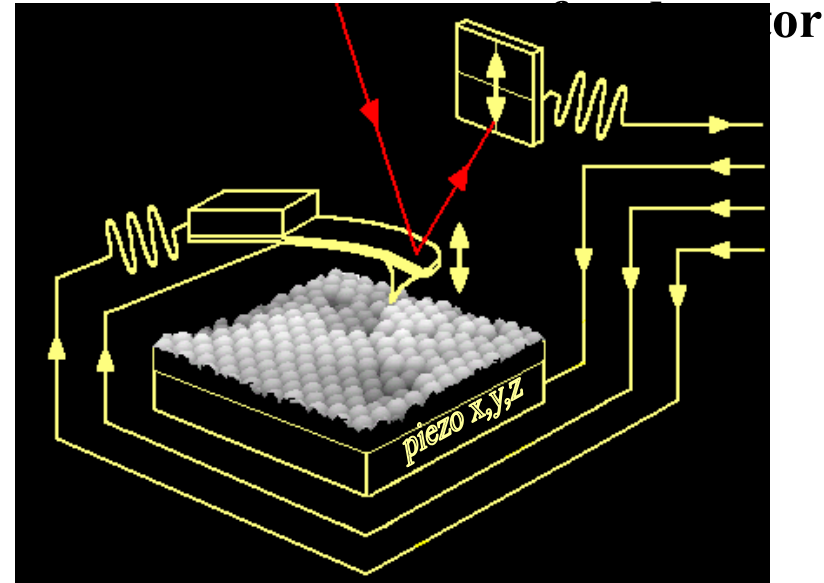
- **Espectroscopia de perda de energia associada à microscopia eletrônica de transmissão (ESI-TEM)**
- **Microscopia de varredura por sonda (SPM)**
- **Microscopia eletrônica por emissão de campo (FESEM)**
- **Espectroscopia de correlação de fótons (PCS)**
- **Espectros no infravermelho**
- **Potencial zeta**
- **Ensaio mecânicos de dureza e tenacidade à fratura**

# Imagens por espectroscopia de elétrons (ESI-TEM)



- TEM com um monocromador de energia de elétrons
- Aquisição de espectros de perda de energia de elétrons
- Os elétrons espalhados inelasticamente fornecem informações da posição dos elementos na amostra
- Alta sensibilidade, inclusive para elementos leves

# Microscopia de varredura de potencial eletrostático (SEPM)



- O contraste da imagem depende da interação eletrostática entre a sonda e a amostra
- Identificação de domínios com diferentes excessos de cargas elétricas
- Aquisição simultânea de imagens topográficas por AFM no modo não contato: mesmo campo

# Preparação das partículas

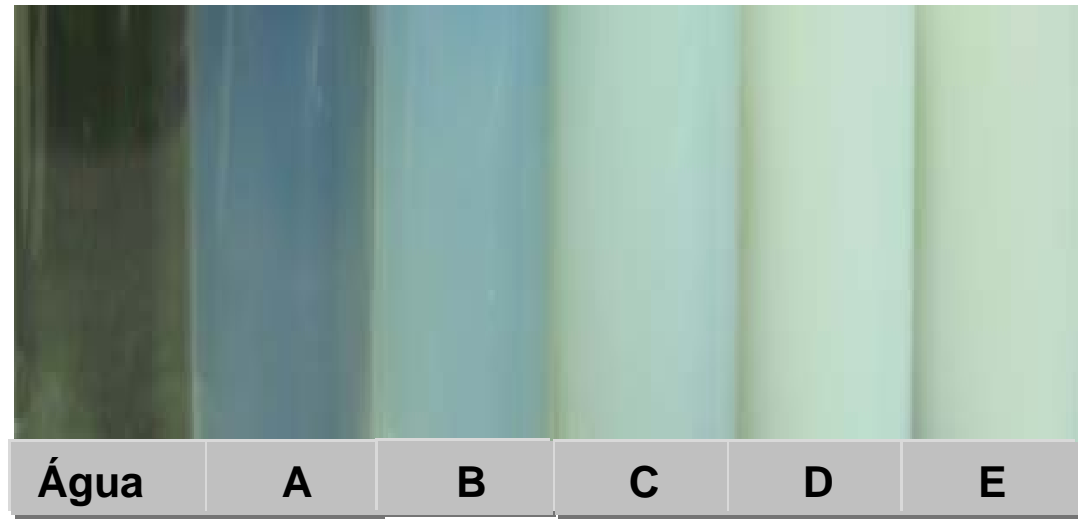
	A	B	C	D	E
amônia sat. (mL) (Synth)	2	2.5	3	3.5	4
TEOS (mL) (Merck)	4	4	4	4	4
etanol (mL) (Merck)	50	50	50	50	50



- sob sonicação contínua: 25 kHz 200 watts  
por 2 horas, 36° C

# Dispersões de sílica em etanol

- incidência indireta de luz branca



laser →

- incidência de um feixe de laser (5 mW e 532nm)



Água



A



B



C



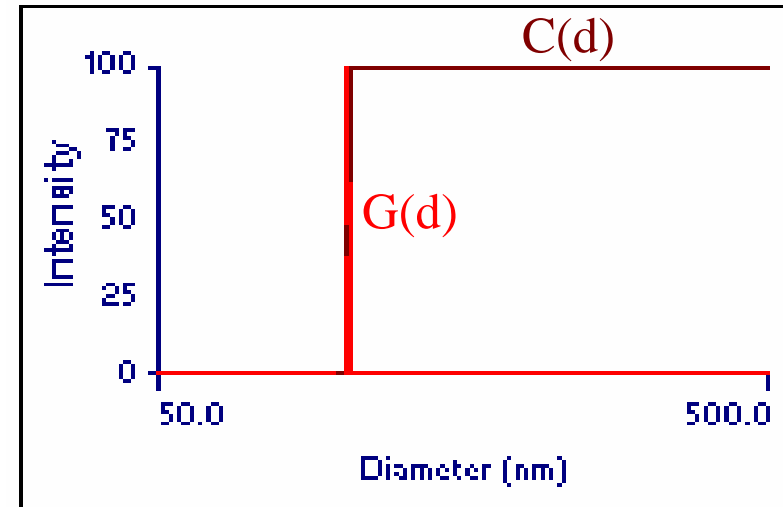
D



E

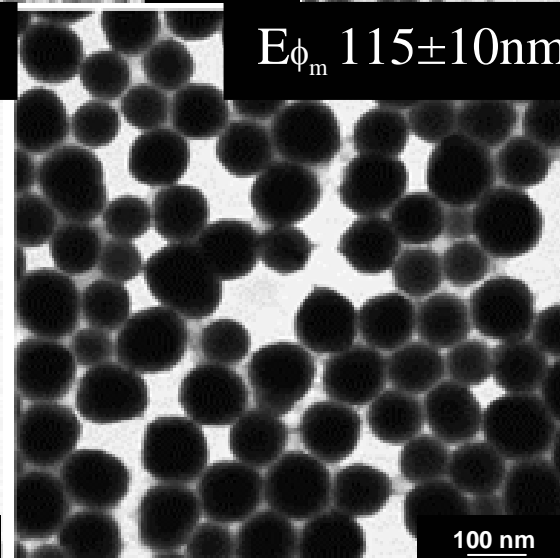
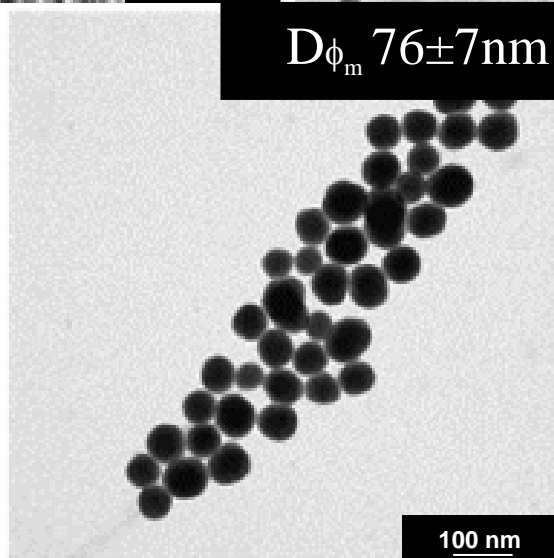
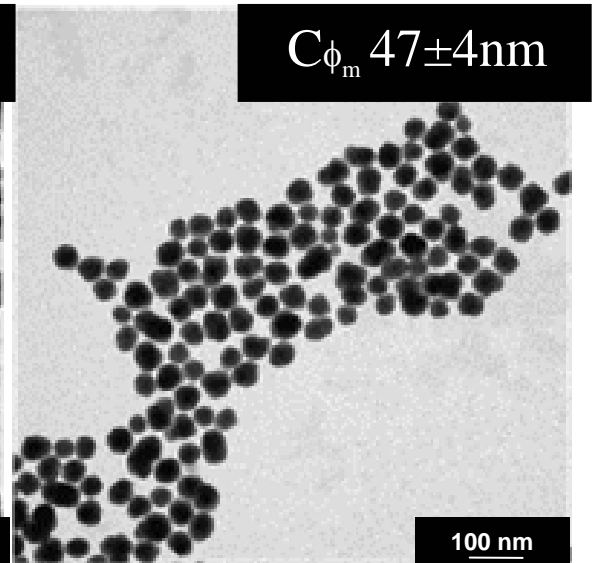
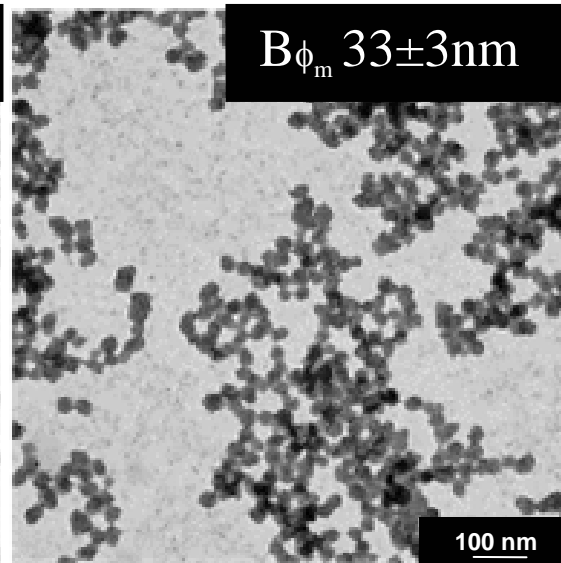
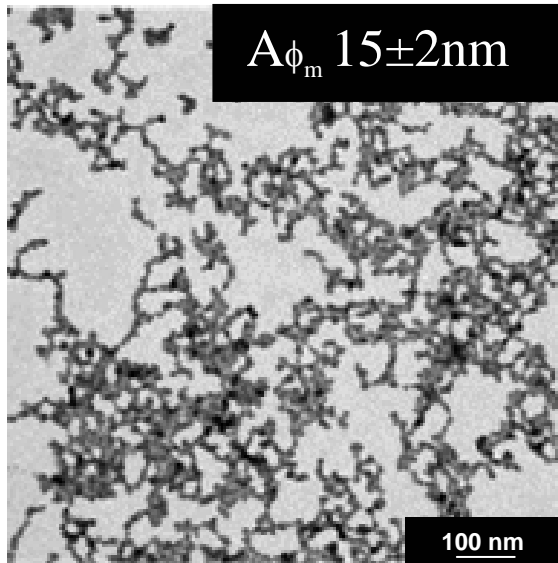
# Determinação dos tamanhos das partículas da amostra D por PCS: diâmetros uniformes

**Effective Diameter:** 102.7 nm  
**Polydispersity:** 0.004  
**Avg. Count Rate:** 399.7 kcps  
**Sample Quality:** 9.9

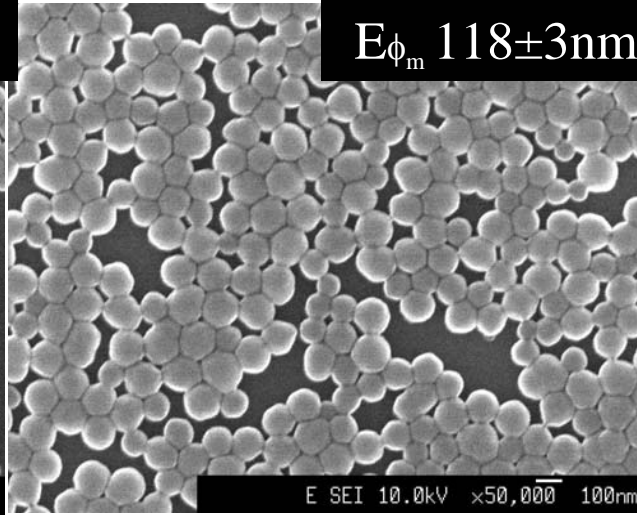
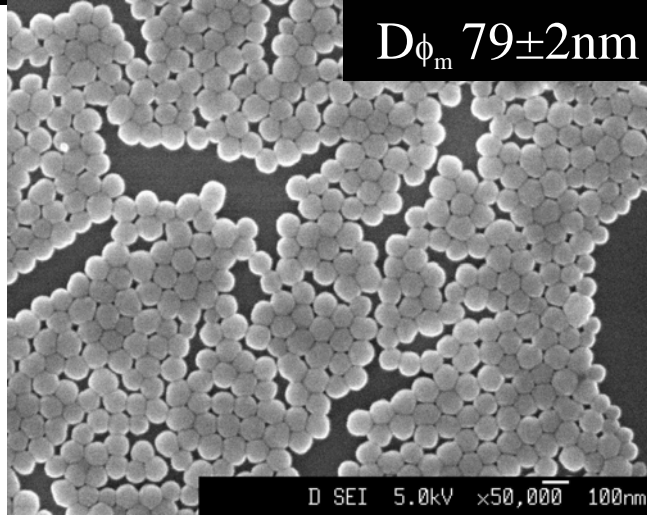
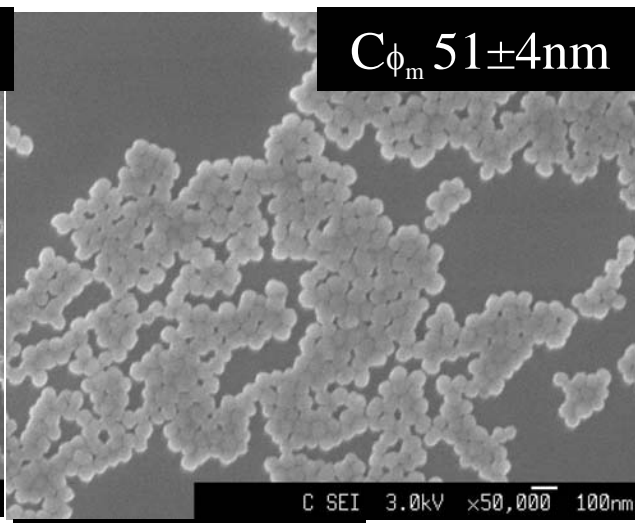
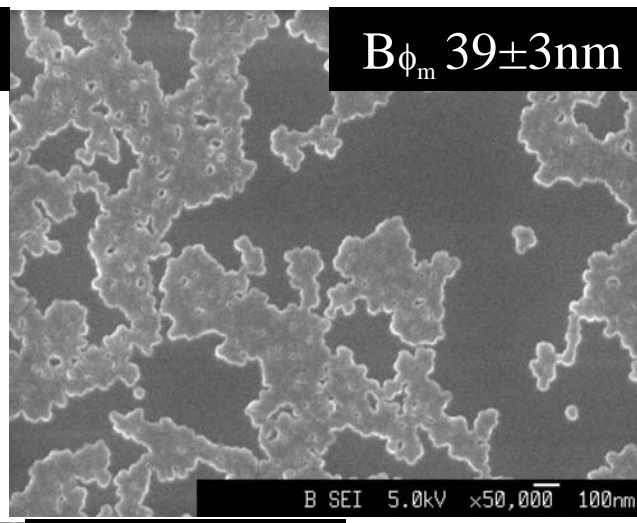
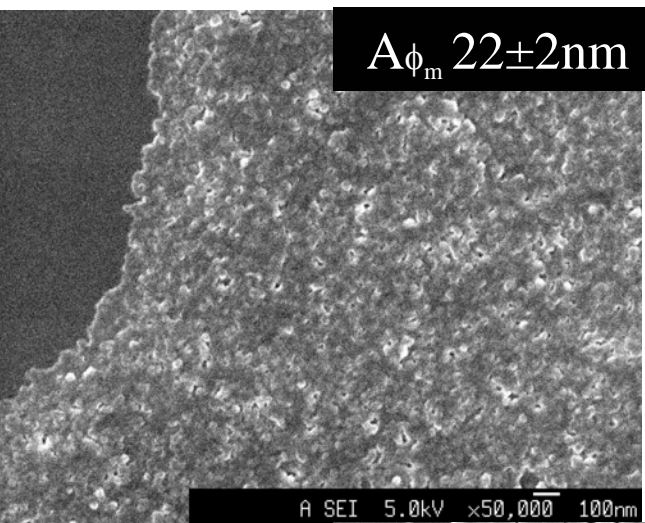


d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
99.7	0	0	101.8	5	1	103.8	0	100
99.9	0	0	102.0	14	4	104.2	0	100
100.1	0	0	102.2	34	10	104.4	0	100
100.2	0	0	102.3	62	23	104.6	0	100
100.4	0	0	102.5	89	40	104.8	0	100
100.6	0	0	102.7	100	60	105.0	0	100
100.8	0	0	102.9	89	77	105.2	0	100
101.0	0	0	103.1	62	90	105.4	0	100

# TEM



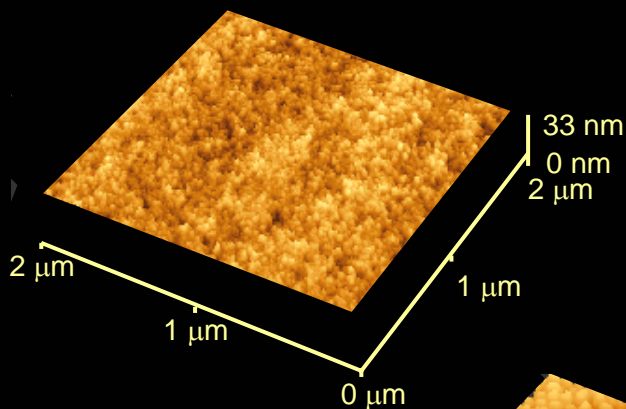
# FESEM



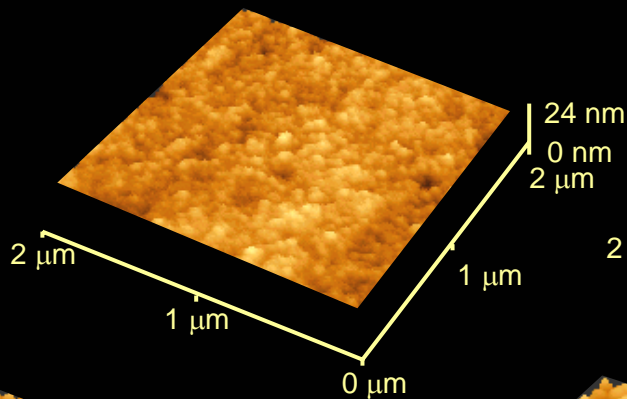


# AFM

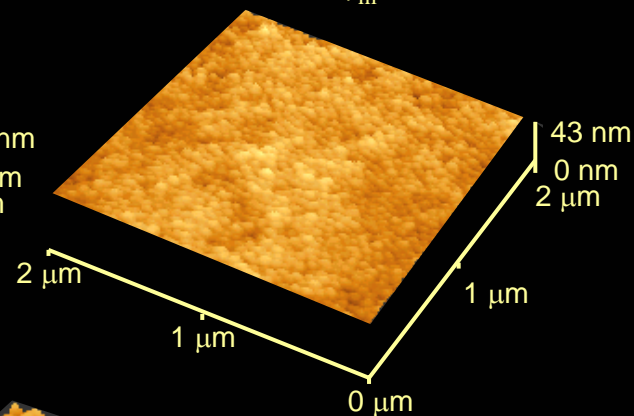
$A_{\phi_m} 33 \pm 2 \text{ nm}$



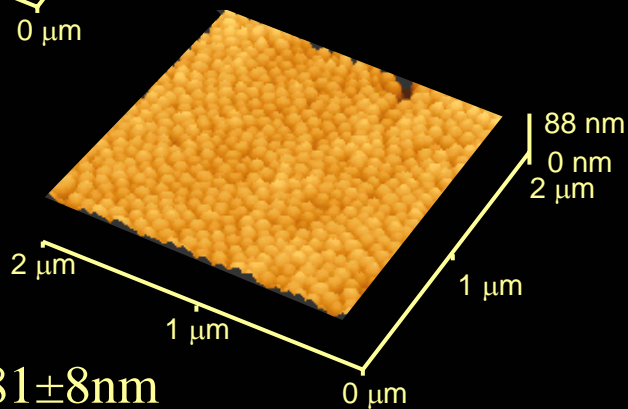
$B_{\phi_m} 45 \pm 4 \text{ nm}$



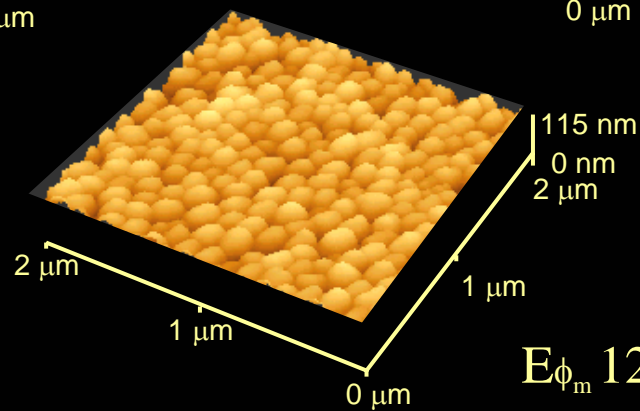
$C_{\phi_m} 57 \pm 5 \text{ nm}$



$D_{\phi_m} 81 \pm 8 \text{ nm}$



$E_{\phi_m} 125 \pm 11 \text{ nm}$

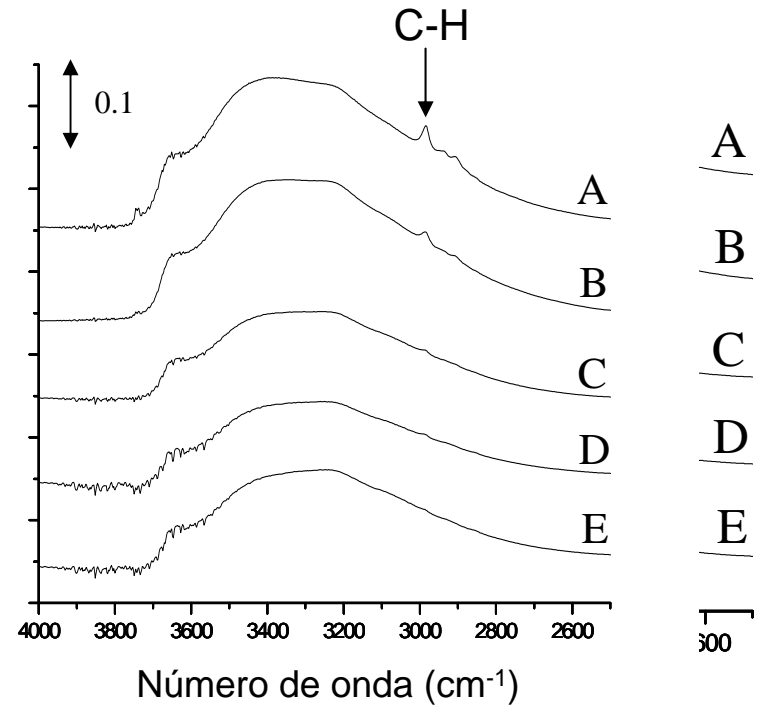
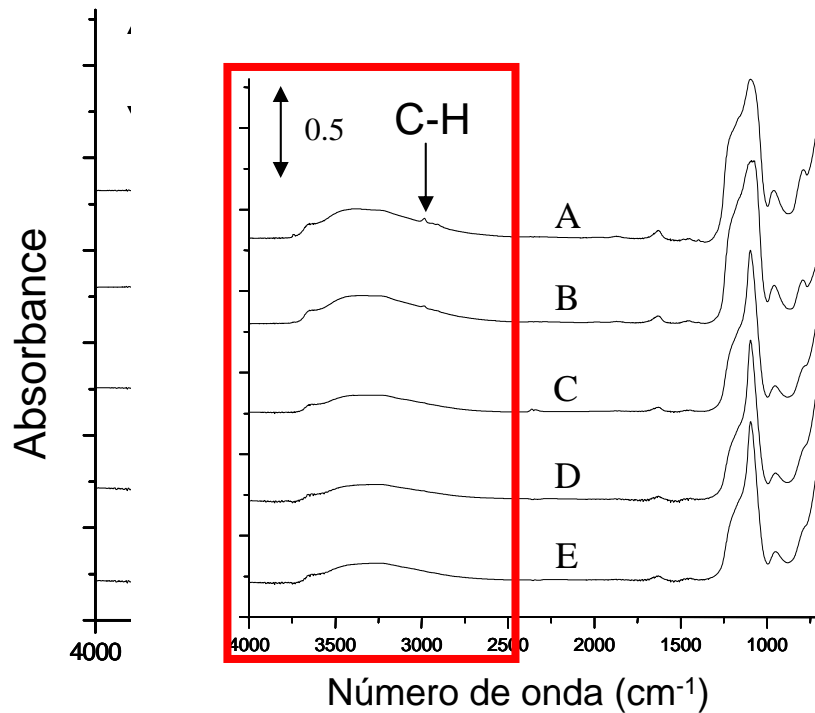


# Diâmetros médios em diferentes meios

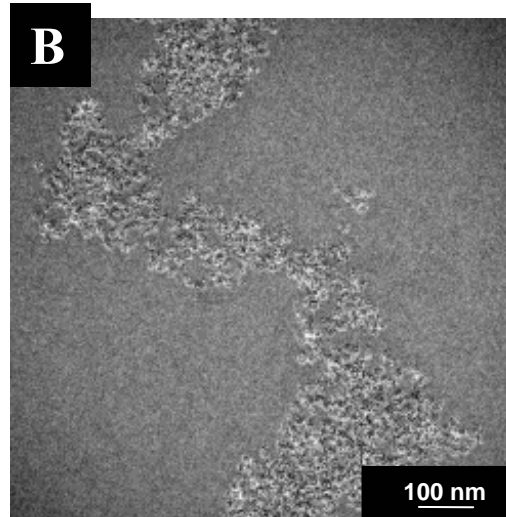
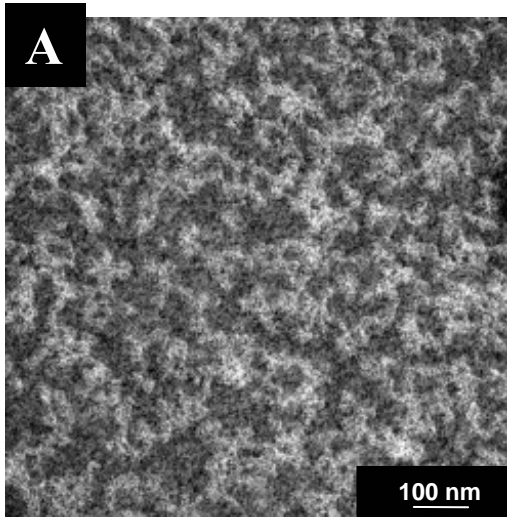
Amostra		A	B	C	D	E
água, 25°C	PCS (nm)	54±5	66±6	77±2	103±1	136±1
etanol, 25°C	PCS (nm)	72±2	74±2	67±6	99±1	131±1
ar, 55% UR, 25°C	AFM (nm)	33±2	45±4	57±5	81±8	125±11
10 <sup>-6</sup> mbar	FESEM(nm)	22±2	39±3	51±4	79±7	118±10
10 <sup>-6</sup> mbar	TEM (nm)	15±2	33±3	47±4	76±7	115±10
Coeficiente de intumescimento em água (% em volume)		4500	700	340	149	65
Coeficiente de intumescimento em etanol (% em volume)		10900	1028	190	121	48
Conteúdo de sólidos (% em massa)		2.7	2.7	2.6	2.5	2.5
Potencial Zeta (em KCl 10 <sup>-3</sup> M) (mV)		-27	-38	-36	-46	-49

- As partículas apresentam grandes variações de volume em função do meio, especialmente as partículas menores.

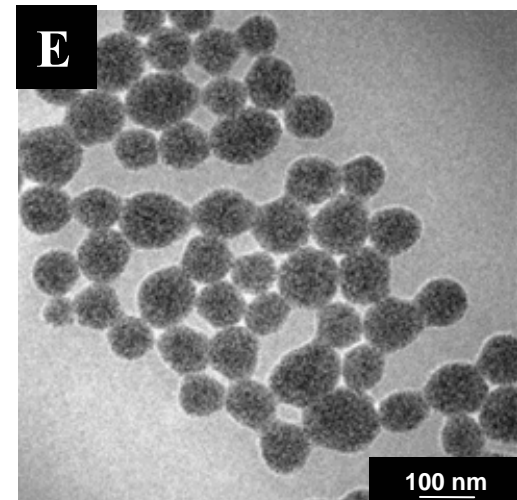
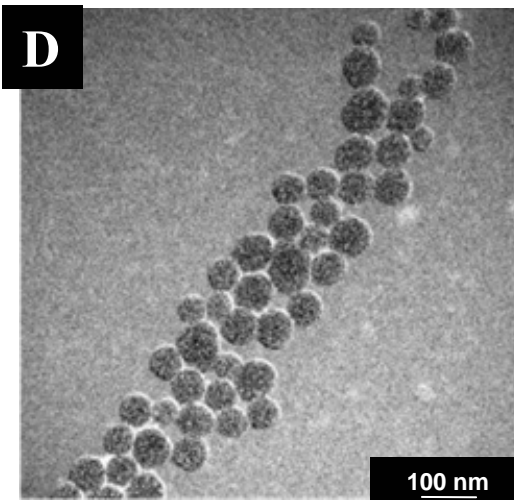
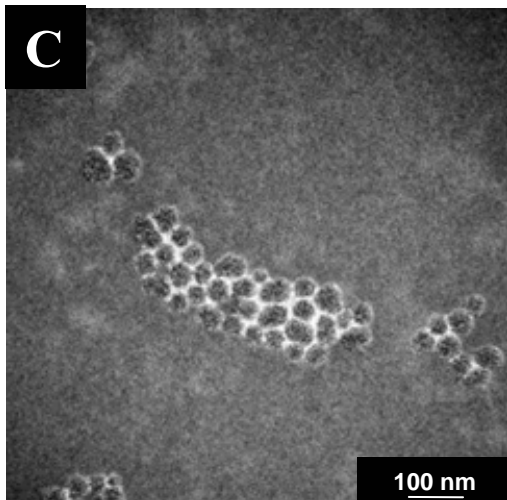
# Espectros de infravermelho



# Mapas de carbono (EELS)



- As partículas menores apresentam carbono distribuído por toda partícula
- As partículas maiores apresentam traços de carbono nos interstícios das partículas



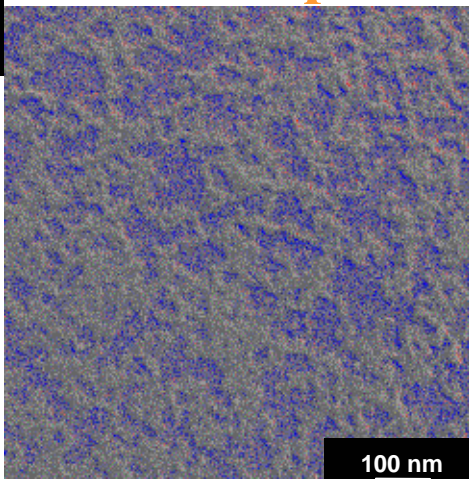


# Espectros de perda de energia e mapas elementares

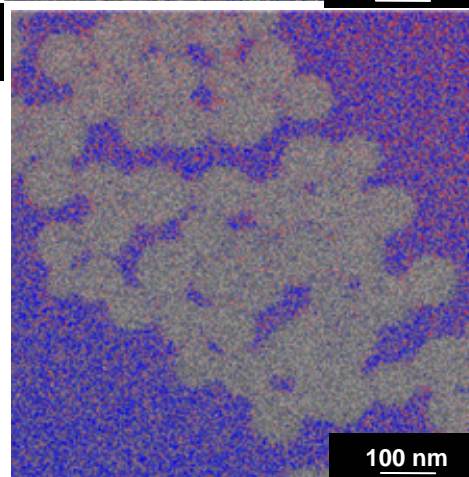
Oxigênio

R-map

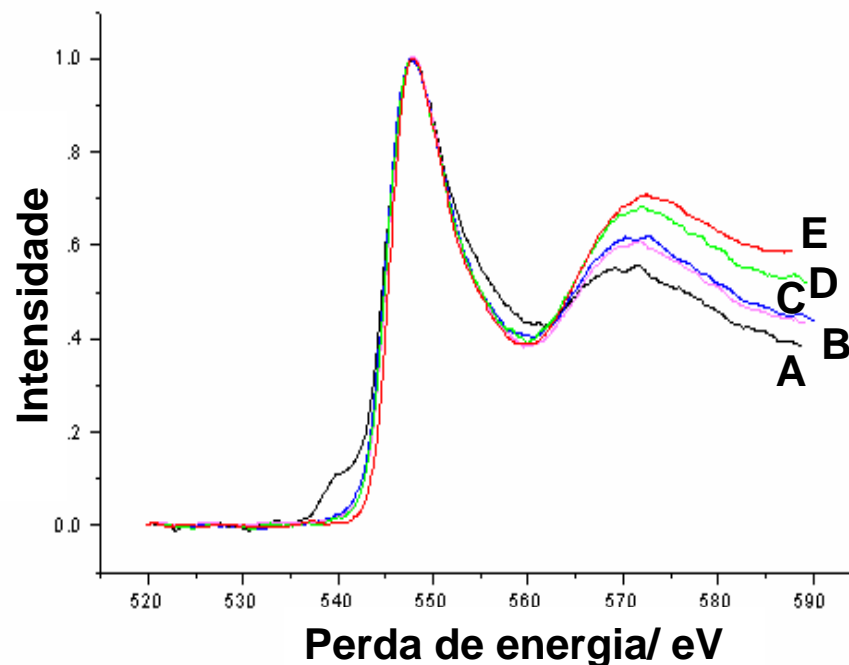
A



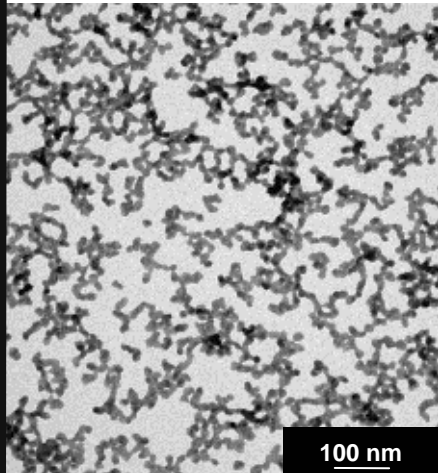
E



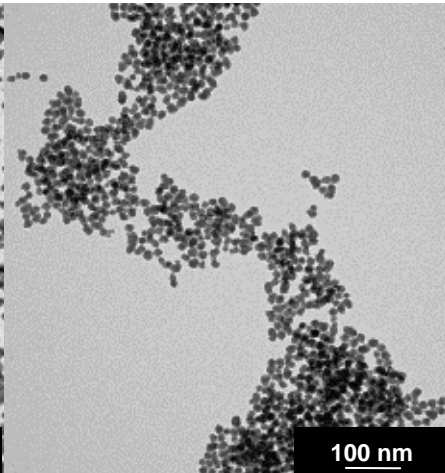
Evidência das mudanças no ambiente químico do oxigênio  
( $-\text{O}-\text{H}$  :  $-\text{O}-\text{Si}$ :  $-\text{O}-\text{C}_2\text{H}_5$ )



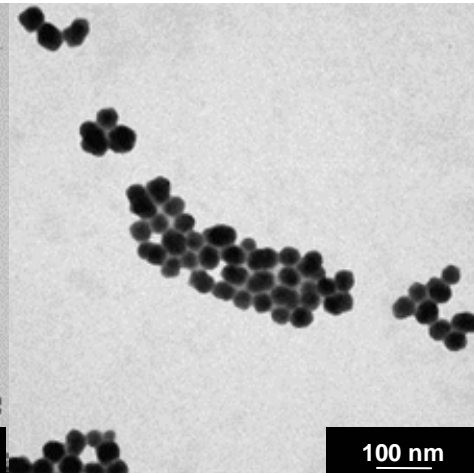
**Campo Claro**



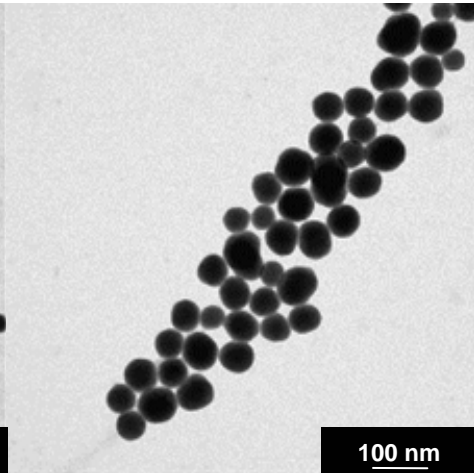
**A**



**B**

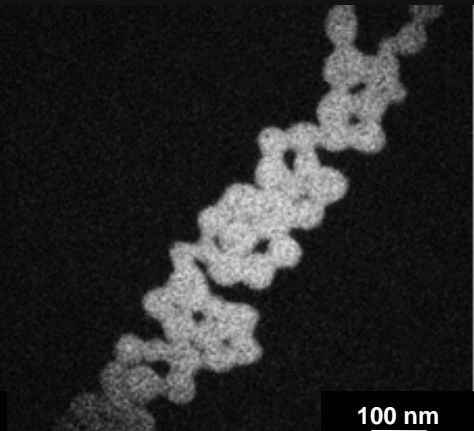
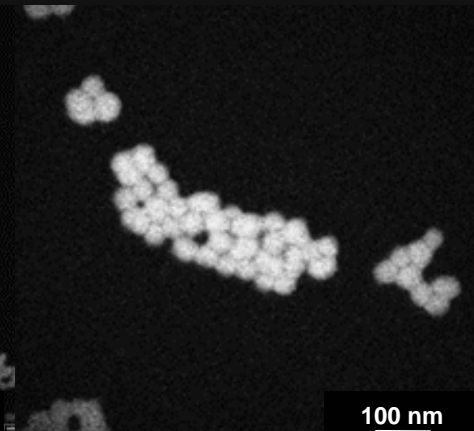
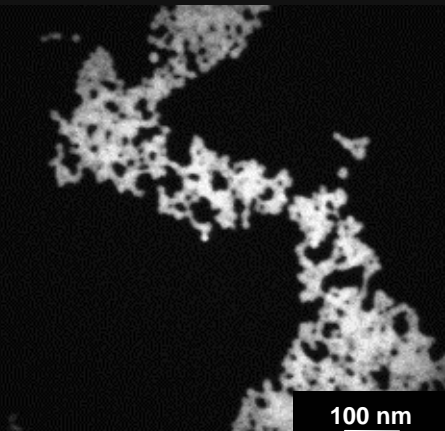
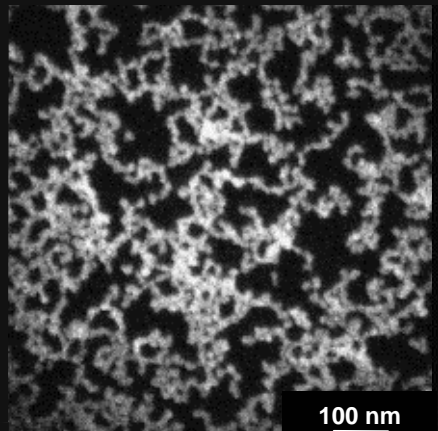


**C**

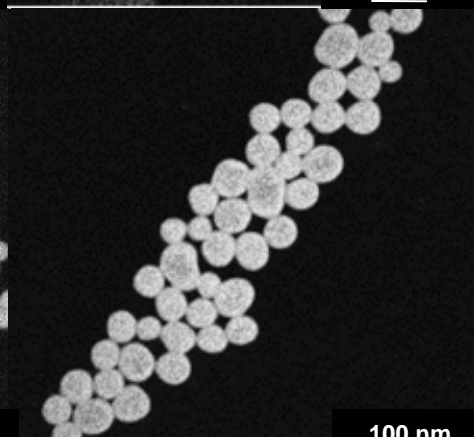
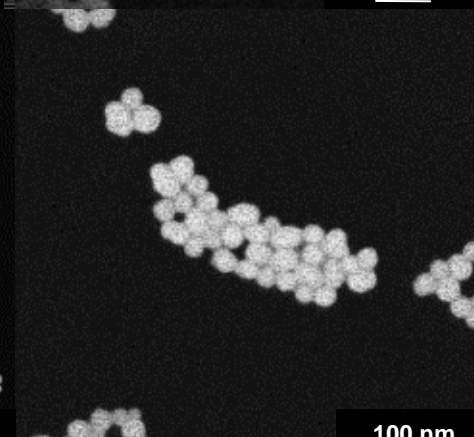
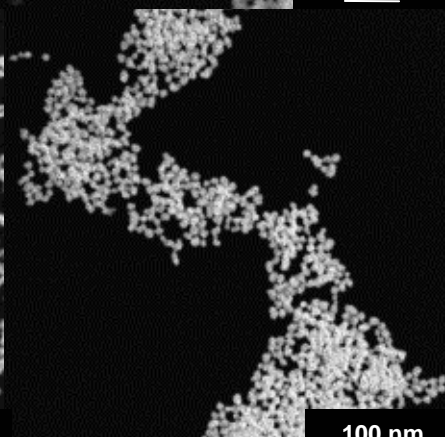
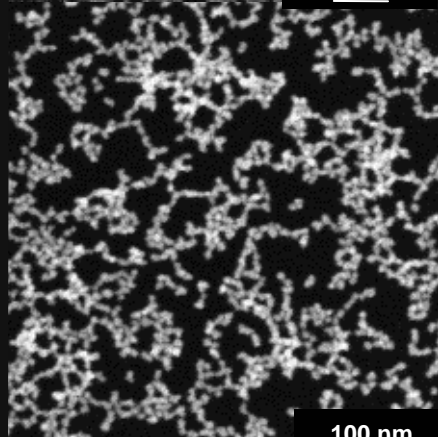


**D**

**Oxigênio**



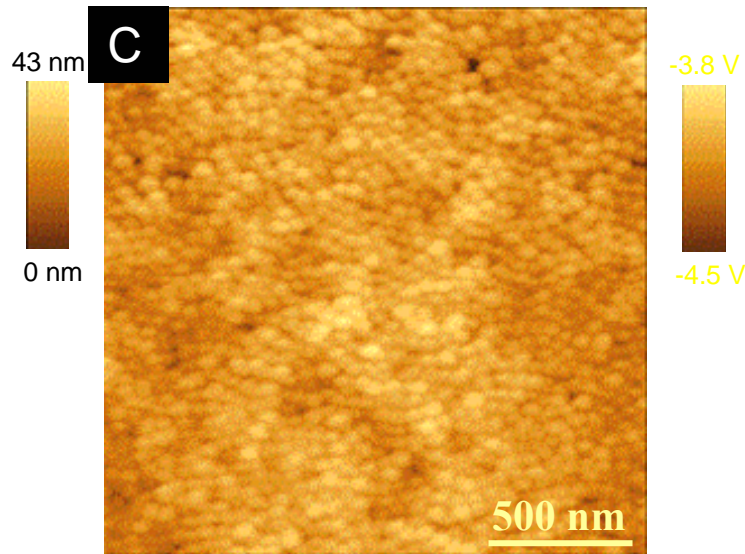
**Silício**



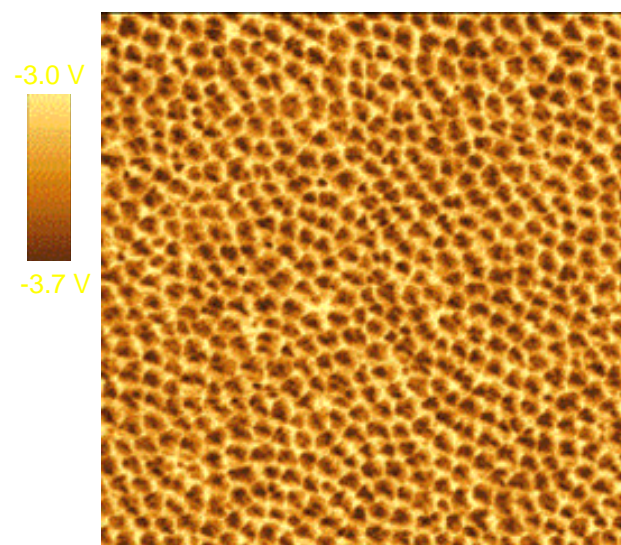
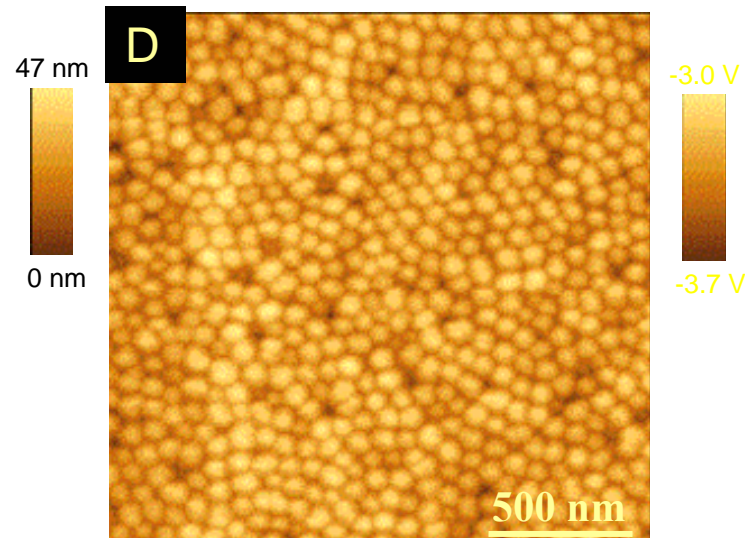
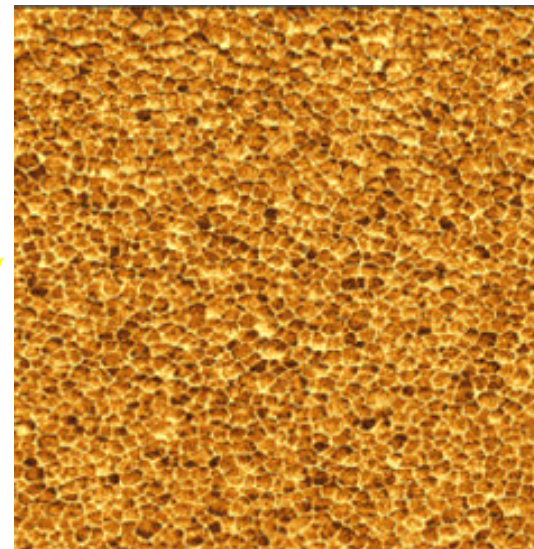


# Imagens de potenciais elétricos

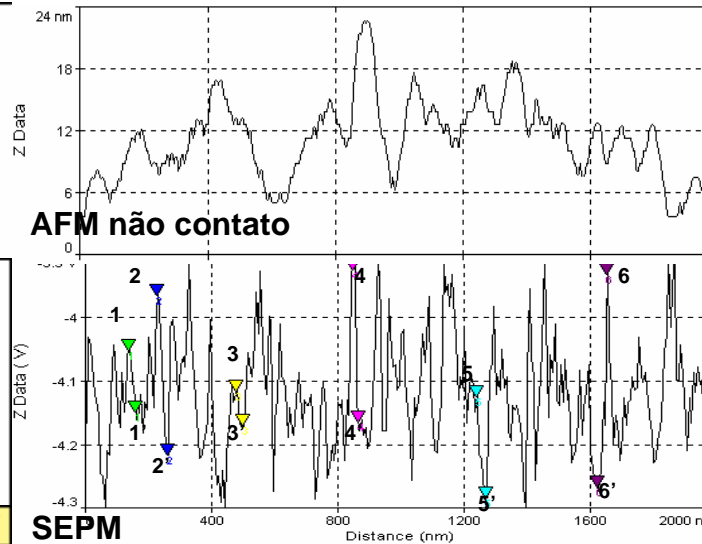
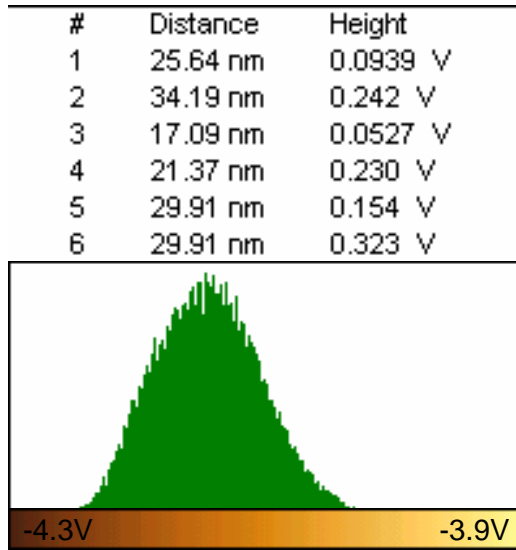
AFM (não contato)



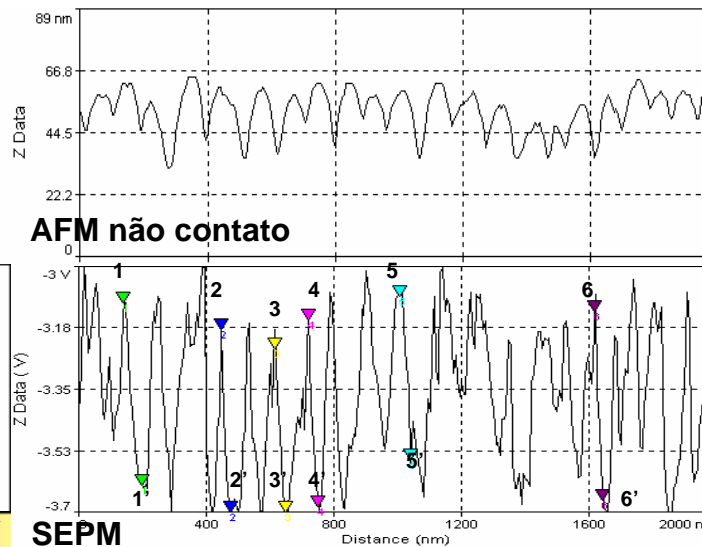
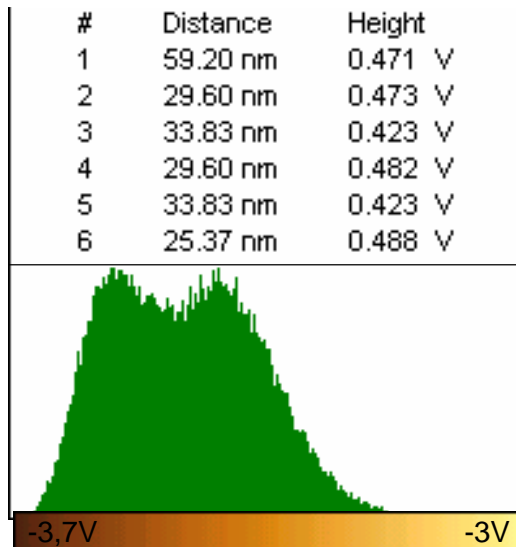
SEPM



# Histograma de potenciais elétricos



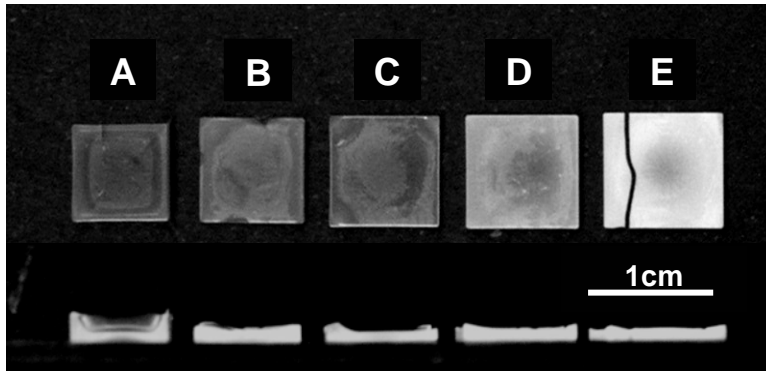
▪ **Amostra B:**  
Baixa correlação entre topografia e distribuição de potencial elétrico



▪ **Amostra D:**  
As partículas são mais uniformemente negativas, mas ainda contém gradientes de potenciais

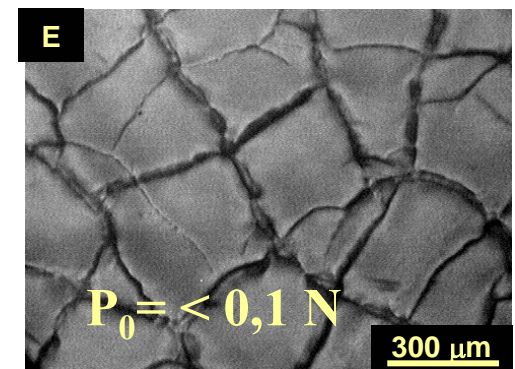
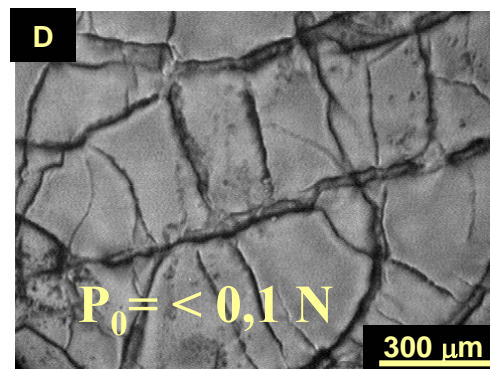
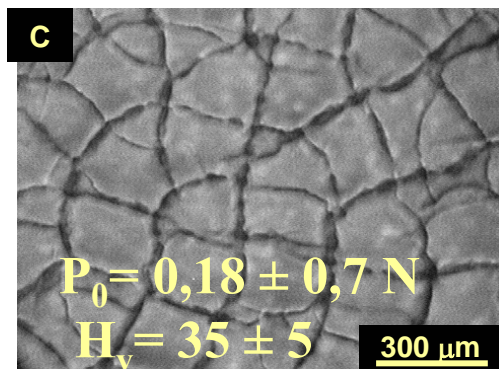
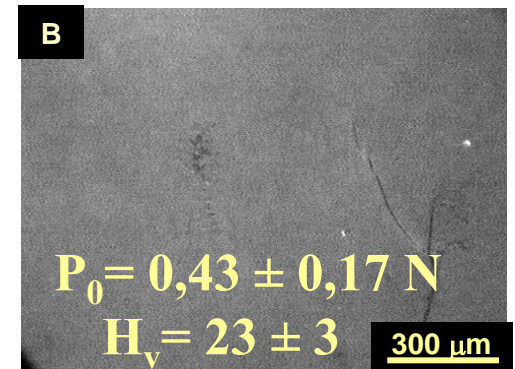
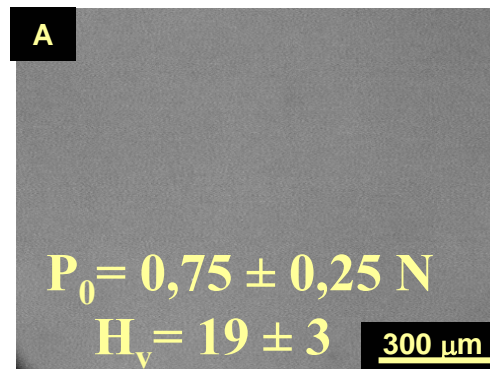


# Monolitos de partículas de sílica



- Monolitos com partículas maiores:
  - menos espessos
  - baixa contração linear
  - mais opacos
  - mais duros e quebradiços

- Monolitos com partículas menores:
  - superfície sem rachaduras
  - mais transparentes
  - elevada contração linear
  - maior tenacidade à fratura



# **Diferenças dependentes do tamanho das partículas**

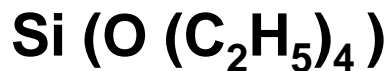
- **Carbono residual**
  - **hidrólise incompleta**
  - **grandes quantidades nas pequenas partículas**
- **Ácido polisilícico solúvel e ésteres, junto com as pequenas partículas**
- **As partículas menores possuem uma maior heterogeneidade de cargas elétricas**

# Caracterização das partículas

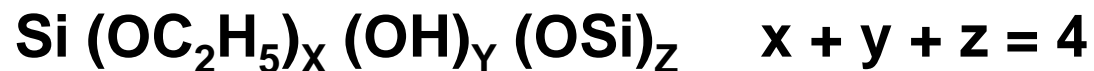
- As partículas menores, preparadas na presença de baixa concentração de base, contém grupos etoxilas residuais que:
  - limitam o crescimento
  - e a reticulação das cadeias de ác. silícico
- Sendo ricas em grupos etoxilas e pouco reticuladas, as partículas menores são mais fortemente intumescidas em etanol e água do que as partículas maiores, e com preferência pelo etanol

*J. Phys. Chem. B, 107  
(2003) 4747-4755*

Monômero

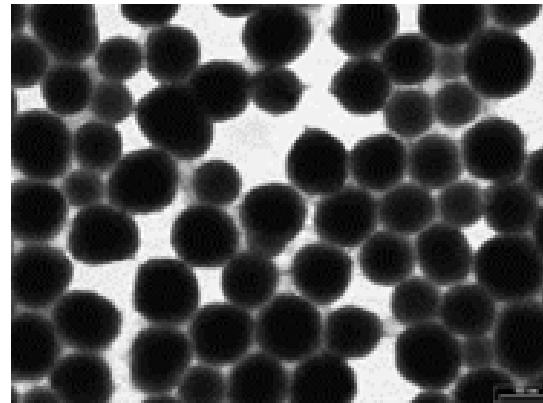
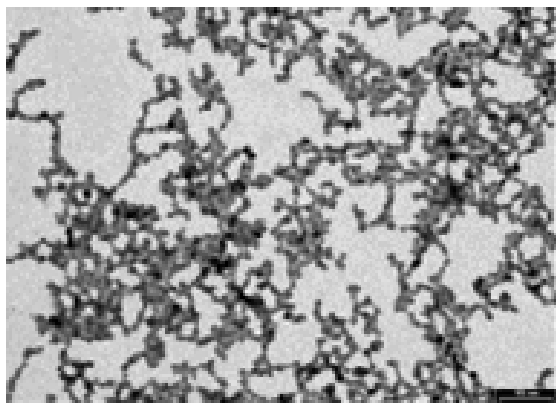
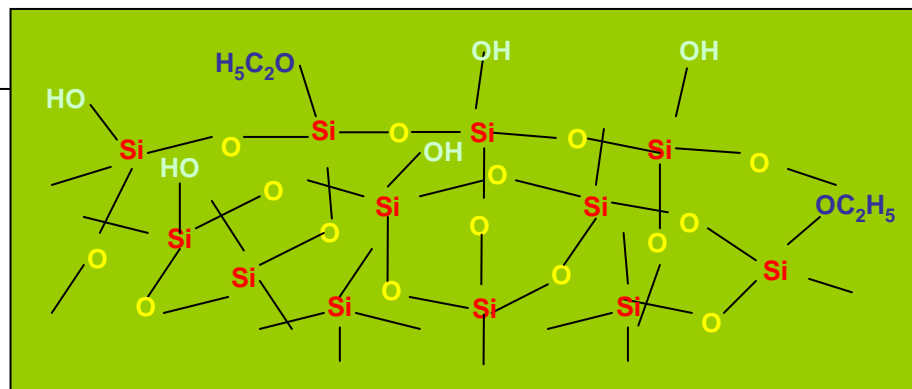
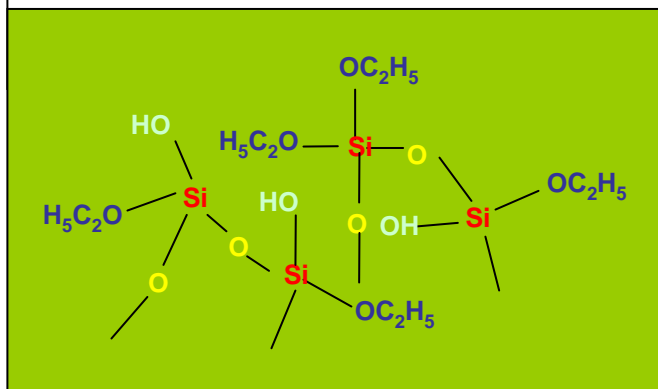


Polímero



Partícula

pH 7-10, na ausência de sal



# **Caracterização dos filmes**

- **Este intumescimento, associado à heterogeneidade de cargas elétricas e o baixo grau de reticulação das nanopartículas contribui para:**
  - **a plasticidade**
  - **e a deformação das partículas na formação de filmes e monolitos preparados por secagem das dispersões**
- **Isto justifica a alta densidade dos filmes, observada em SEM e AFM, e a formação de monolitos com superfície mais lisa, menos duros**

# **Sorção em sílica de Stöber: um estudo microquímico**

- **Sorção de íons:**
  - sorção de cátions e ânions em partículas com  $\zeta < 0$
  - entre diferentes partículas e o substrato
- **Sorção de polímeros:**
  - efeitos da concentração, massa molar e temperatura
- **Sorção de tensoativos:**
  - aniônicos, catiônicos e não-iônicos
  - efeitos da concentração
  - sorção do contra-íon

# Experimental

**Diluição (1:9) : dispersão de sílica ( $\phi_{\text{TEM}}=77\text{nm}$ ) em soluções de íons, polímeros ou tensoativos**

**Sonicação**

**30 min de repouso a T constante**

**Diluição (1:40) em água**

**Secagem a T constante, sob umidade relativa de 55%**

# Sorção de NaCl

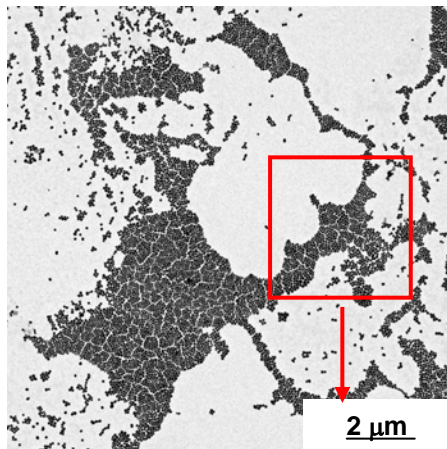
- **Observação direta, com uma descrição quantitativa, do padrão de sorção de íons  $\text{Na}^+$  e  $\text{Cl}^-$  em submonocamadas de partículas de sílica, utilizando ESI-TEM**



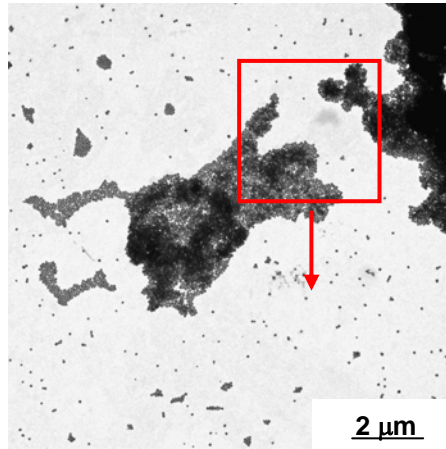
# Imagens de TEM das partículas de sílica

## Efeito da concentração de NaCl

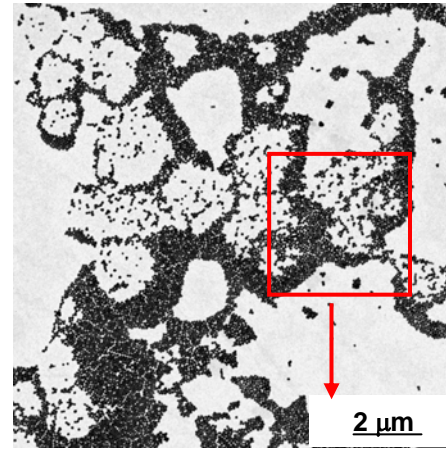
Sem NaCl



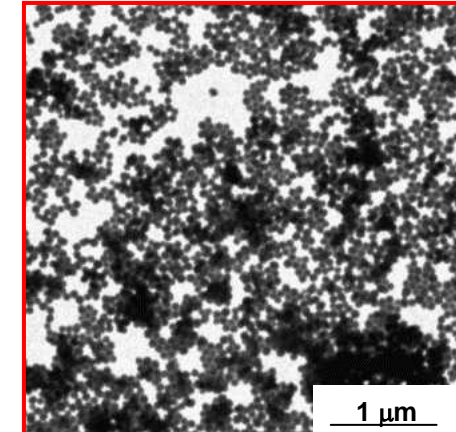
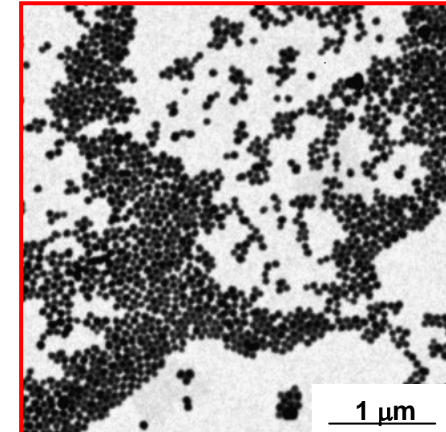
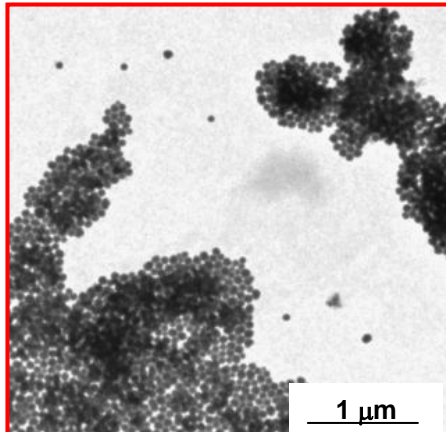
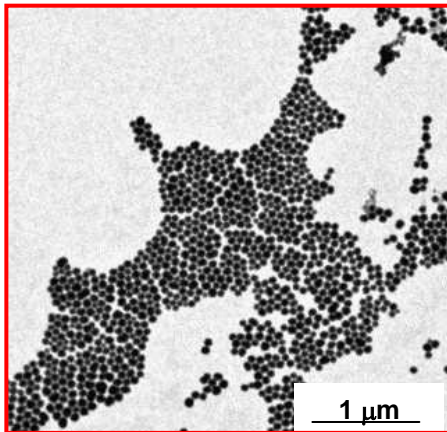
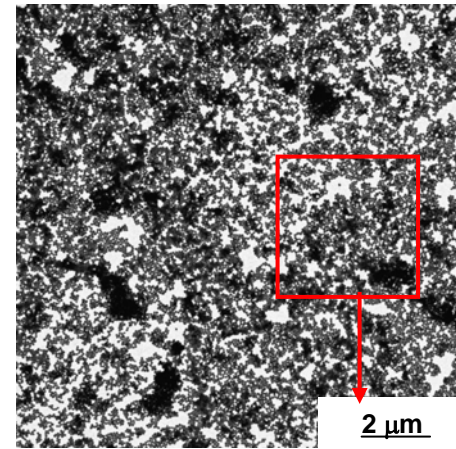
$10^{-5}$  M



$10^{-3}$  M

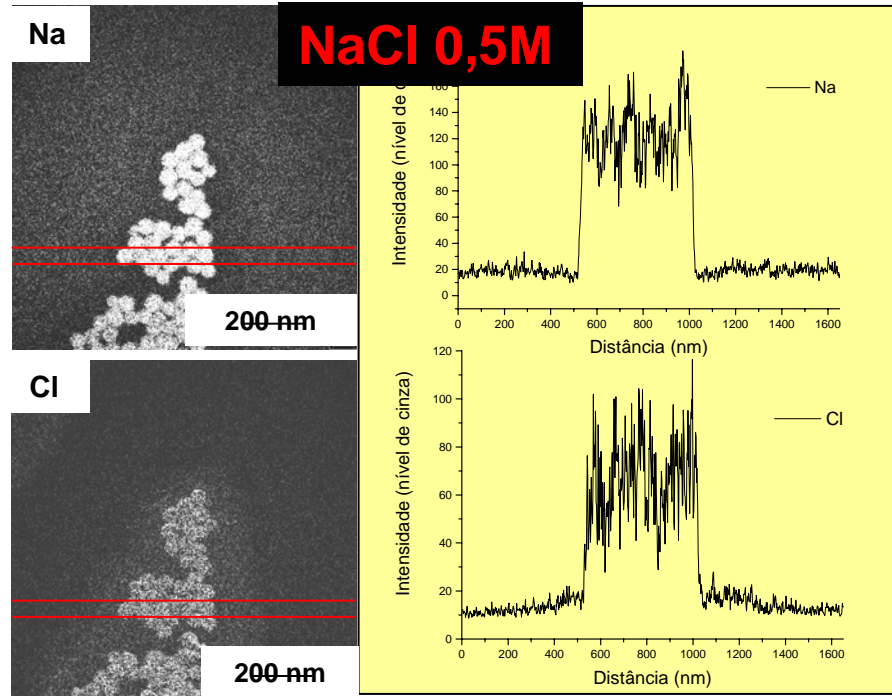
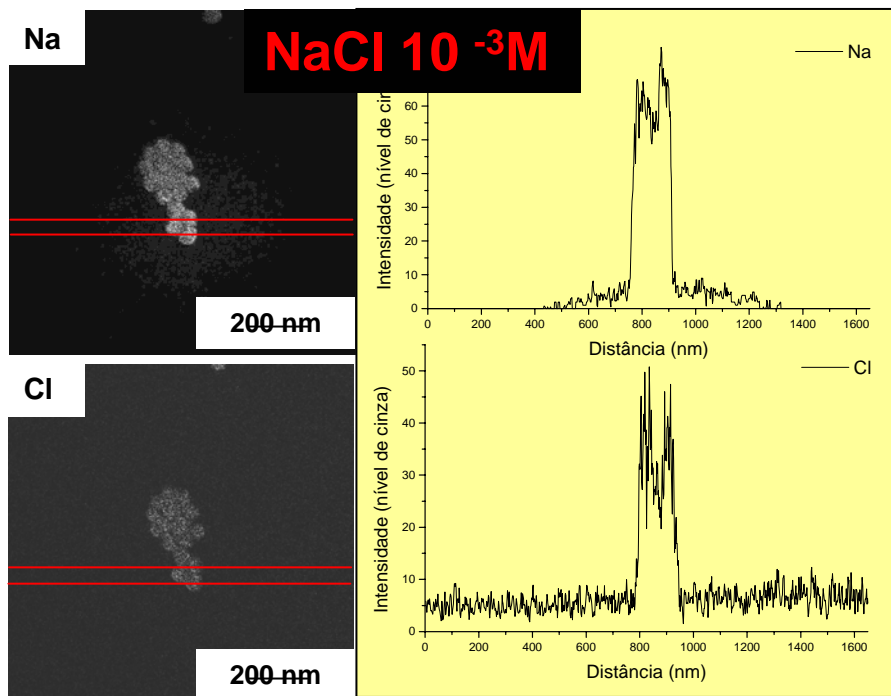
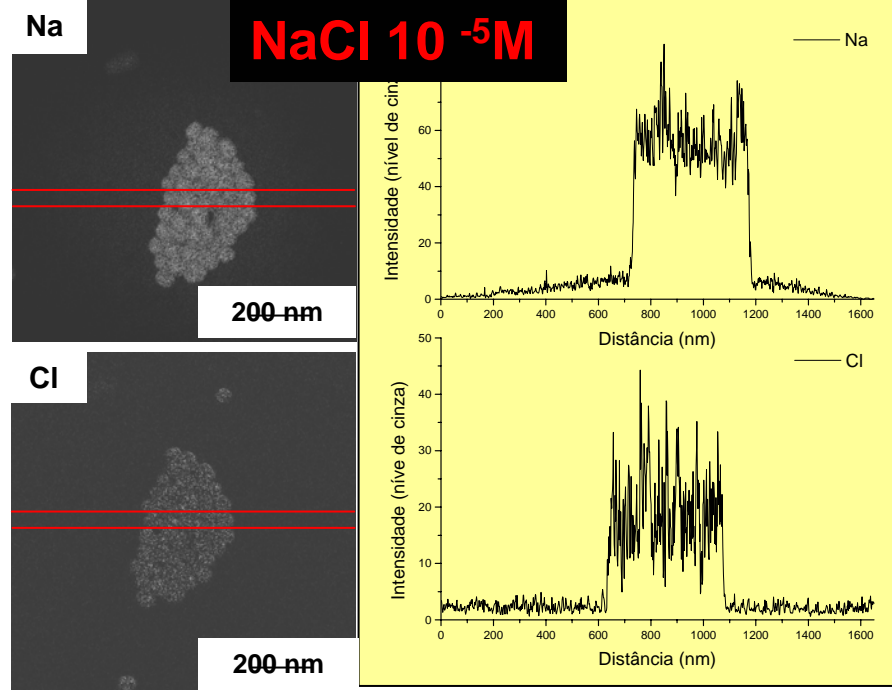


0,5 M



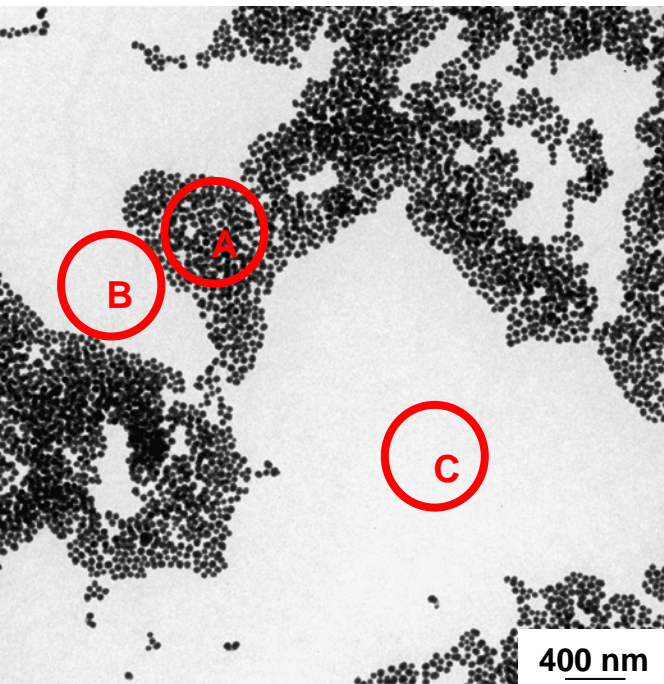
# Mapas elementares de Na e Cl

## Efeito da concentração de NaCl

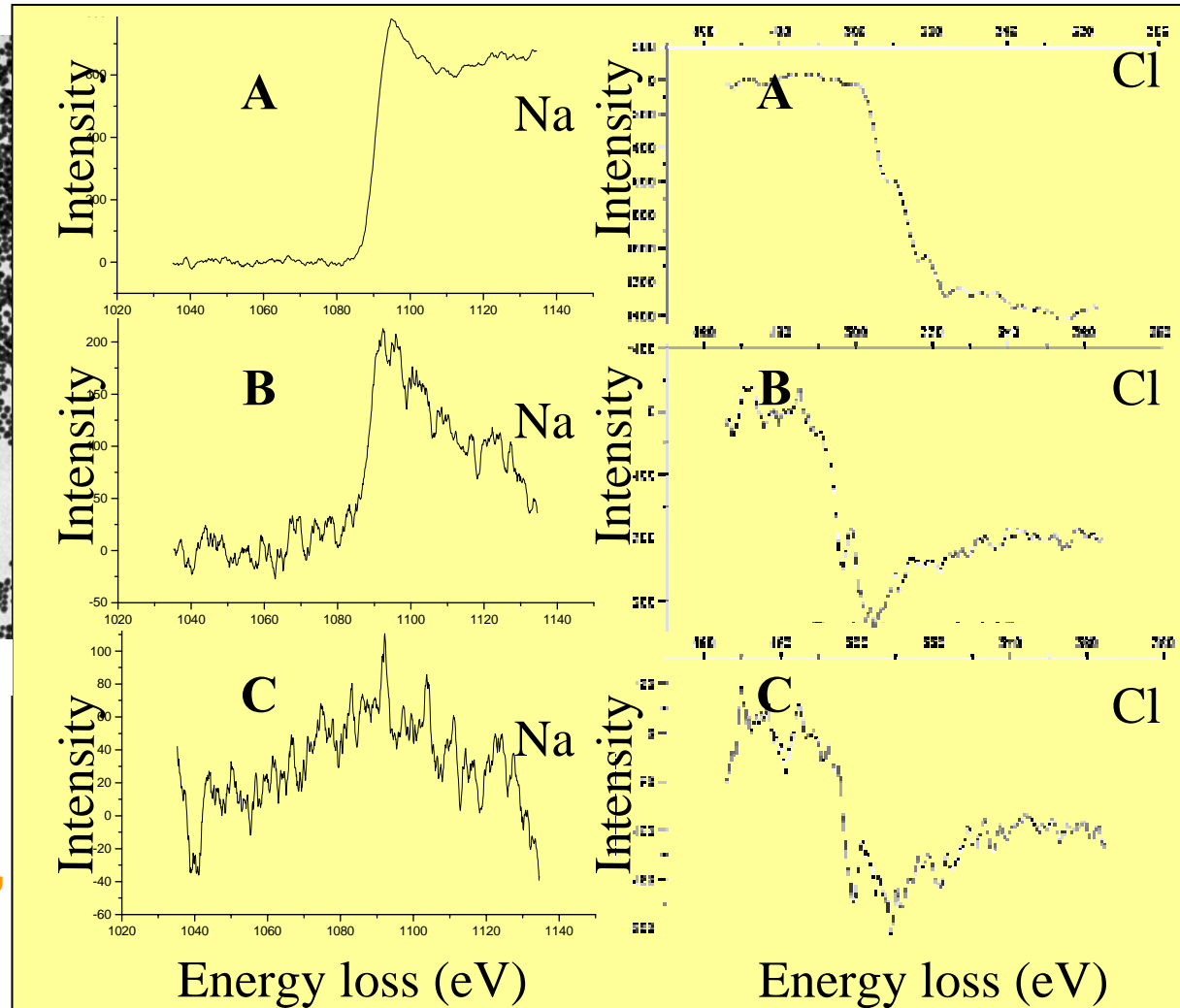


# Espectros de perda de energia

NaCl 0,5 M



Região A - Área de  $0,6\mu\text{m}^2$ , coberta 80,9% com partículas de sílica, sendo que em 15,3% desta área as partículas estão superpostas



# Quantificação por EELS

- Relação entre a área do pico de ionização  $A_i$  e o número  $N_i$  de átomos do elemento  $i$ :

$$A_i = c_i N_i$$

onde  $c_i$  é uma constante que depende da seção de choque do elemento analisado, e dos parâmetros de aquisição utilizados na aquisição do espectro.

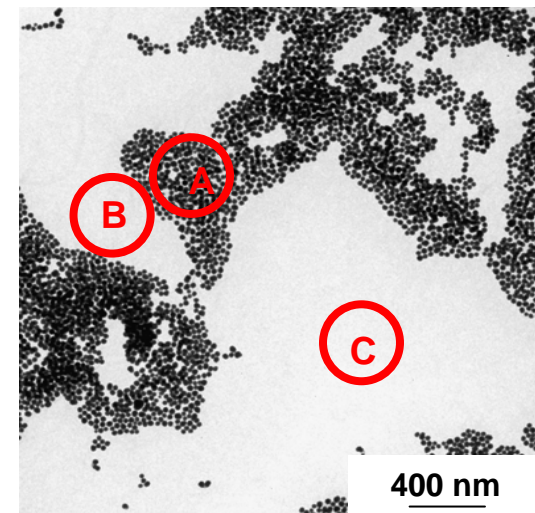
- Adquirindo sob condições constantes para  $k$  e  $i$ , em diferentes áreas 1 e 2:

$$N_{k2} / N_{i2} = (N_{k1} / N_{i1}) \cdot (A_{k2} / A_{i2}) \cdot (A_{i1} / A_{k1})$$



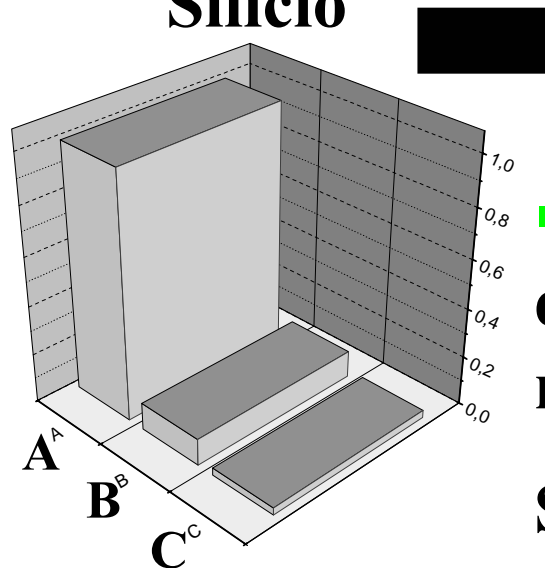
# Razão entre as quantidades relativas de Si, O, Na e Cl entre as regiões A, B e C

$$N_{k2} / N_{i2} = (N_{k1} / N_{i1}).(A_{k2} / A_{i2}).(A_{i1} / A_{k1})$$



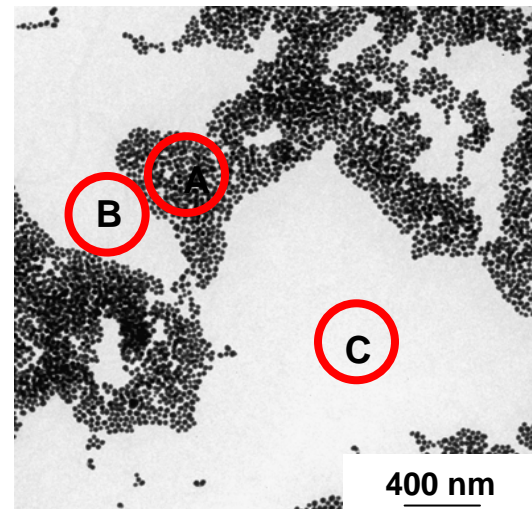
$N_X / N_Y$		X											
		Região A				Região B				Região C			
		Si	O	Na	Cl	Si	O	Na	Cl	Si	O	Na	Cl
Região A	Si	1	a	b	c	0,11				0,03			
	O	1/a	1	d	e		0,66				0,44		
	Na	1/b	1/d	1	f			0,21				0,11	
	Cl	1/c	1/e	1/f	1				0,23				0,12
Região B	Si	9,00				1	5,94a	1,89b	2,07c	0,29			
	O		1,51			0,17/a	1	0,32d	0,35e		0,67		
	Na			4,79		0,52/b	3,15/d	1	1,10f			0,51	
	Cl				4,35	0,48/c	2,88/e	0,91/f	1				0,52
Região C	Si	30,76				3,42				1	13,53a	3,38b	3,69c
	O		2,26				1,49			0,07/a	1	0,25d	0,27e
	Na			9,38				1,96		0,30/b	4,00/d	1	1,13f
	Cl				8,34				1,92	0,27/c	3,70/e	0,88/f	1

## Silício

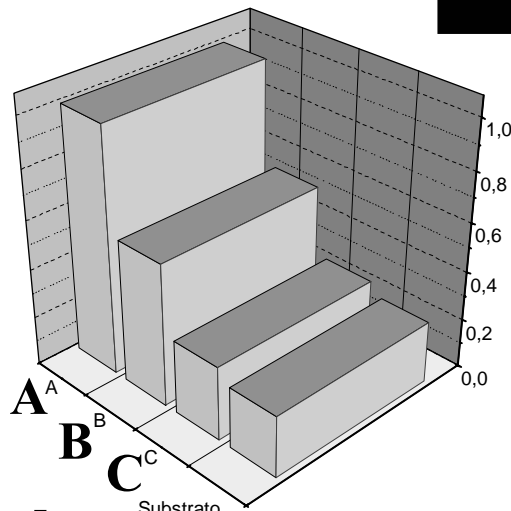


■ Presença de compostos de Si não-particulados nas regiões B e C.

Si em A:B:C (1: 0,11: 0,03)



## Oxigênio

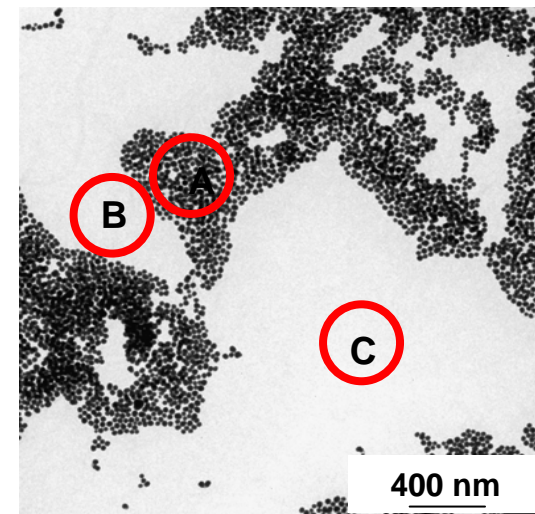
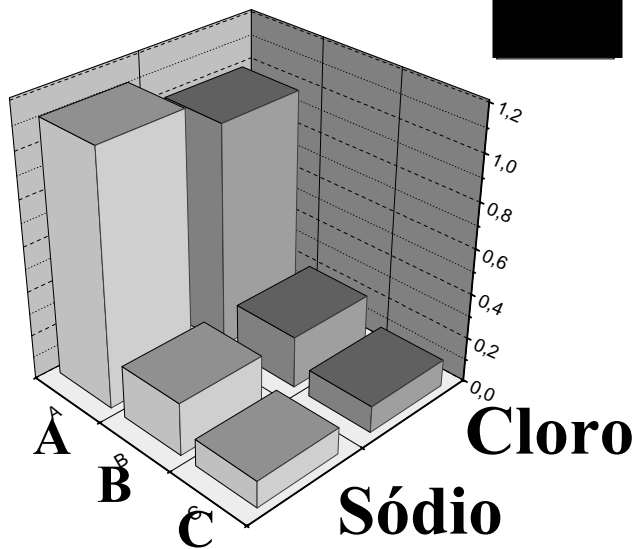


Substrato

■ O oxigênio está presente tanto na sílica como na água de hidratação e no substrato de parlódio

■ A hidratação do Si aumenta na região C em relação as regiões B e A

O/Si em A:B:C (1: 5,2: 9,2)



**Na em A:B:C (1: 0,21: 0,11)**

**Cl em A:B:C (1: 0,23: 0,12)**

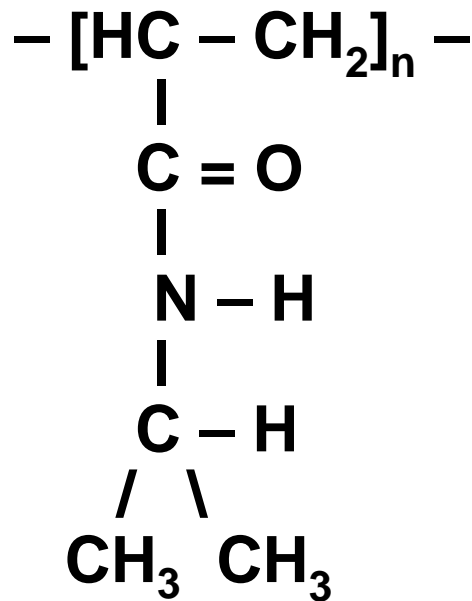
- Na e Cl são sorvidos próximos da razão estequiométrica do NaCl
- Excesso de  $\text{Na}^+$  nas partículas e nos compostos de Si solúveis
  - » as partículas de sílica e os ácidos silícicos possuem um potencial zeta negativo

# **Sorção de polímero**

- **Influência das camadas de polímeros adsorvidas na organização das partículas em duas dimensões**
  - **Observação direta da organização das partículas**
  - **Medidas diretas da camada de polímero adsorvida**
  - **Efeito da temperatura**



# Poli(N-isopropilacrilamida) (PNIPAM)



- Polímero termosensível com uma baixa temperatura crítica de solução (LCST), entre 30°C e 35°C
- $T < \text{LCST}$ , a água é um bom solvente, o polímero forma um novelo solúvel
- $T > \text{LCST}$ , a água é um solvente ruim, o polímero colapsa, resultando em separação de fase

# Imagens de TEM das partículas de sílica

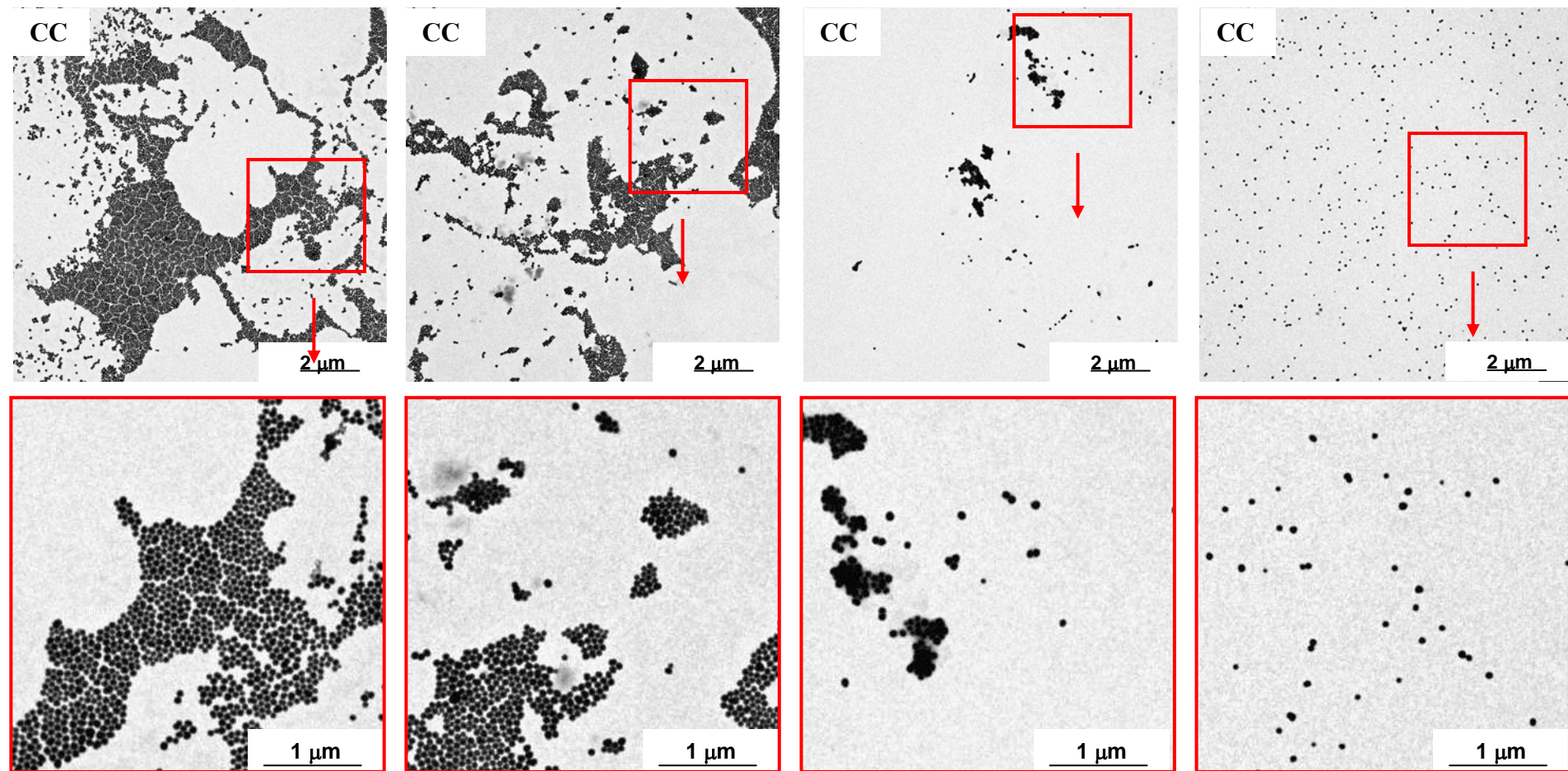
Efeito da concentração do polímero  
( $T = 20\text{ }^{\circ}\text{C}$ ) (Massa molar = 90 Kg/Mol)

Sem polímero

$10^{-5}\text{ g/mL}$

$10^{-4}\text{ g/mL}$

$10^{-3}\text{ g/mL}$



A dispersão das partículas aumenta com a concentração do polímero

# Mapas elementares de carbono

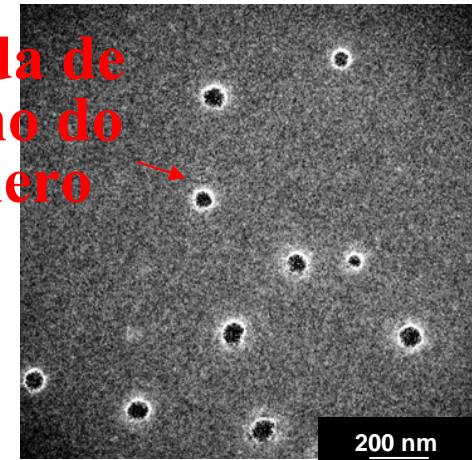
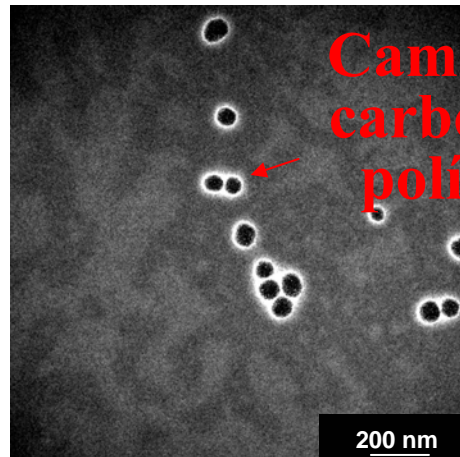
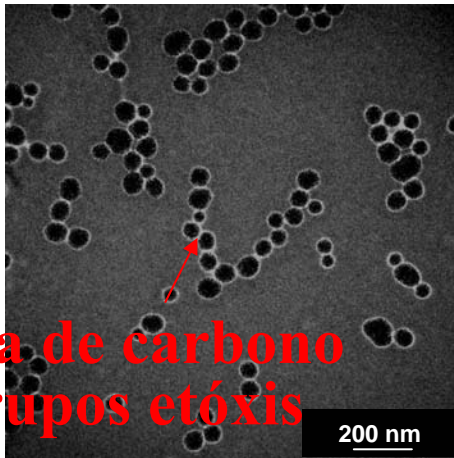
$$\Delta E = 284 \pm 8 \text{ eV}$$

## Efeito da concentração do polímero

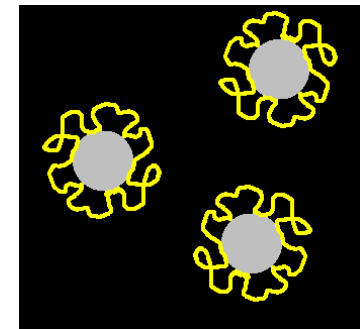
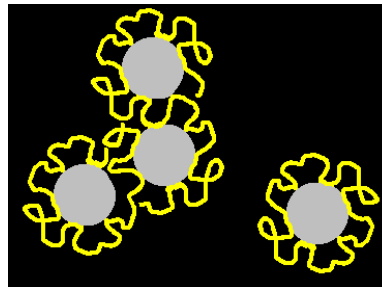
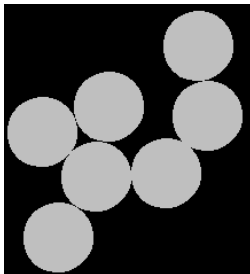
Sem polímero

$10^{-4} \text{ g/mL}$

$10^{-3} \text{ g/mL}$

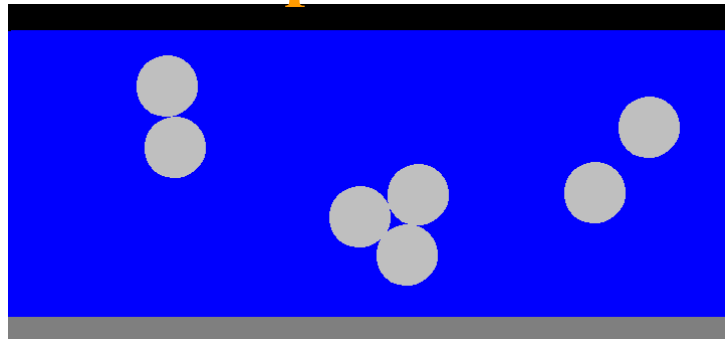


Dispersão das partículas devido a camada de polímero adsorvida



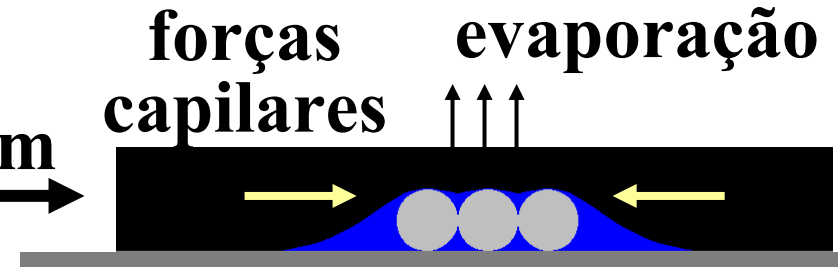
# Estágios finais da secagem

**sem polímero**



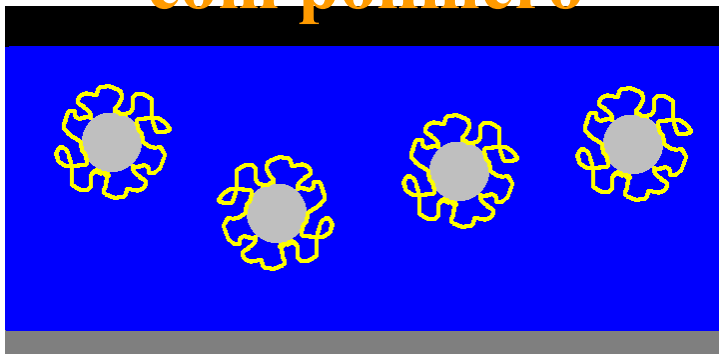
**agregação de  
algumas partículas**

**secagem**



**empacotamento  
fechado em 2D**

**com polímero**



**dispersão das partículas  
por repulsão estérica**

**secagem**



**partículas dispersas**

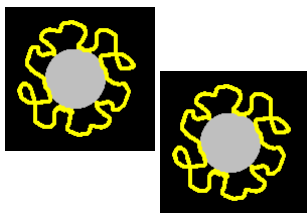
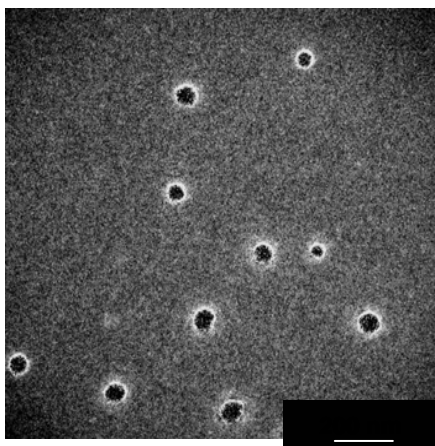


# Mapas elementares de carbono

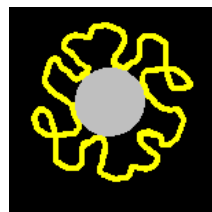
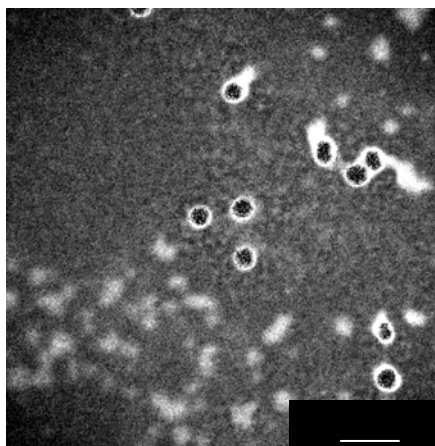
Efeito da massa molar

$C_p = 10^{-3} \text{ g/mL}$ ,  $T = 20^\circ\text{C}$

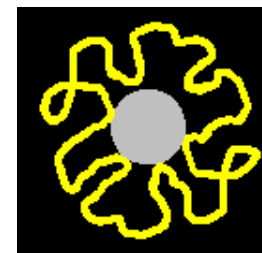
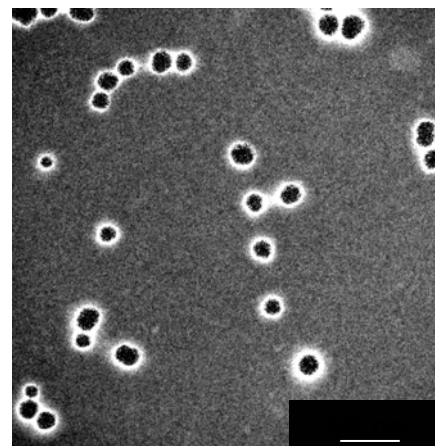
90 kg / Mol



190 kg / Mol

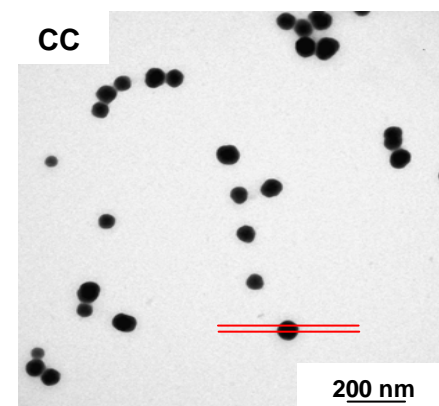
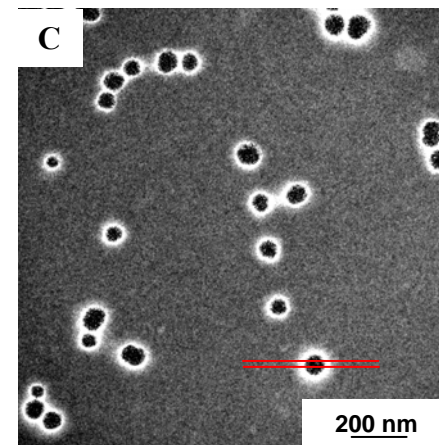
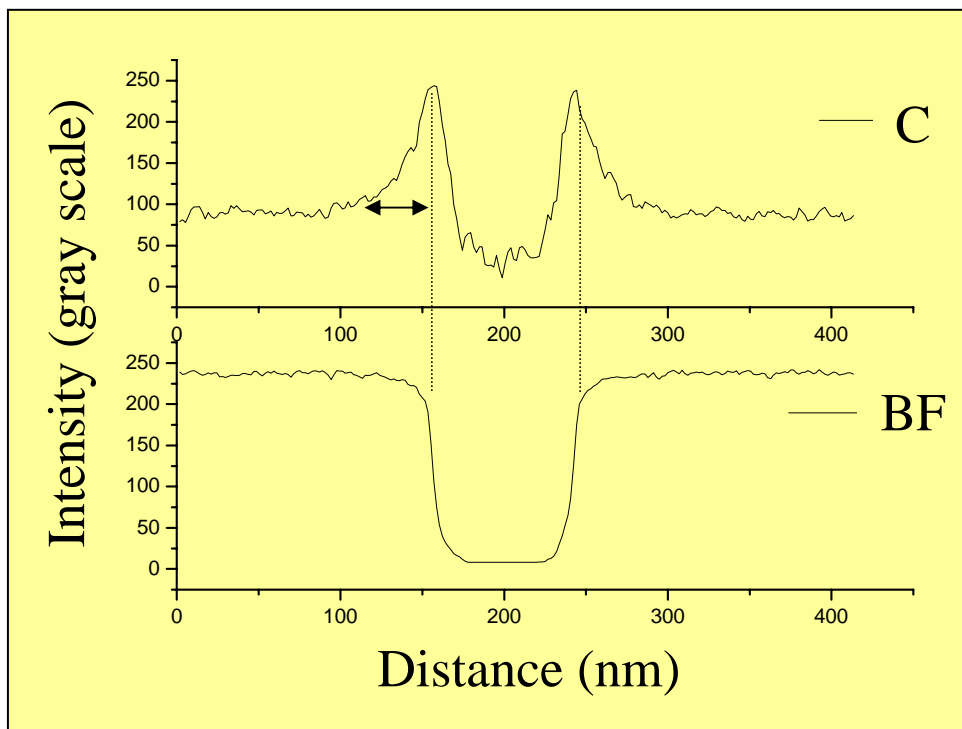


1050 kg / Mol



A espessura da camada adsorvida aumenta com a massa molar

# Efeito da massa molar

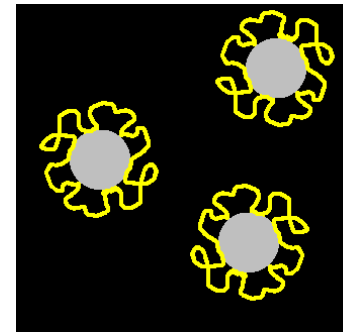
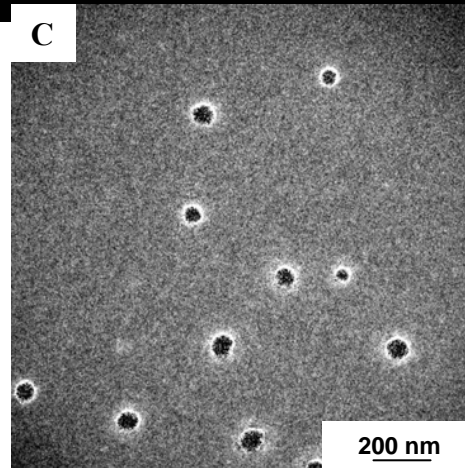
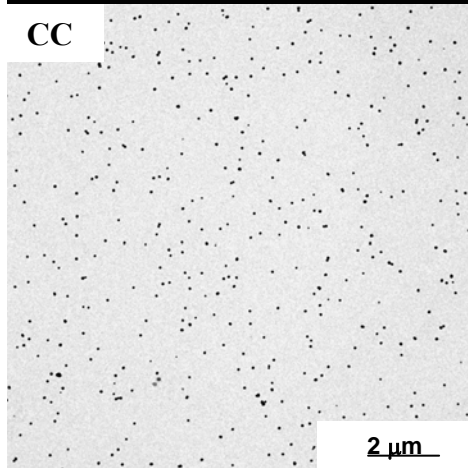


## Espessura da camada de polímero adsorvida

Mw(Kg/Mol)	90	190	1050
TEM (nm)	$10 \pm 5$	$21 \pm 5$	$38 \pm 5$
PCS (nm)	$10 \pm 2$	$35 \pm 2$	$129 \pm 3$

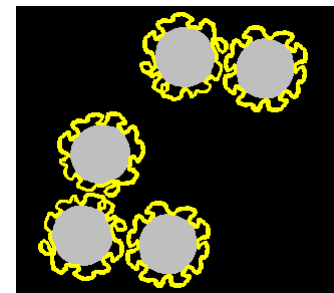
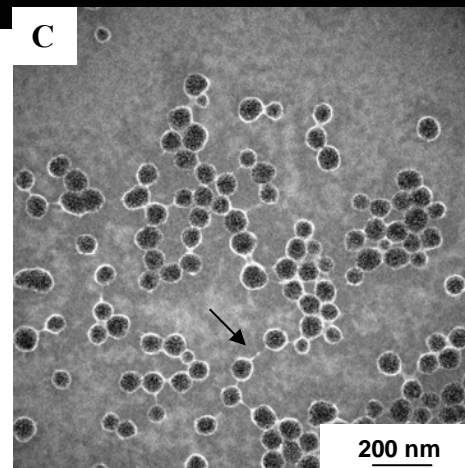
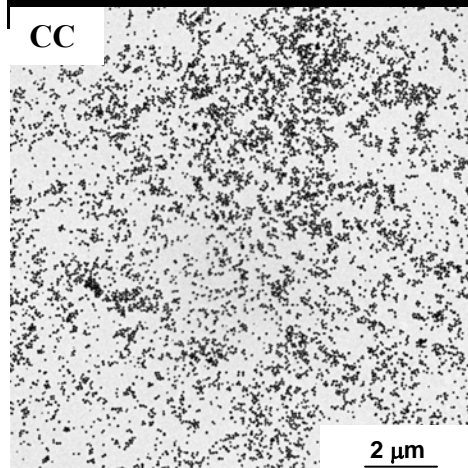
# Efeito da temperatura de secagem

**$T = 20^{\circ}\text{C}$  ( $T < \text{LCST}$ , condições boas de solvência)**



**repulsão  
estérica**

**$T = 40^{\circ}\text{C}$  ( $T > \text{LCST}$ , condições ruins de solvência)**



**colapso da  
camada  
adsorvida →  
atração**

# **Sorção de tensoativos**

- **Estudo da influência da sorção de tensoativos na organização das partículas em duas dimensões**
  - **Observação direta da organização das partículas**
  - **Observação direta da sorção do tensoativo e do contra-íon**



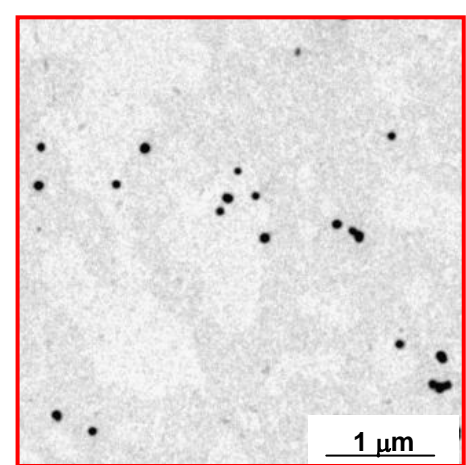
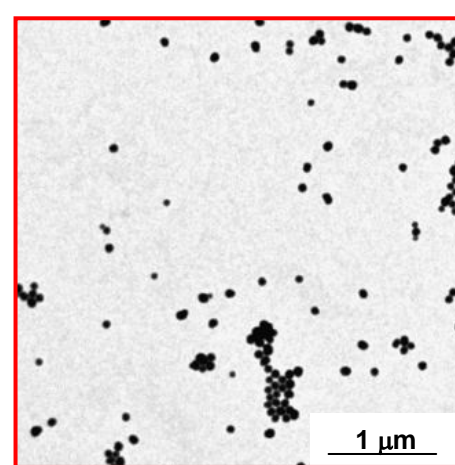
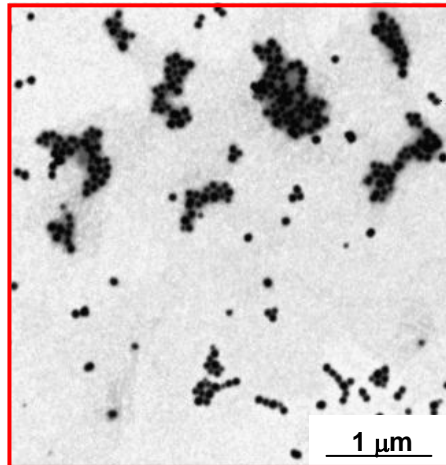
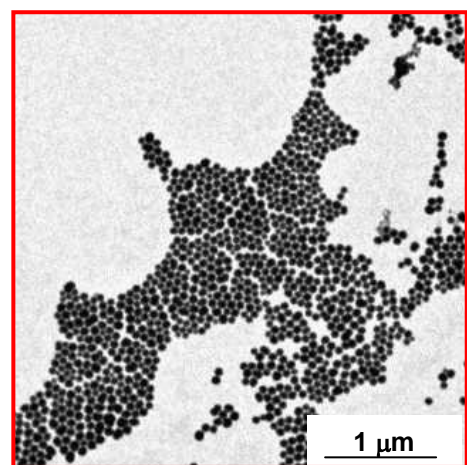
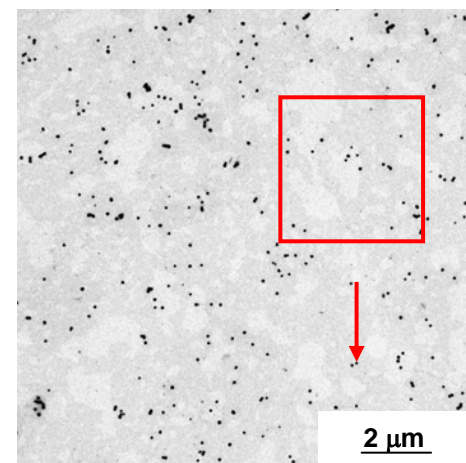
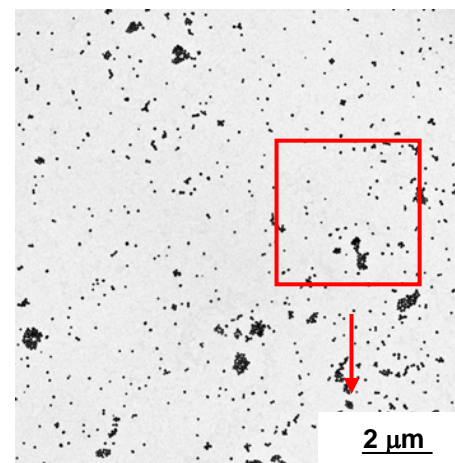
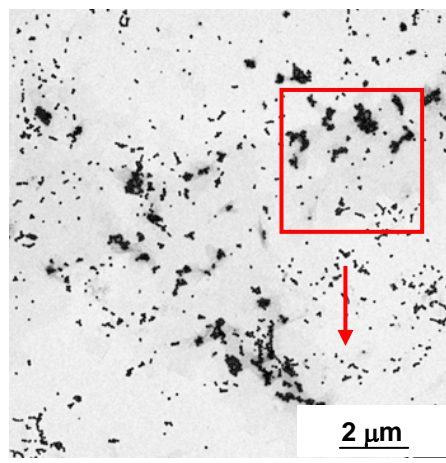
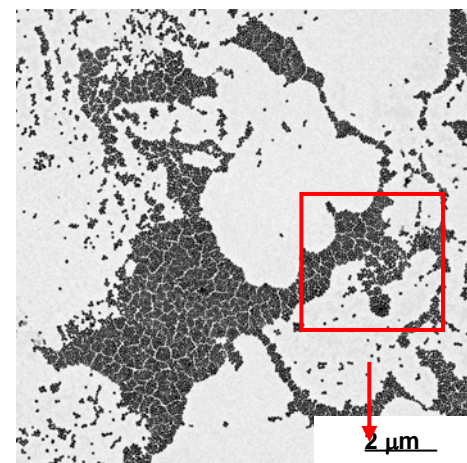
# Efeito da concentração de SDS

Sem SDS

$10^{-5}$  M

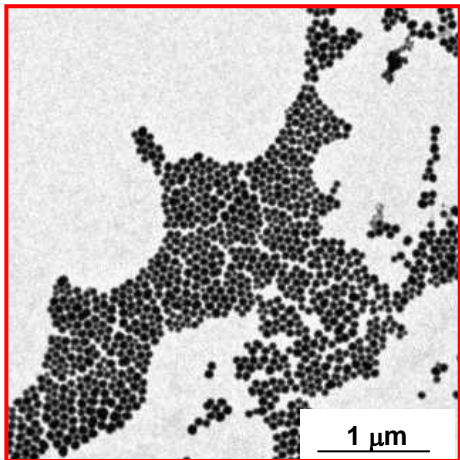
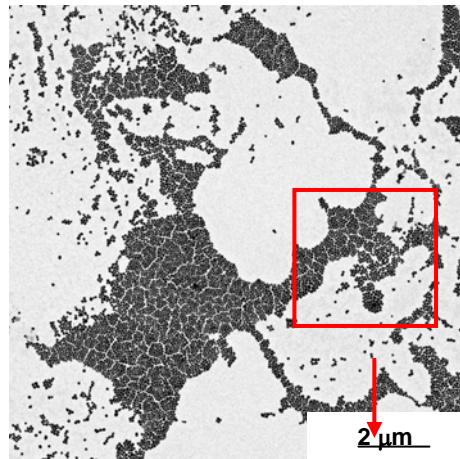
$10^{-3}$  M

$10^{-1}$  M

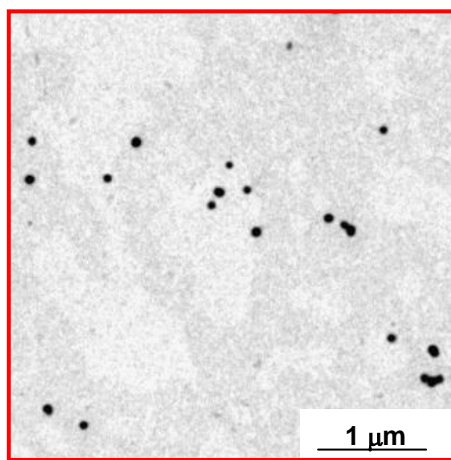
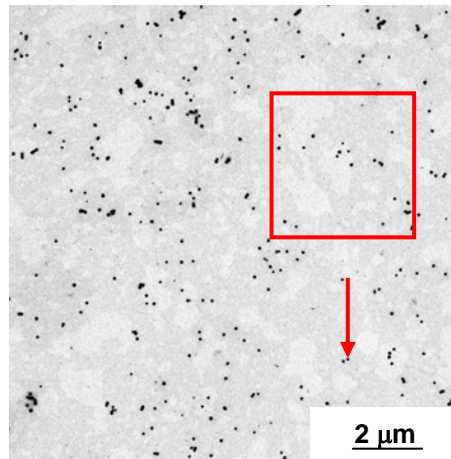


# Sorção de diferentes tensoativos

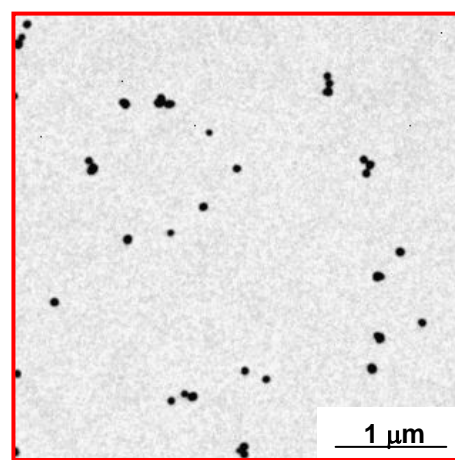
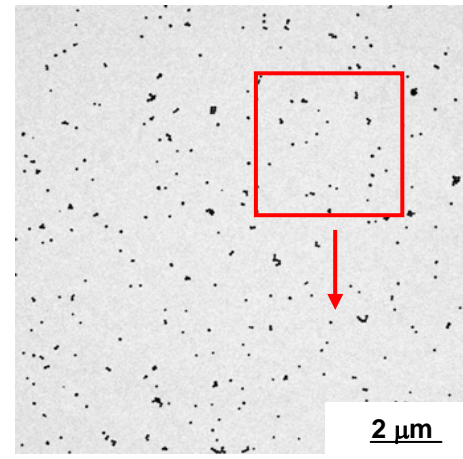
**Sem tensoativos**



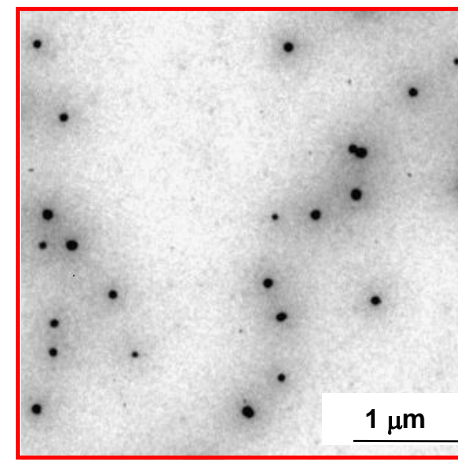
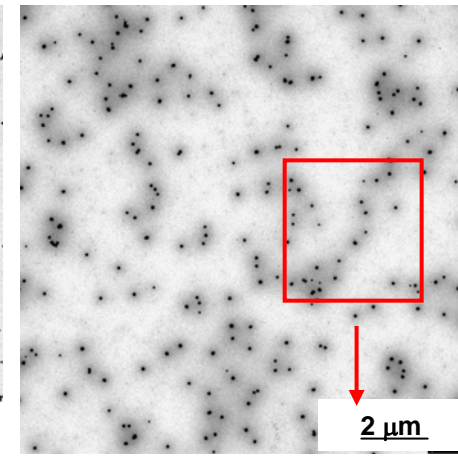
**SDS  $10^{-1}$  M**



**CTAB  $10^{-1}$  M**



**RENEX  $10^{-1}$  M**

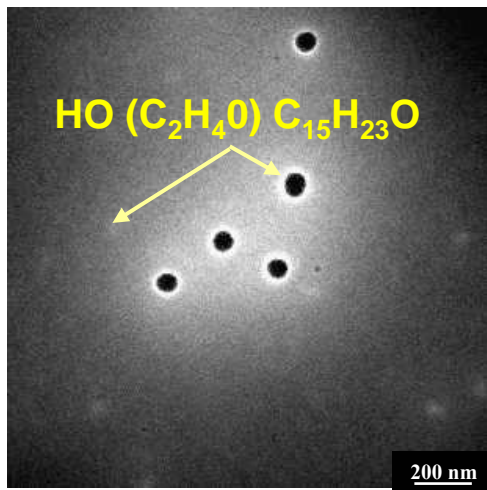




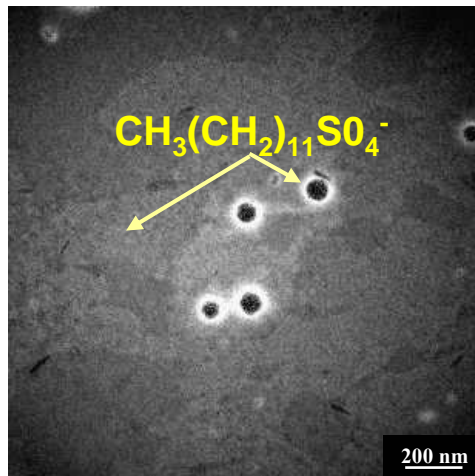
# Sorção de tensoativos

Mapas elementares de carbono  $\Delta E = 284 \pm 8$  eV

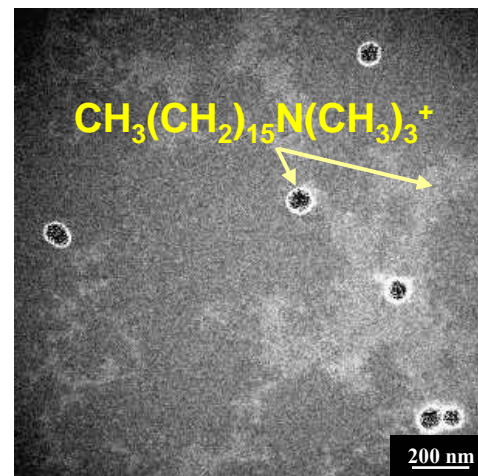
**RENEX  $10^{-1}$  M**



**SDS  $10^{-1}$  M**



**CTBA  $10^{-1}$  M**



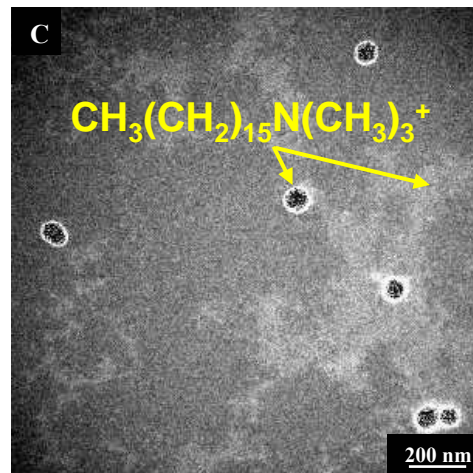
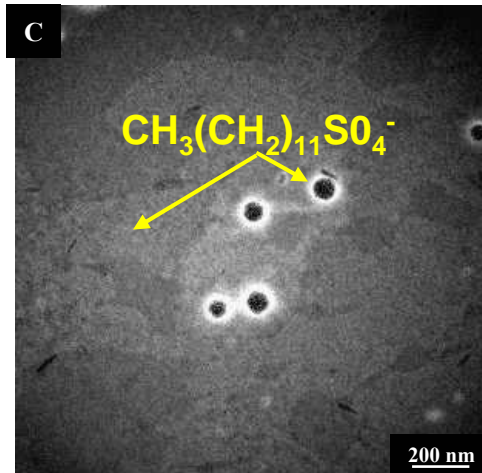
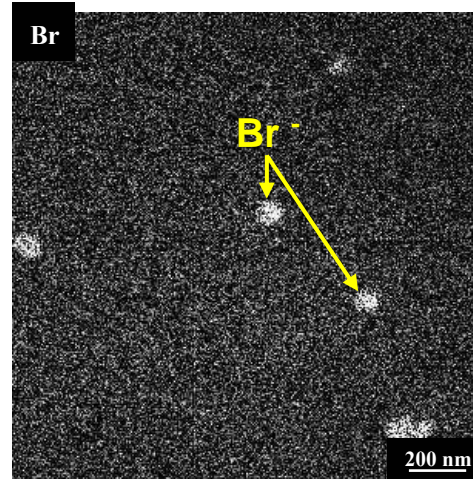
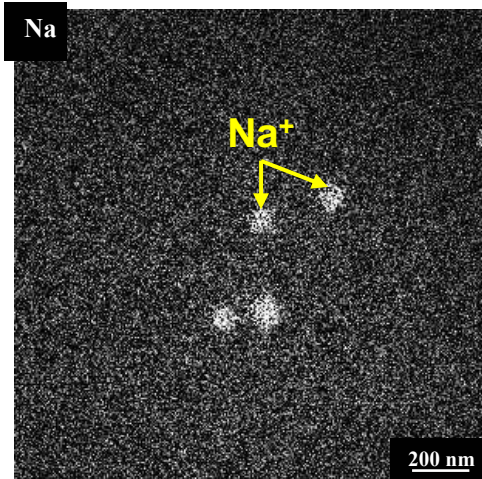
- Os tensoativos são retidos na superfície das partículas, não sendo verificada sua presença no interior destas
- São observados depósitos de tensoativos distribuídos com formato irregular em algumas regiões sobre o substrato

# Sorção dos contra-íons

## Mapas elementares de sódio, bromo e carbono

**SDS  $10^{-1}$  M**

**CTBA  $10^{-1}$  M**



■ Os contra-íons são sorvidos no interior das partículas

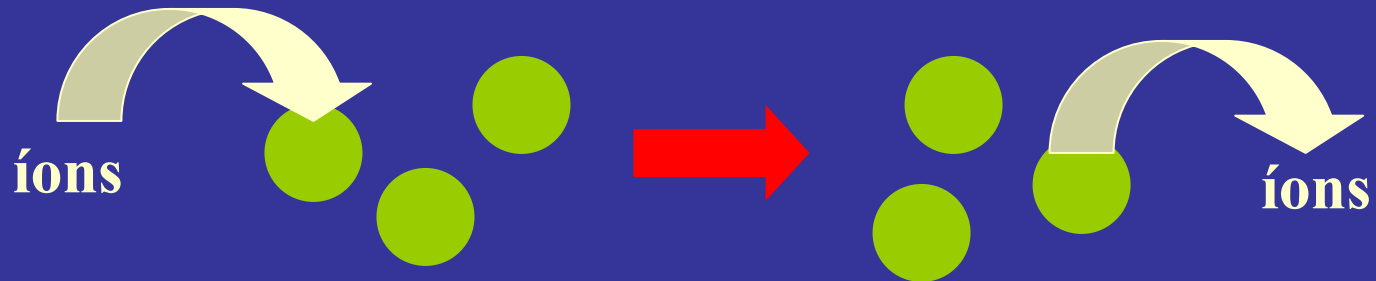
■ Os contra-íons não estão acumulados sobre o tensoativo no substrato

# Conclusões

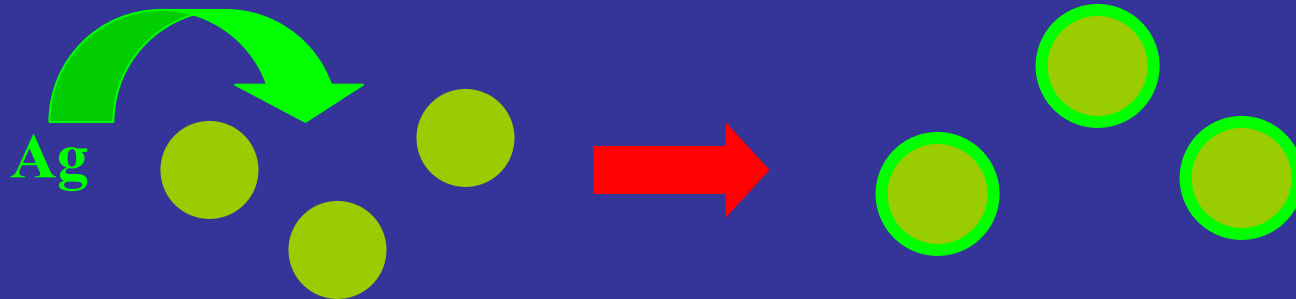
- Os resultados apresentados mostram que a Sílica de Stöber apresenta características podem levar ao seu uso como transportadoras de moléculas e íons, devido ao seu pequeno tamanho, alta estabilidade coloidal e capacidade de sorção

# Considerações finais

transportadoras de íons



nanoespelhos esféricos



# transportadoras de drogas

Y anticorpo  
● ● drogas  
PNIPAM

