Materiais Nanoestruturados à base de carbono: filmes finos e nanotubos

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Laboratório de Revestimentos Protetores e Materiais Nanoestruturados

Ciência dos Materiais

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Dra. Marta Dotto
Estudantes de doutorado: Renato, Dunieskys e Pillar
Estudantes de IC: Fernando Henrique e Jorge

Nanociência e Nanotecnologia:

- Top-Down

Miniaturização

- Bottom-up

Desenvolvimento de técnicas de análise e manipulação em escala atômica:

- microscopia eletrônica de alta resolução
- diferentes microscopias de varredura por sonda: STM, AFM, MFM, LFM, SNOM....

"Os princípios da física, assim como eu os vejo, não falam contra a possibilidade de se fabricar objetos manipulando átomo a átomo. Isso não viola nenhuma lei. É uma coisa que, a princípio, pode ser feita; mas, na prática, ainda não foi realizado por sermos muito grandes."

Richard Feynman, 1959

"There´s Plenty of Room at the Bottom"

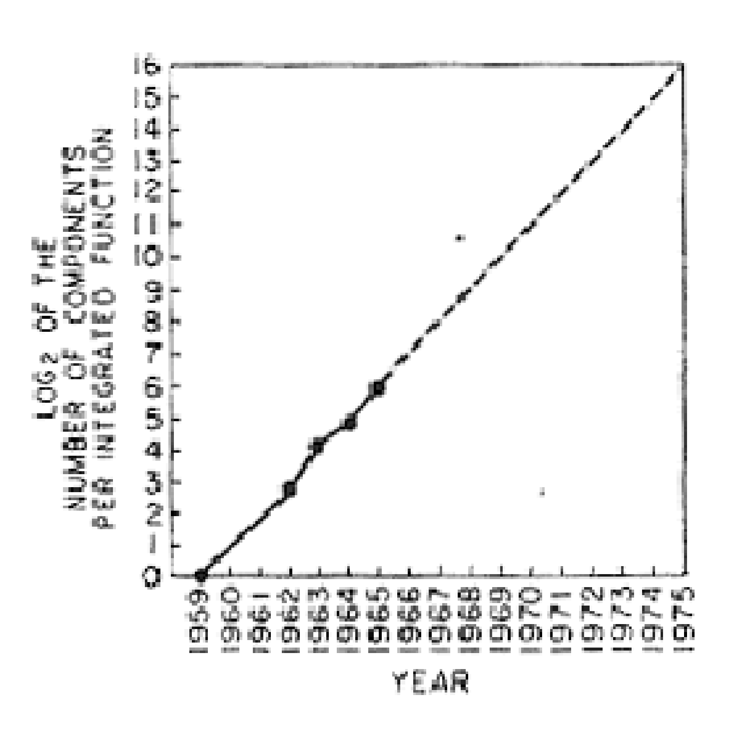
Eng. Sci. 23 (1960) 22

SHAPING THE WORLD ATOM BY ATOM

The emerging fields of nanoscience and nanoengineering are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. This is likely to change the way almost everything–from vaccines to computers to automobile tires to objects not yet imagined–is designed and made.

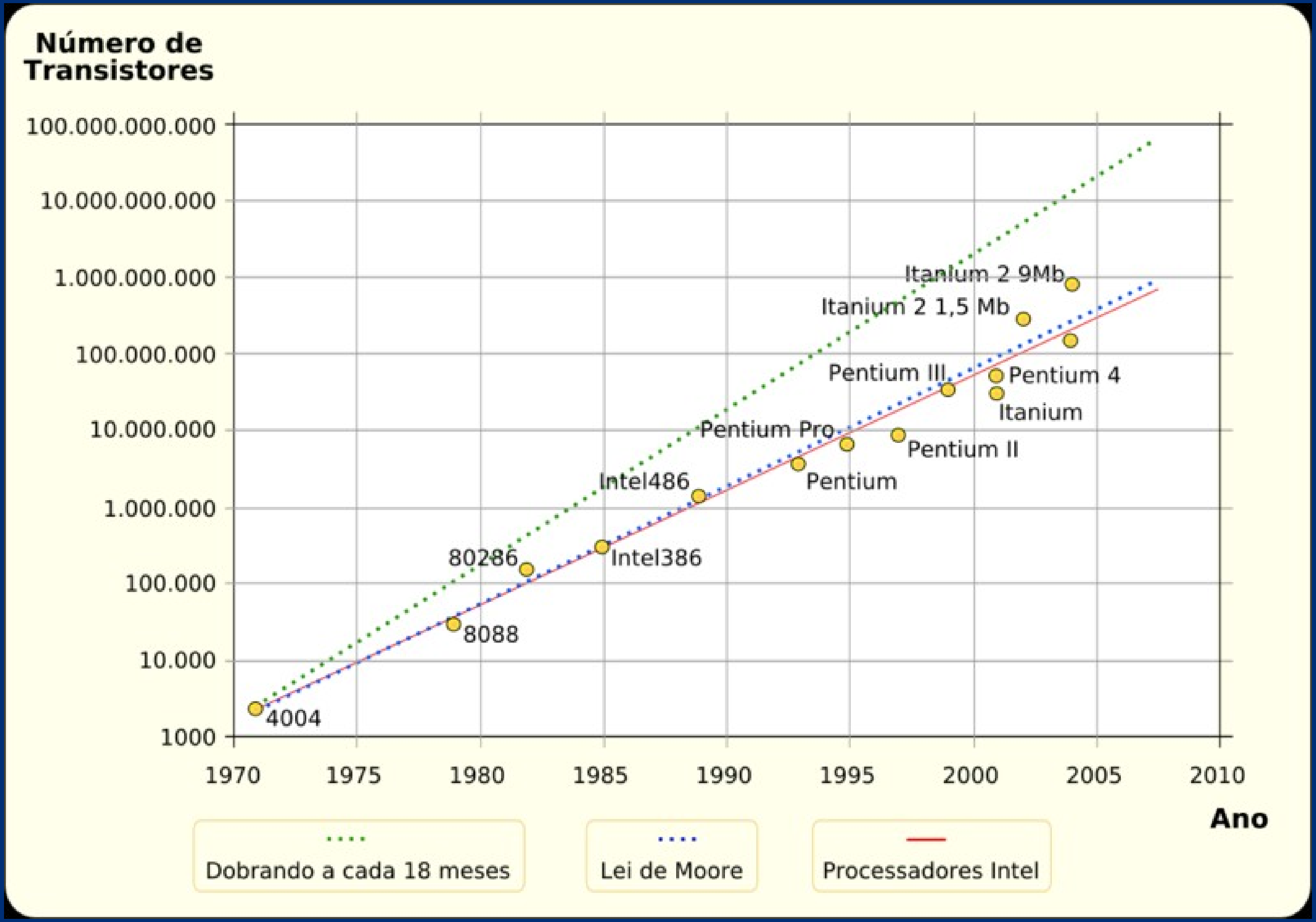
National Nanotechnology Initiative (1999)

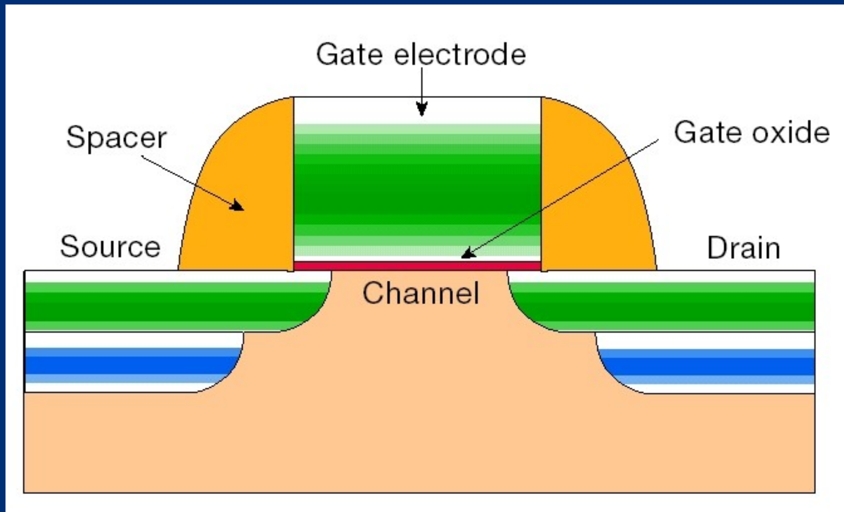
Top-down: miniaturização

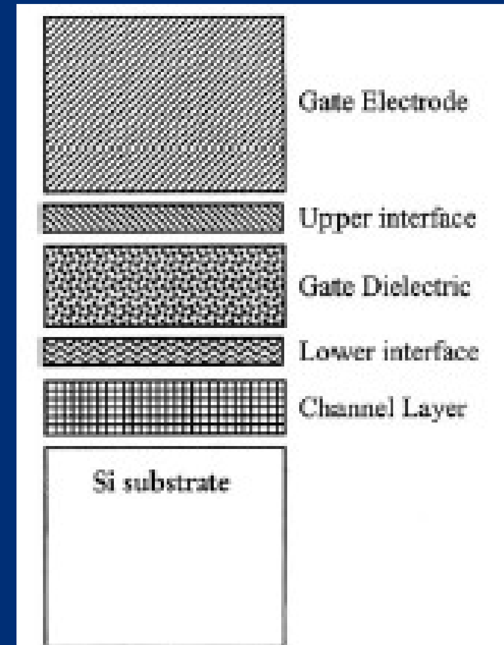


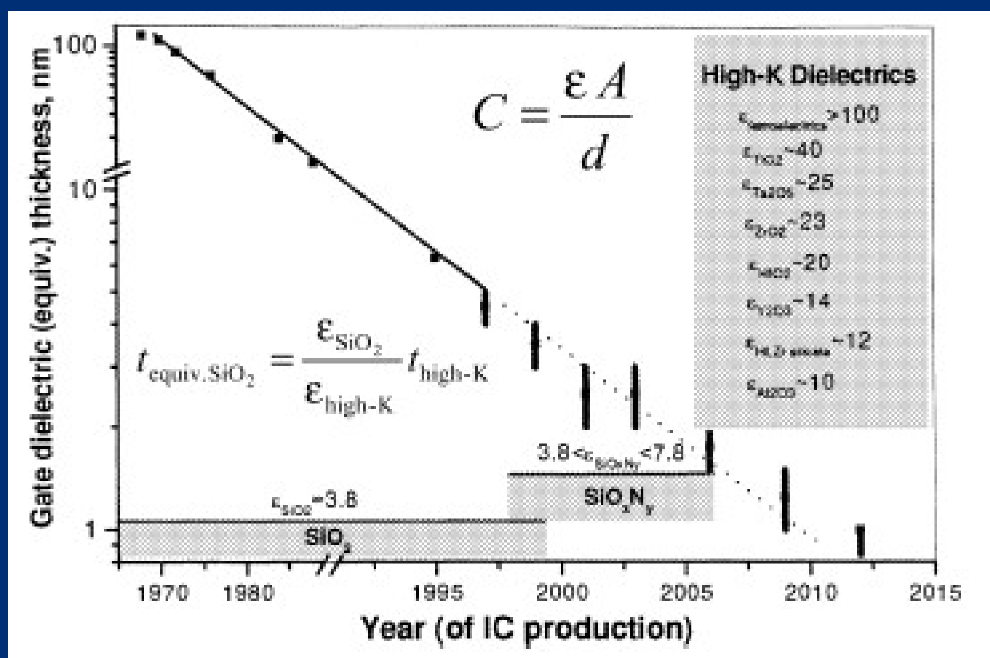
Lei de Moore

Top-down: miniaturização

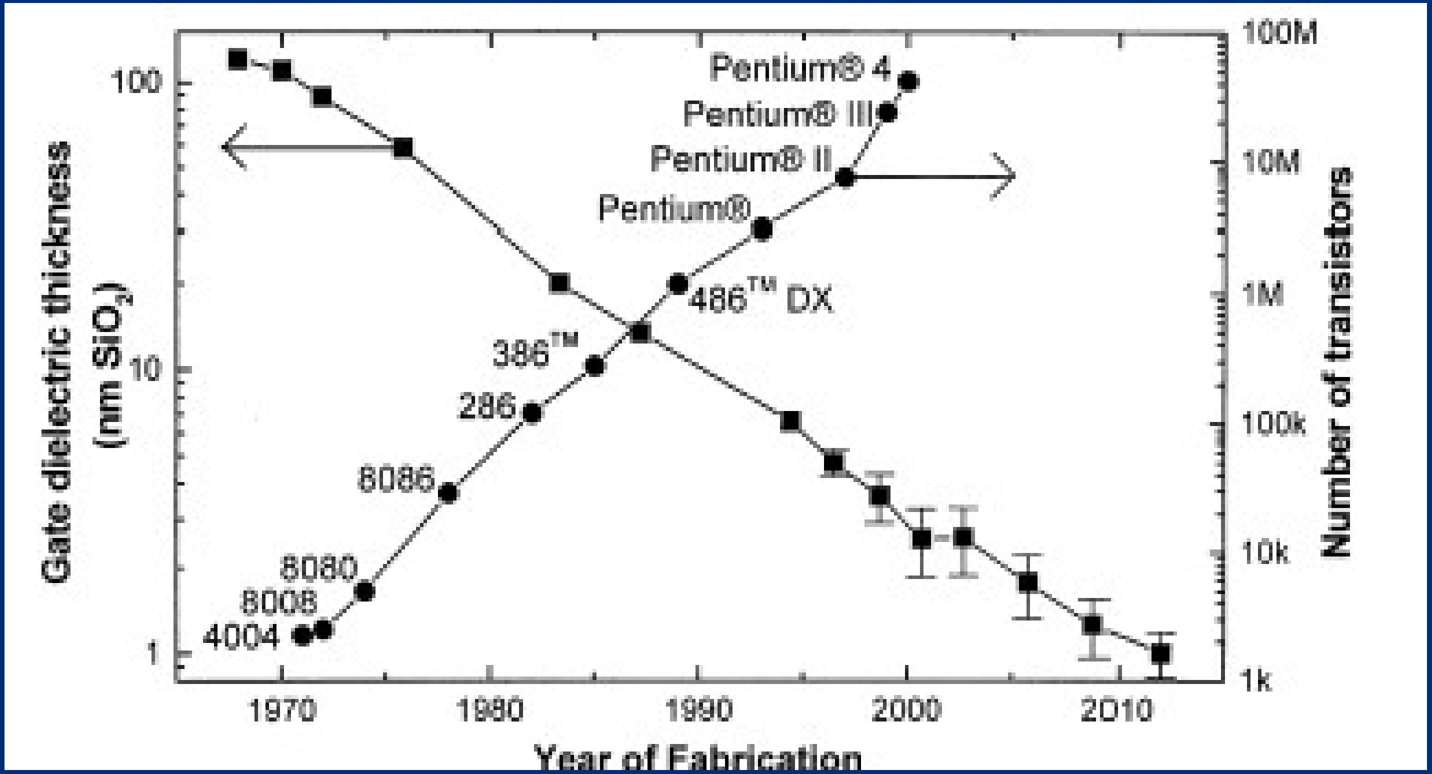



Gate electrode
Spacer
Gate oxide
Source
Drain
Channel


Gate Electrode
Upper interface
Gate Dielectric
Lower interface
Channel Layer
Si substrate


High-K Dielectrics
$C = \frac{\varepsilon A}{d}$
$t_{equiv.SiO_2} = \frac{\varepsilon_{SiO_2}}{\varepsilon_{high\text{-}K}} t_{high\text{-}K}$
ε_{SiO2}~3.8
SiO_2
SiO_xN_y
Gate dielectric (equiv.) thickness, nm
Year (of IC production)

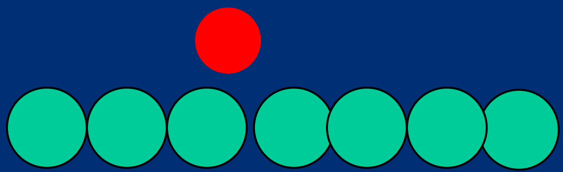
High-K dielectrics

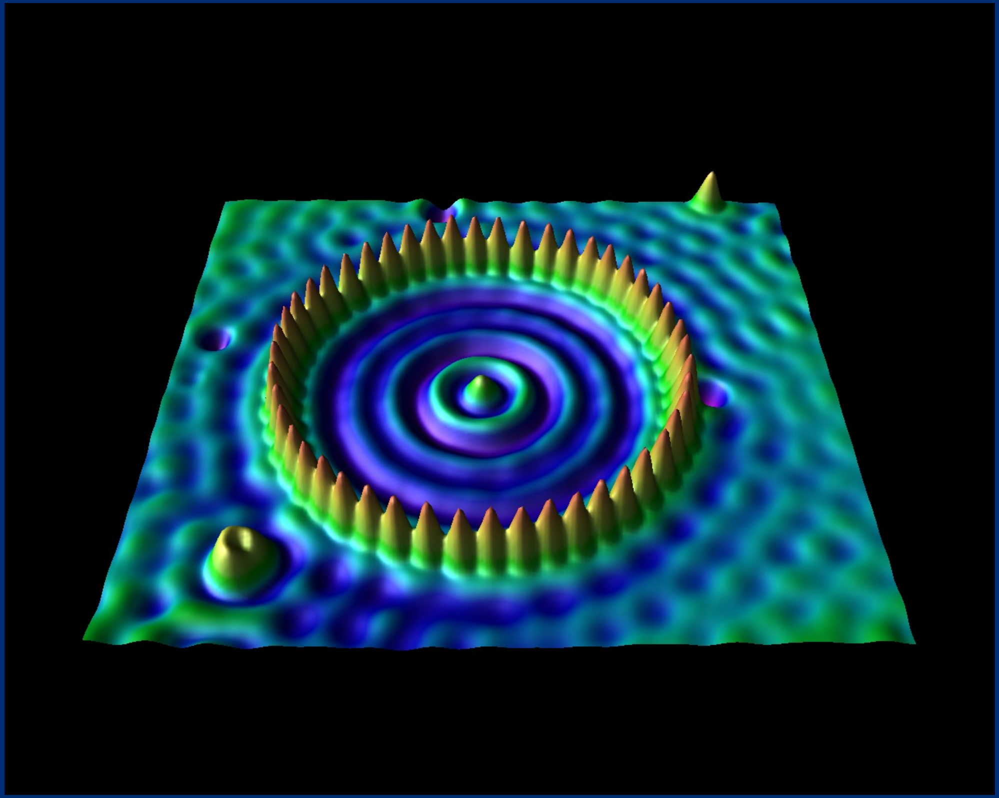


Lei de Moore

Óxido de Silício substituído por Óxido de Háfnio

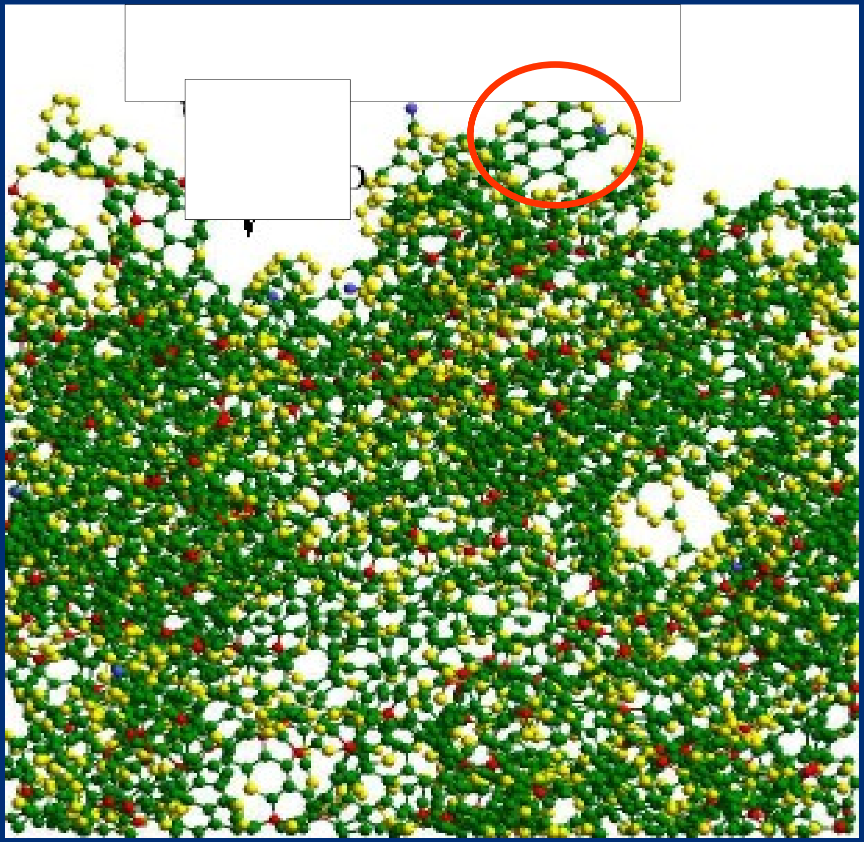
Manipulação atômica





Surface state electrons on Cu(111) were confined to closed structures
defined by barriers built from Fe adatoms. The barriers were assembled
by individually positioning Fe adatoms using the tip of a low temperature scanning tunneling microscope (STM). A circular corral of radius 7.1 nm was constructed in this way out of 48 Fe

Filmes de carbono amorfo: clusters de carbono sp2 interligados por átomos de carbono sp3, nanoporos e hidrogênio

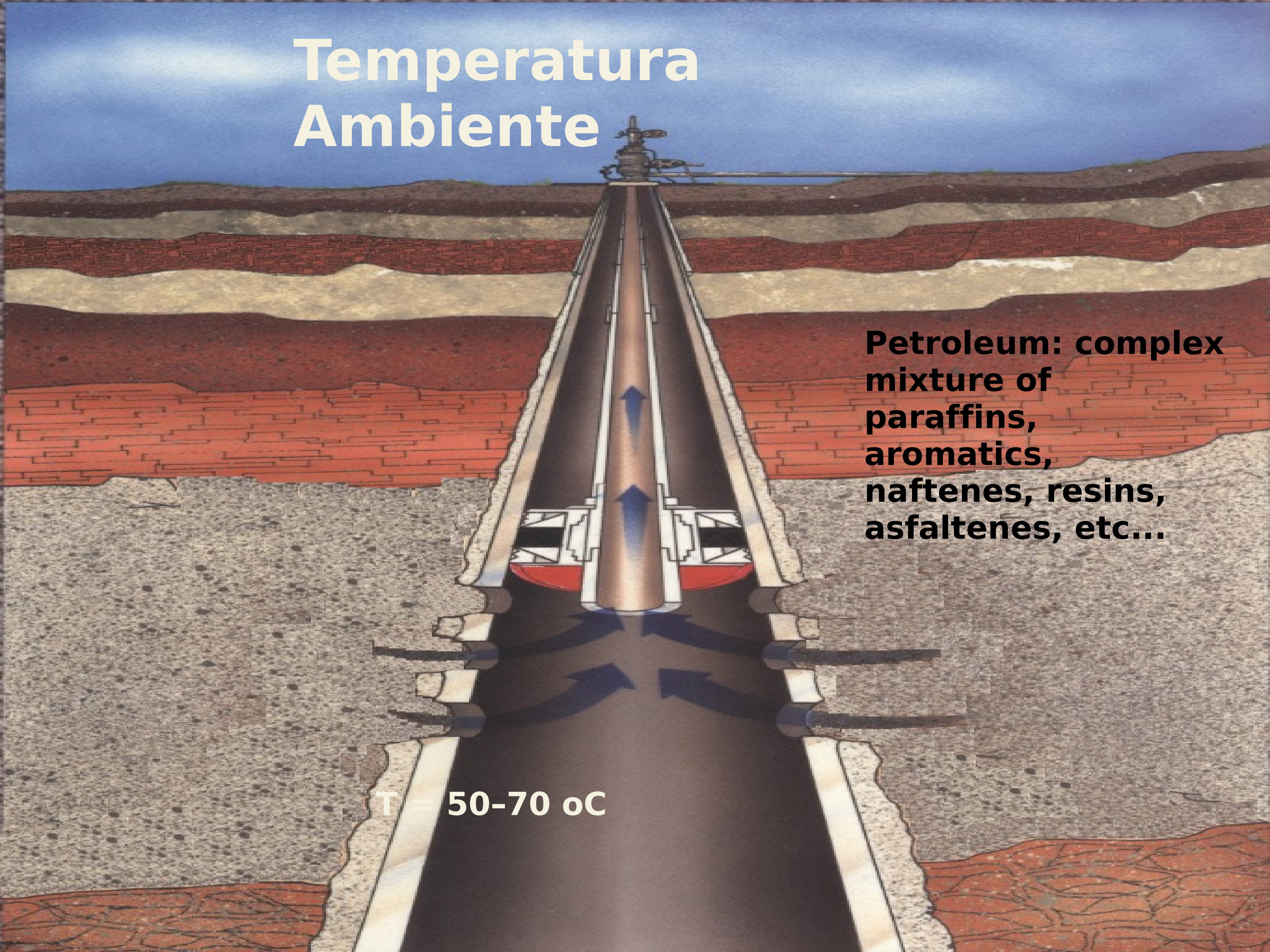


Cluster sp2

Indústria Aerospacial

Painéis solares: solda fria (Rede de Pesquisa em Revestimentos Nanoestruturados, INPE)

Temperatura Ambiente

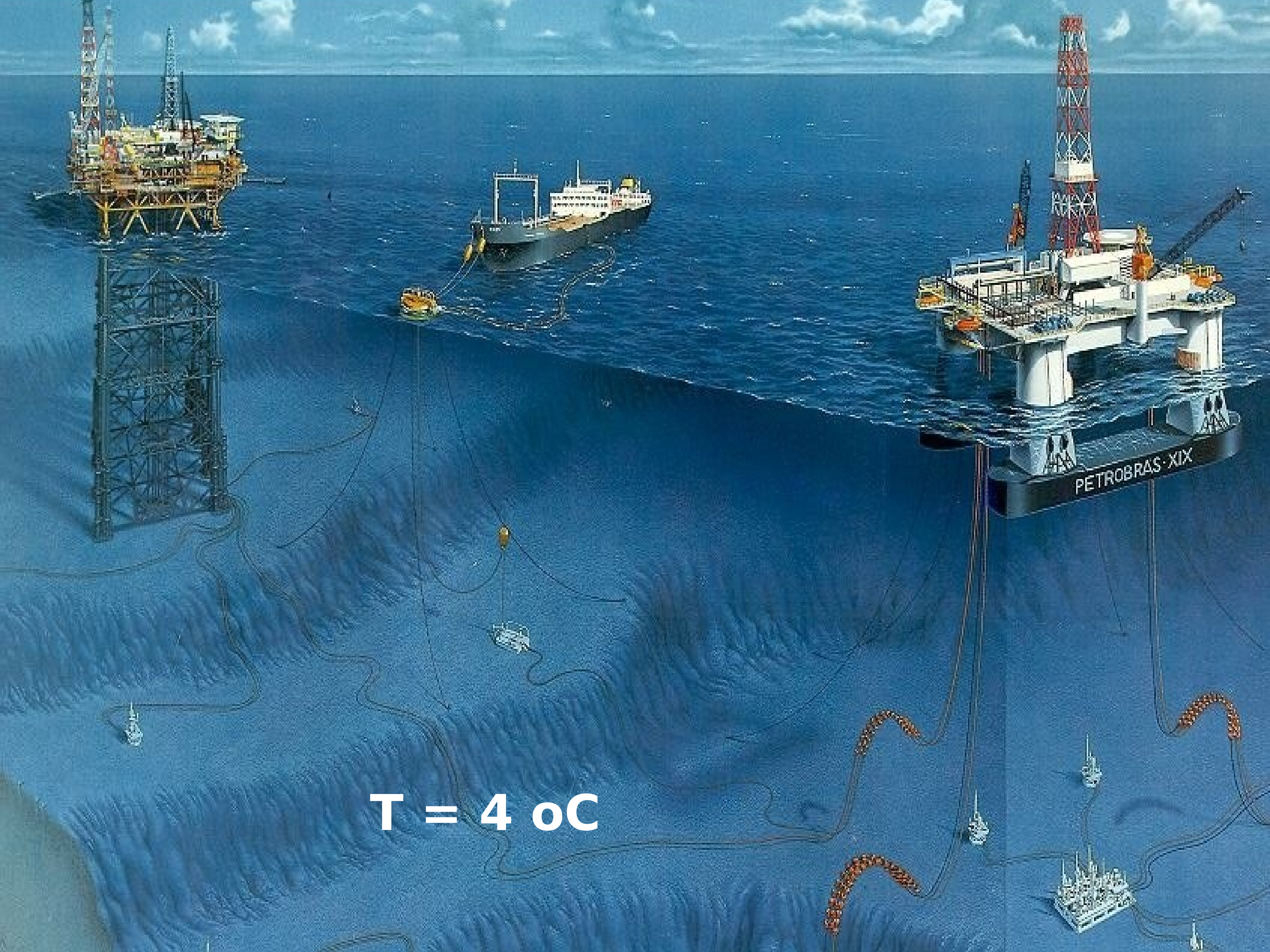


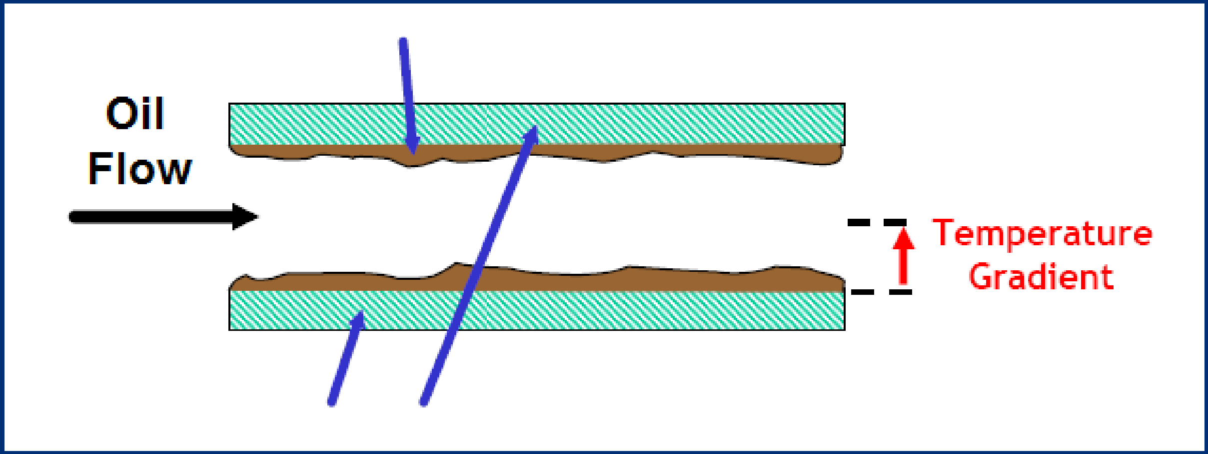
Petroleum: complex mixture of paraffins, aromatics, naftenes, resins, asfaltenes, etc...

T = 50–70 oC

Formação de depósitos de parafina

Redução do fluxo, bloqueio de dutos, interrupção da produção


PETROBRAS · XIX
T = 4 oC

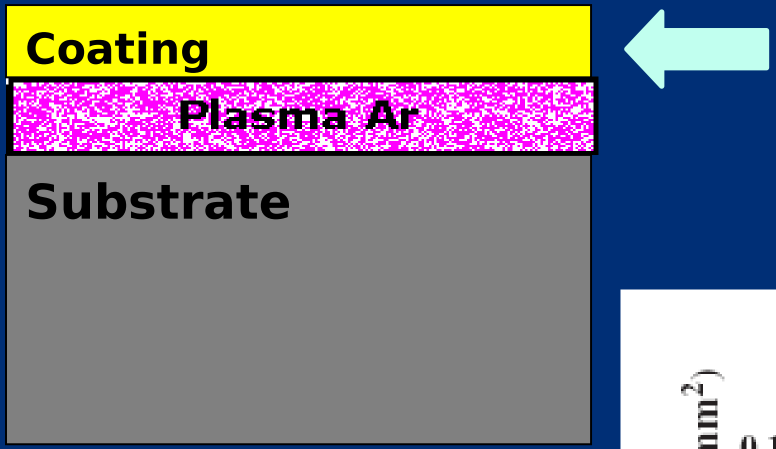


Mechanismos de transporte e deposição da parafina:

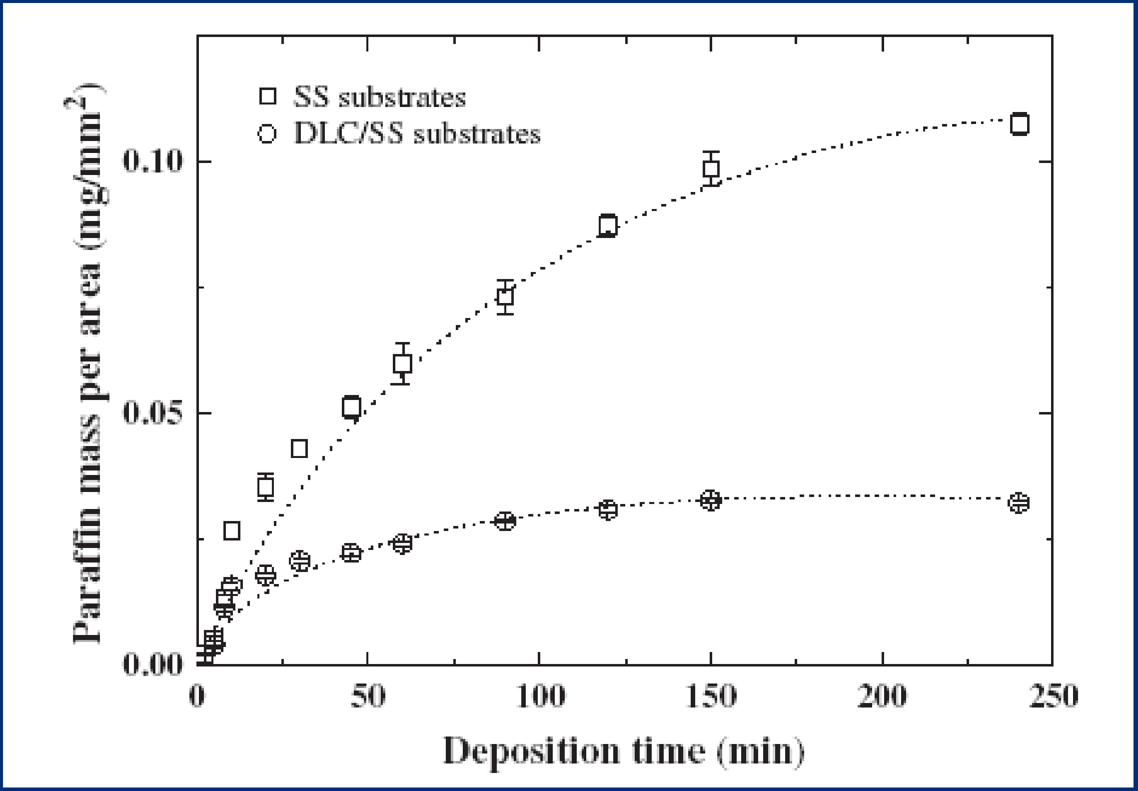
- **Difusão Molecular**
- **Movimento Brownian**
- **Gravidade**

Parametros Importantes:

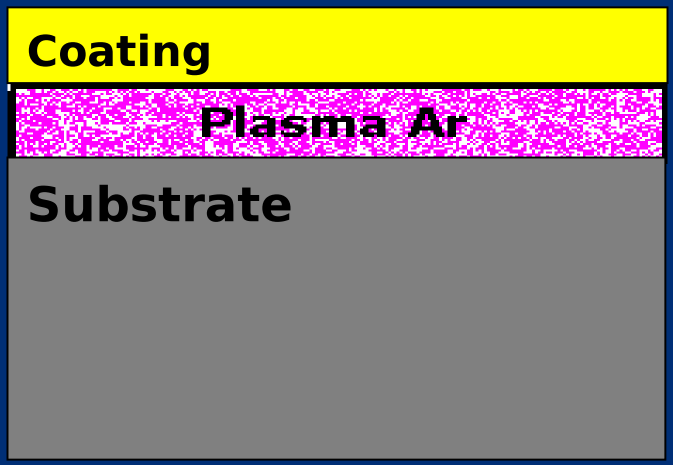
- **Temperatura**
- **Pressão**
- **Fluxo**
- **Fluído multifásico**

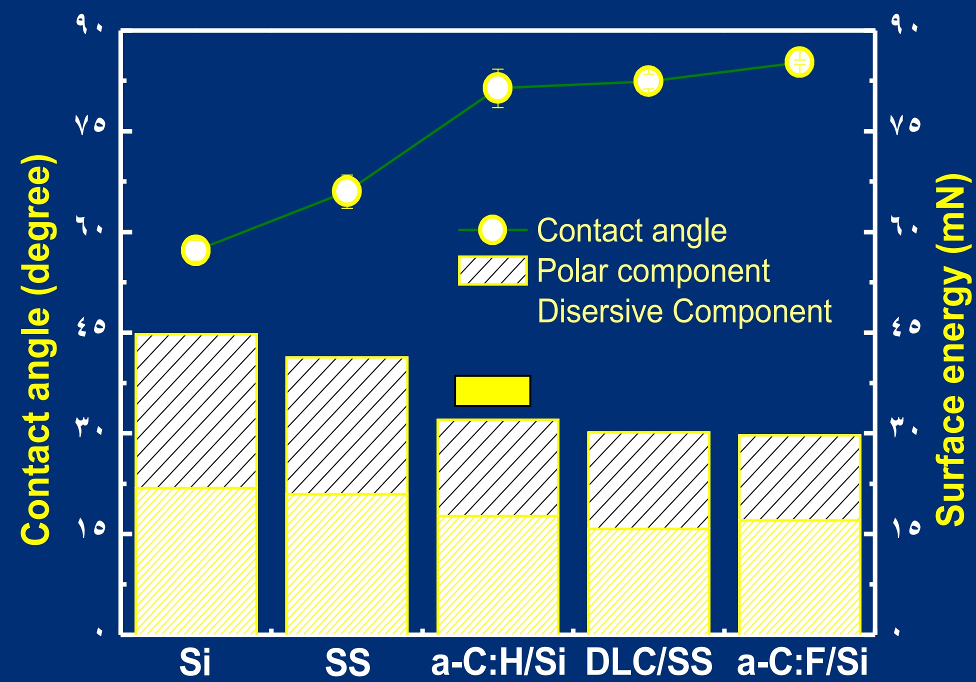


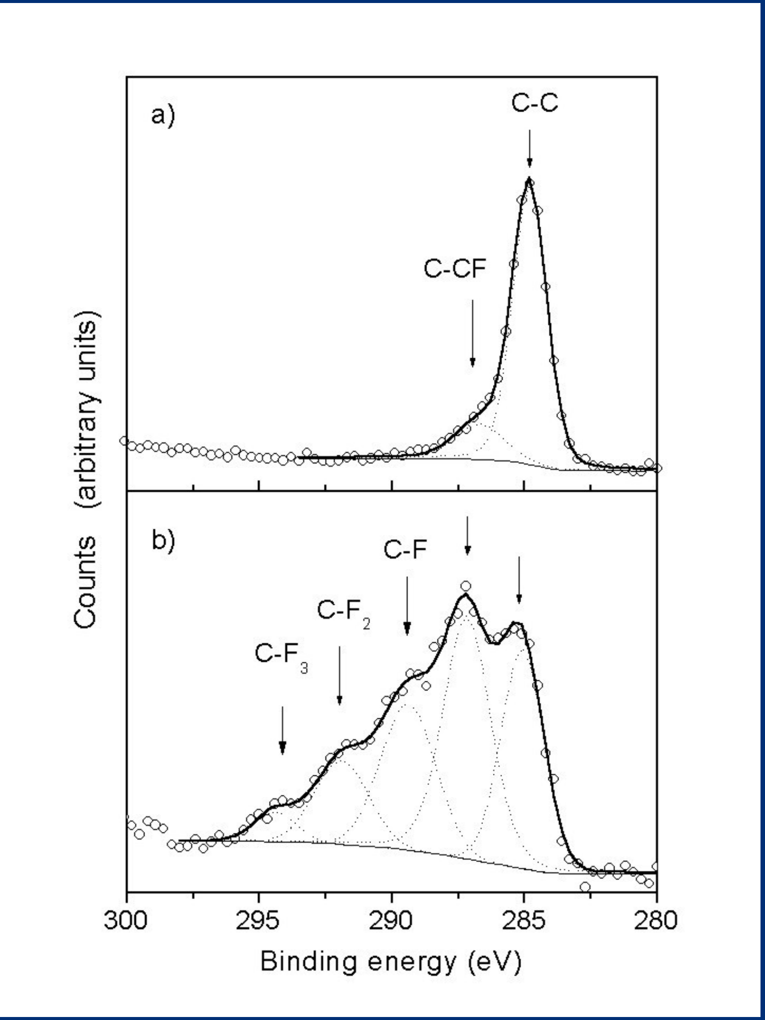
a-C:H, rf-PECVD, CH_4



M.E.R. Dotto et al, Surface and Coating Technology, 200 (2006) 6479


Coating
Plasma Ar
Substrate

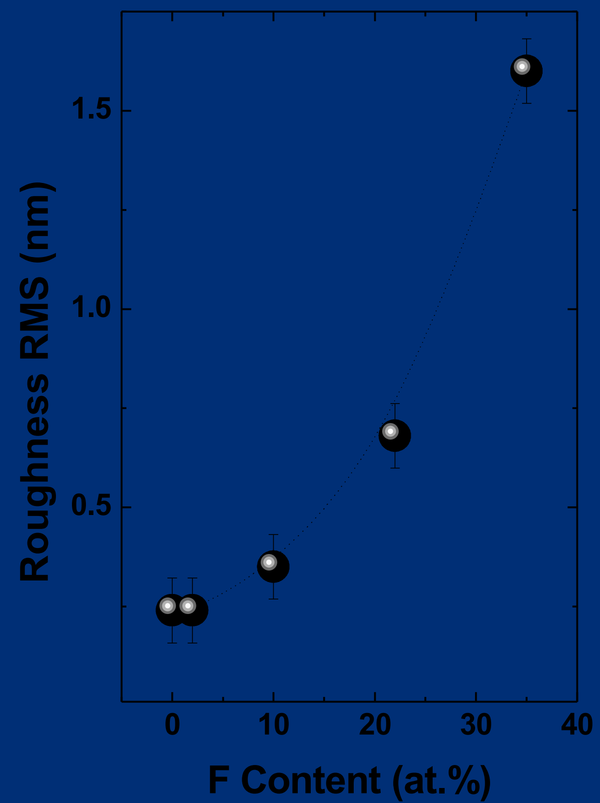

Contact angle (degree)
Surface energy (mN)
٠
١٥
٣٠
٤٥
٦٠
٧٥
٩٠
Contact angle
Polar component
Disersive Component
Si
SS
a-C:H/Si
DLC/SS
a-C:F/Si



F = 10 at.%

F = 35 at.%

XPS



Ângulo de contato e rugosidade

Dureza

L.G. Jacobsohn et al., Diamond and Related Materials, 12 (2003) 2037

Amostra: DLC depositado por rf-PECVD usando acetileno:

P= 3 Pa ; Vb = -350V H = 20 GPa

= 1.4 x 1023 at/cm3

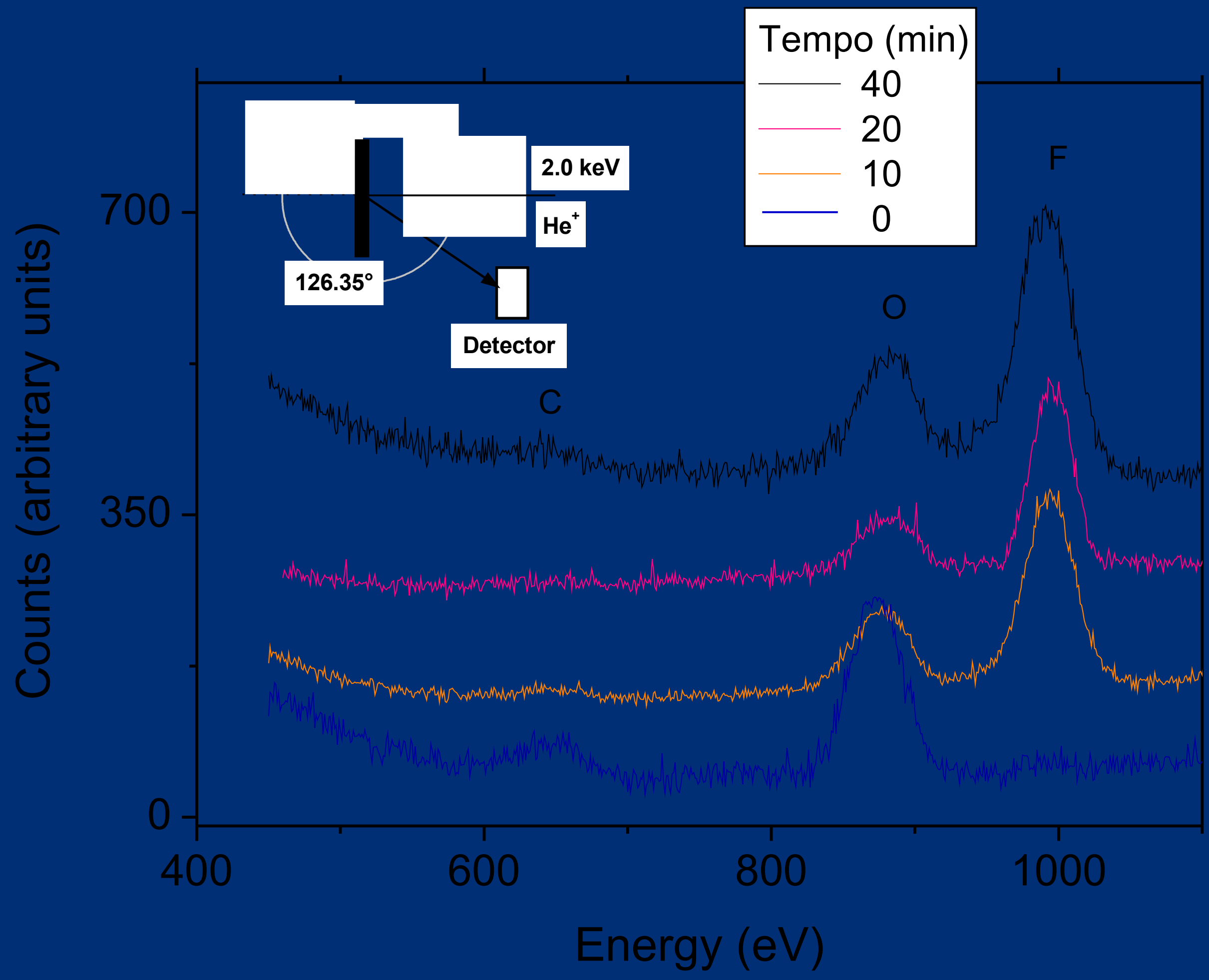
Condiçıes do tratamento por plasma

Atmosfera: CF4 a 3 Pa

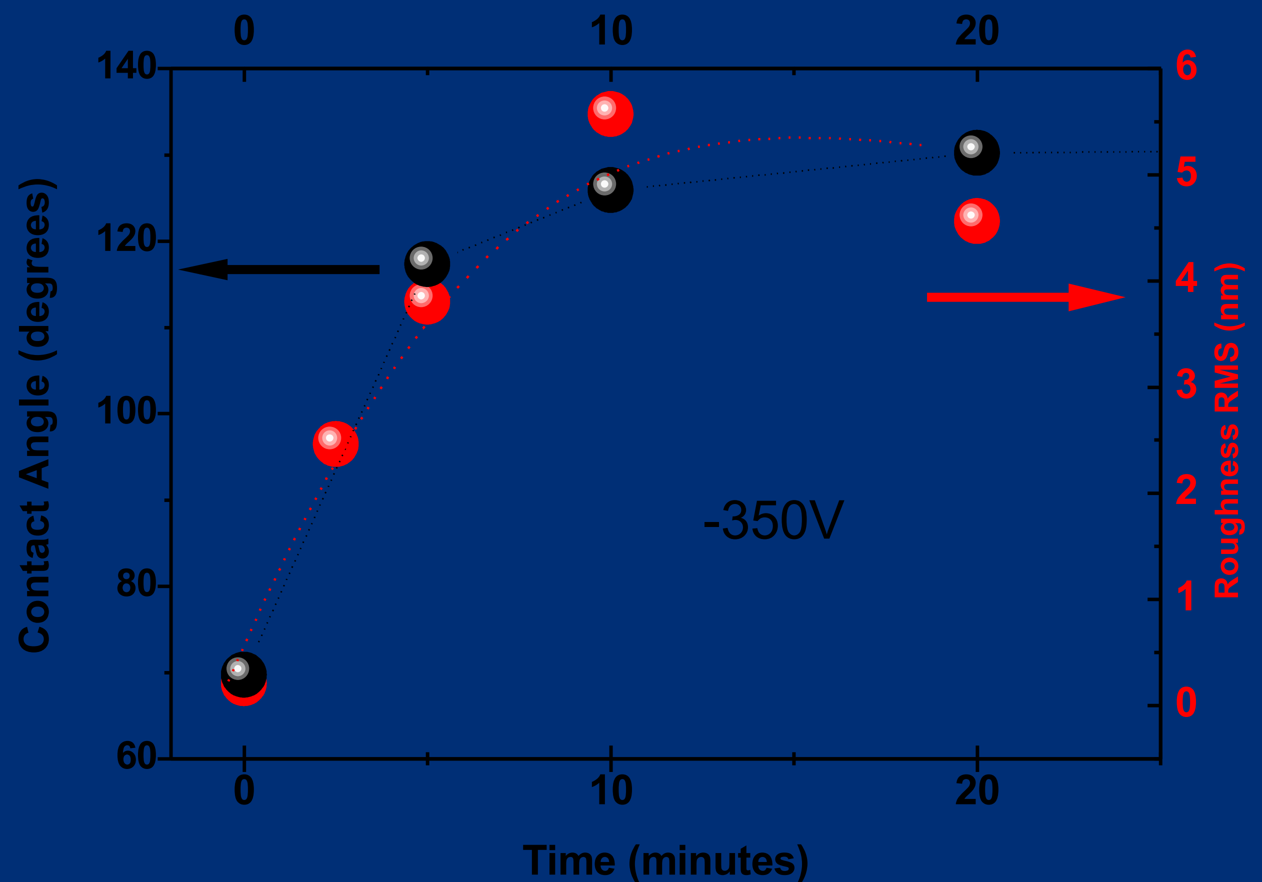
Tensão de auto-olarização: -100V ô -600V

Tempo: 5 minutos a 3 horas

M.E.H. Maia da Costa et al, Diamond and Related Materials (submitted)

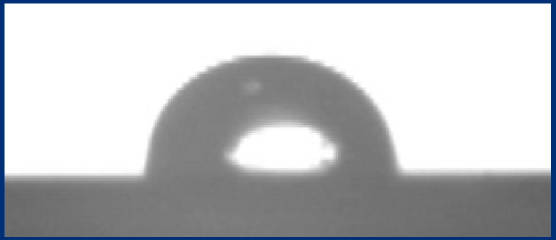


LEIS Spectra obtained from samples treated at -350V

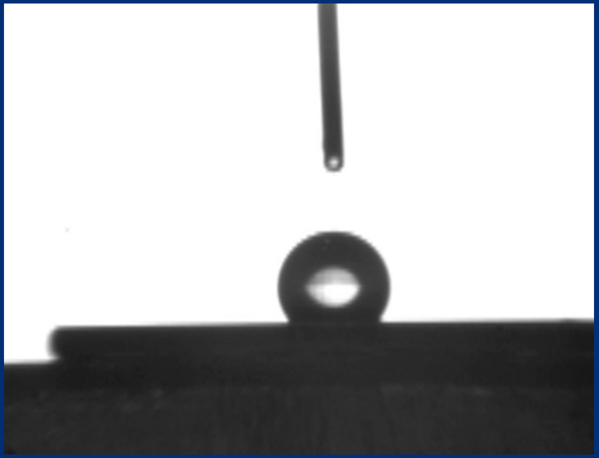


Contact angle and roughness obtained from samples treated at -350V

Revestimentos Hidrofóbicos



Filmes de carbono-fluor



Filmes DLC tratados por plasma de CF_4

Nanotubo de carbono

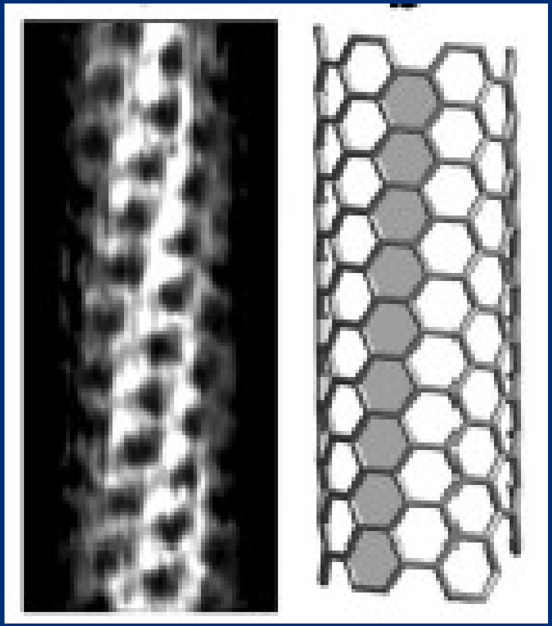
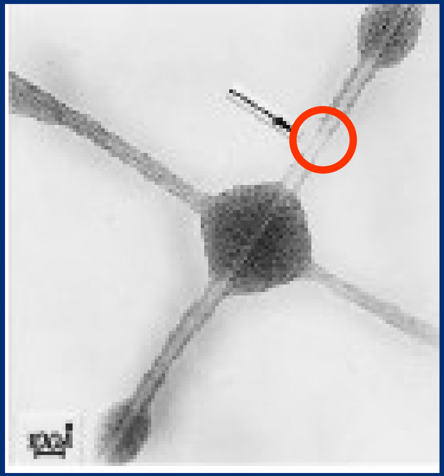
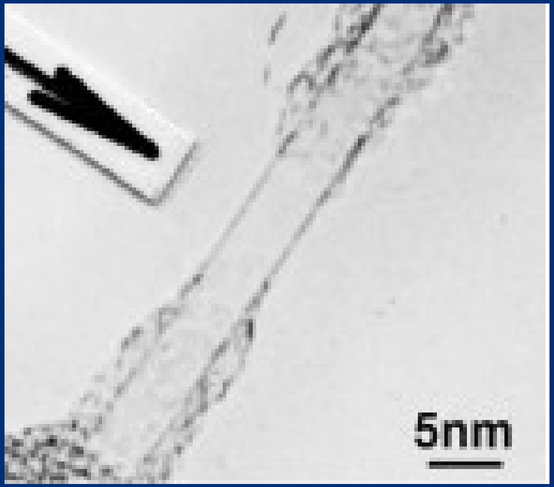


Imagem obtida por STM



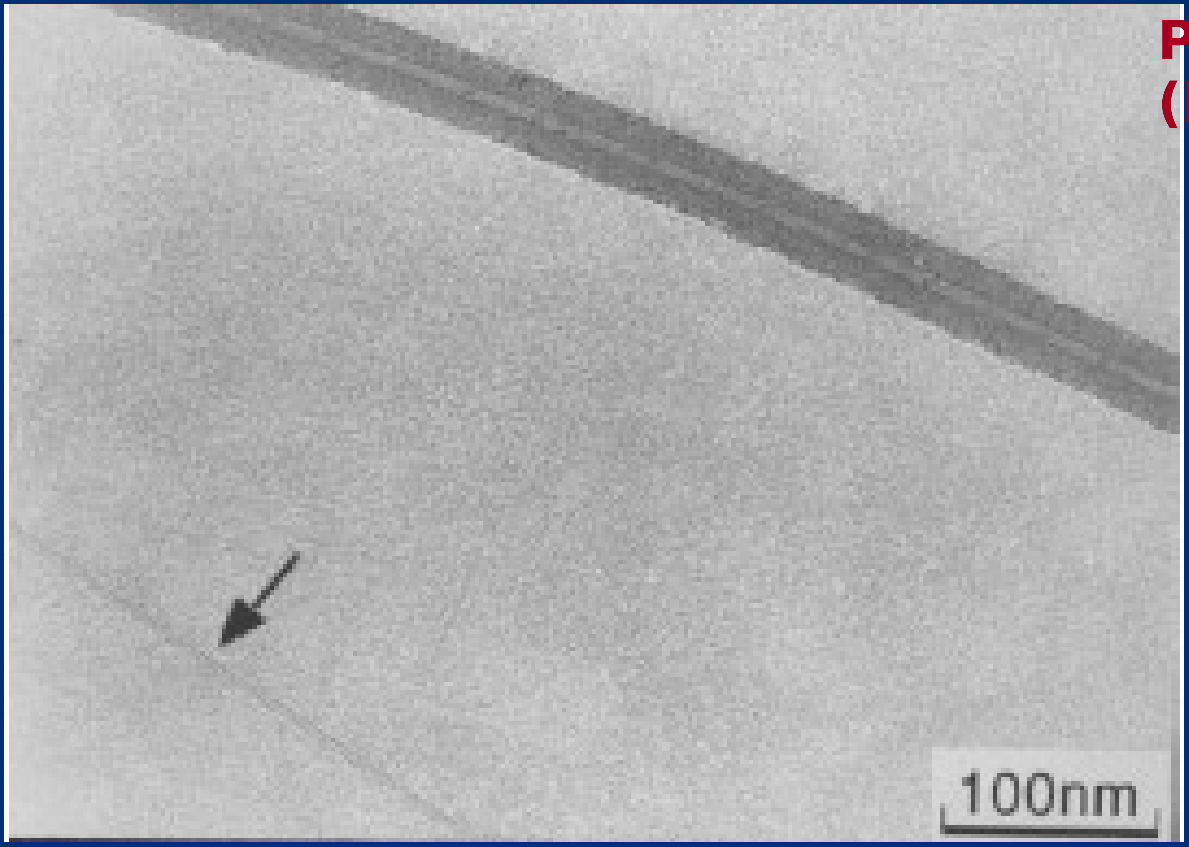


Carbono amorfo

Fibras de carbono produzidas por pirólise de benzeno e ferroceno a 1000o C.

A. Oberlin, M. Endo, T. Koyama, J. Cryst. Growth 32 (1976) 335

1985: Descoberta dos fullerenos; H.W. Kroto, J.R. Heath, S. C. O. Brein, R.E. Smaley, Nature 318 (1985) 162.

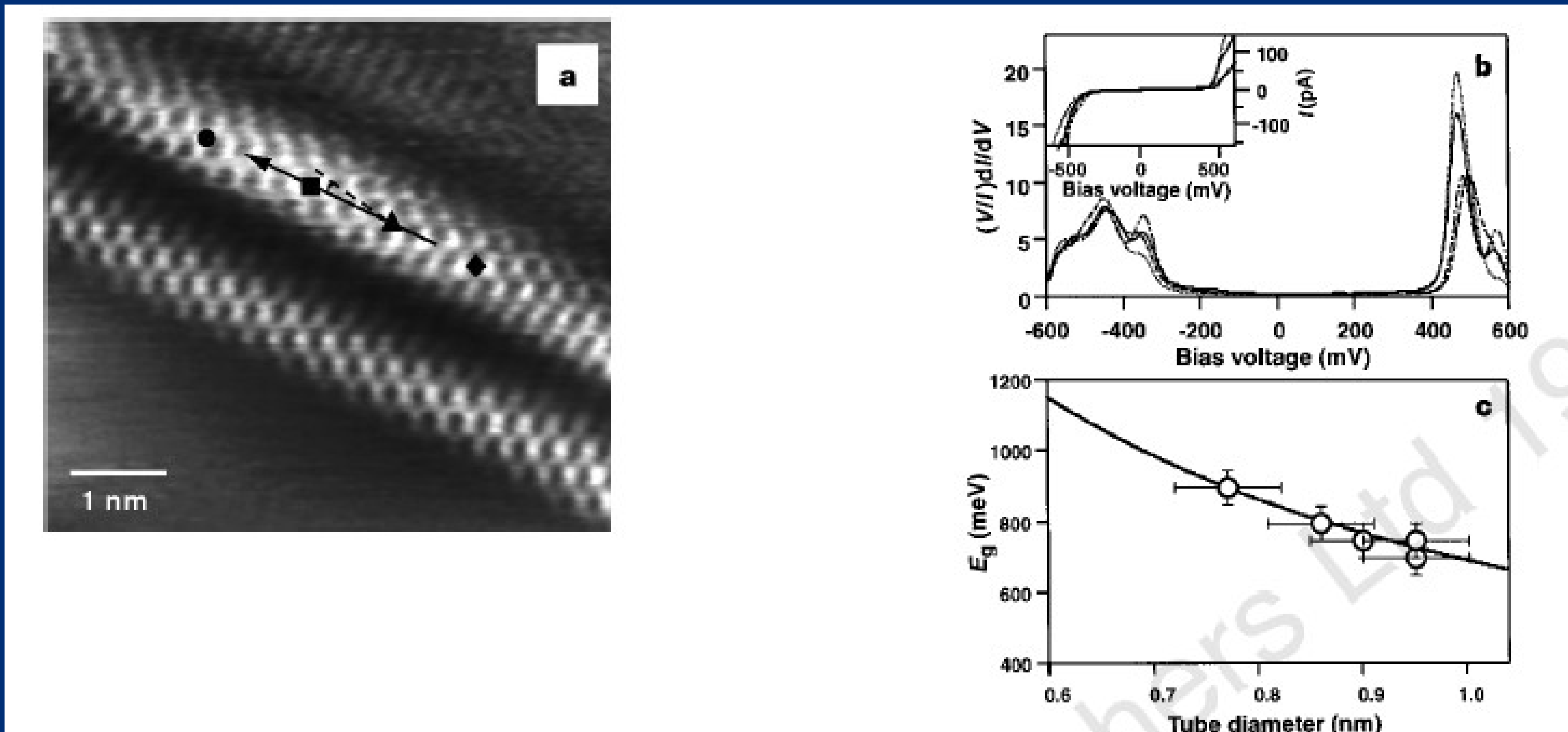


Paredes múltiplas (MWNT)

Parede simples
Single wall
(SWNT)

1991: Observação dos nanotubos de carbono *multi-wall* por S. Ijima, Nature 354 (1991) 56.

Propriedades elétricas



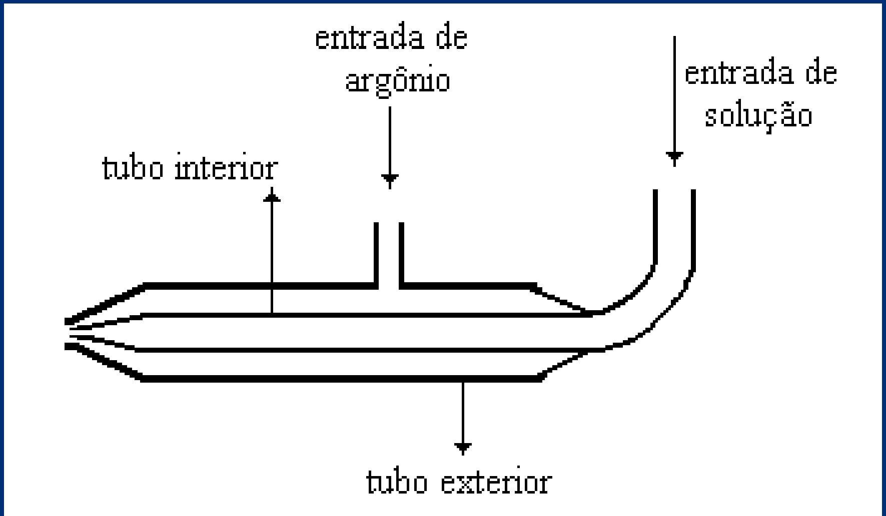
gem de nanotubo semicondutor isolado em uma superfície de Au, condutância,
p de energia em função do diâmetro do tubo.

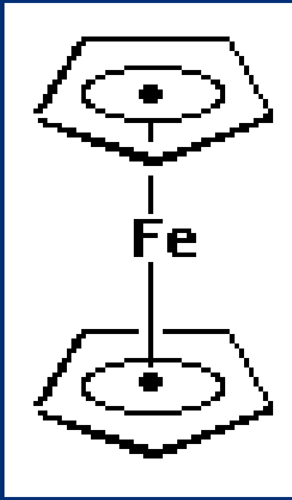
Desafio:

Produzir nanotubos de modo controlado:

- **diâmetro.**
- **semicondutores ou metálicos.**
- **dopagem (tipo n com N e tipo p com B).**

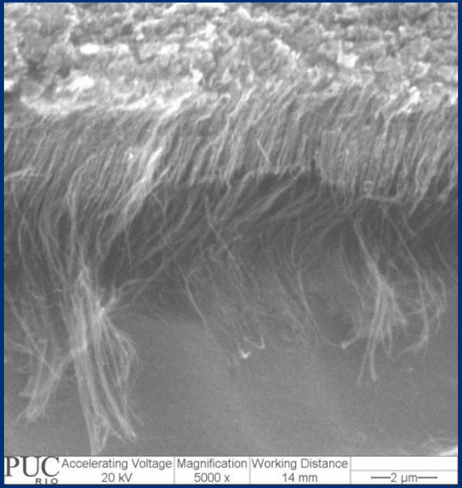
Spray pirólise

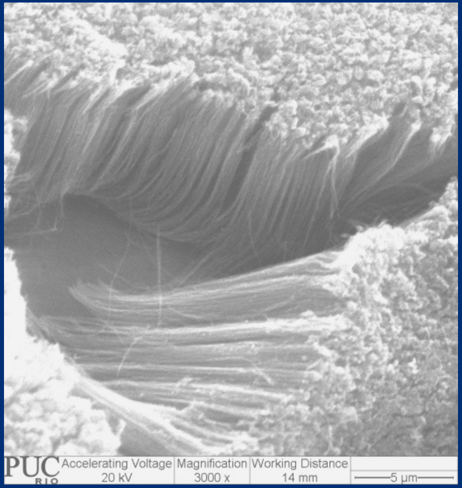


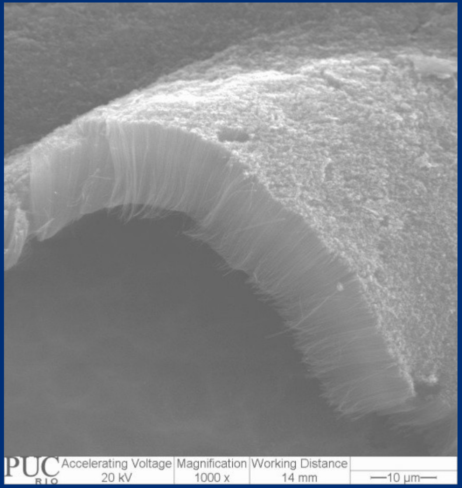


Tolueno e ferroceno

Antes do centro do forno

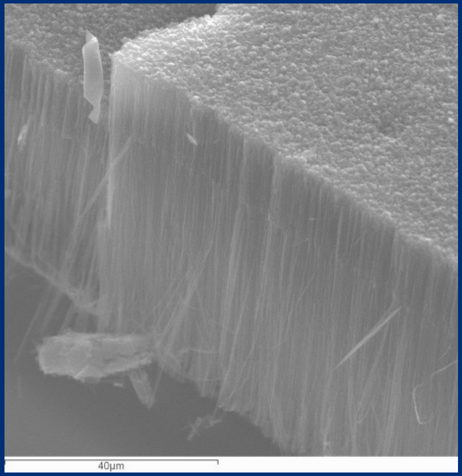


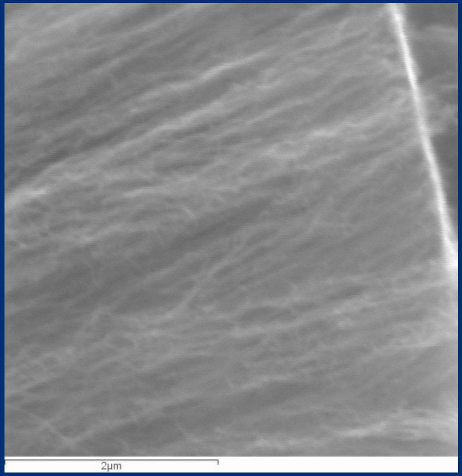


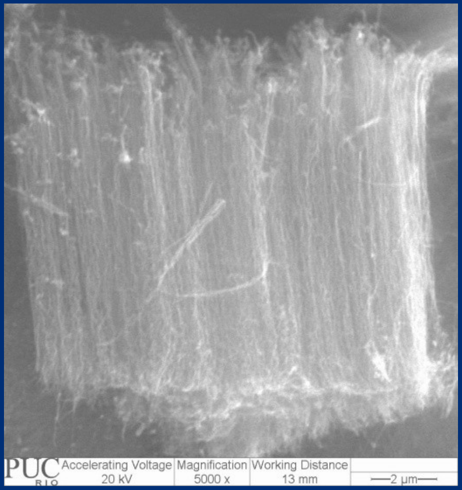


No centro

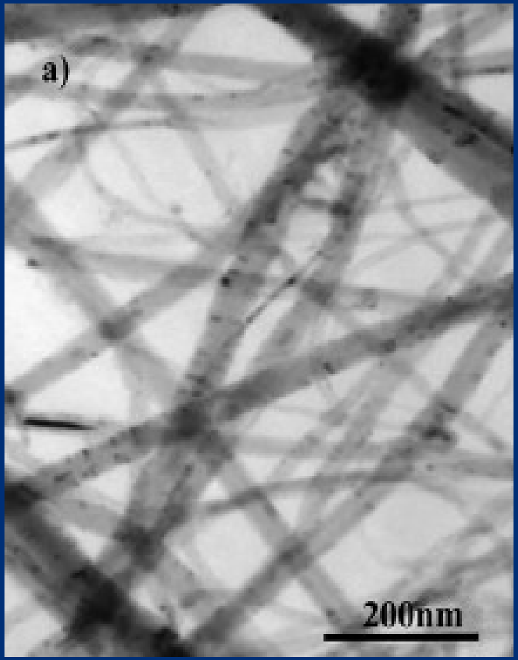
Depois do centro



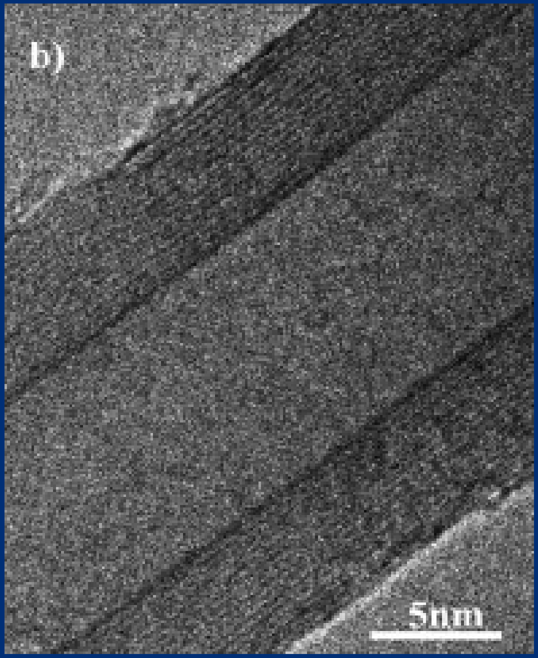




Nanotubos de parede múltipla

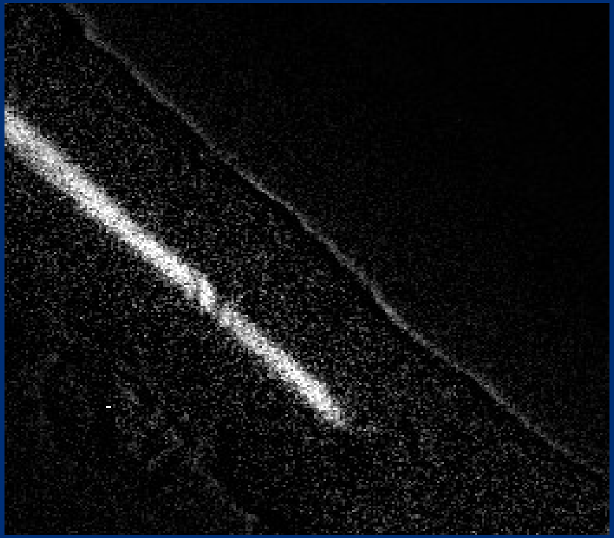


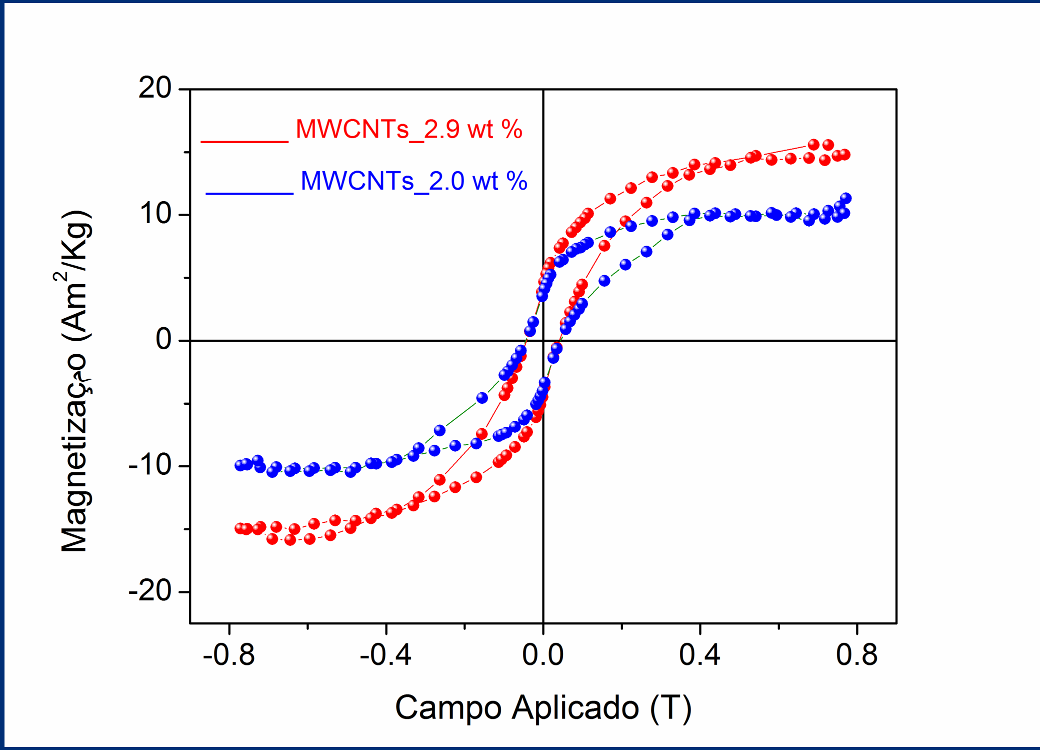
TEM



HRTE
M

Precursores: ferroceno e tolueno (C_7H_8)
Temperatura: 800oC

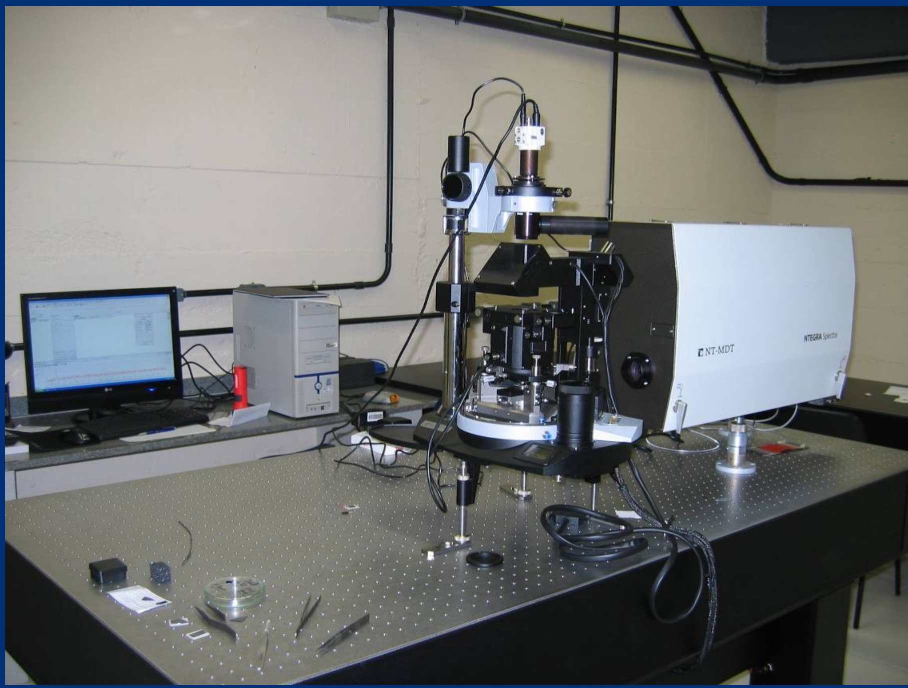


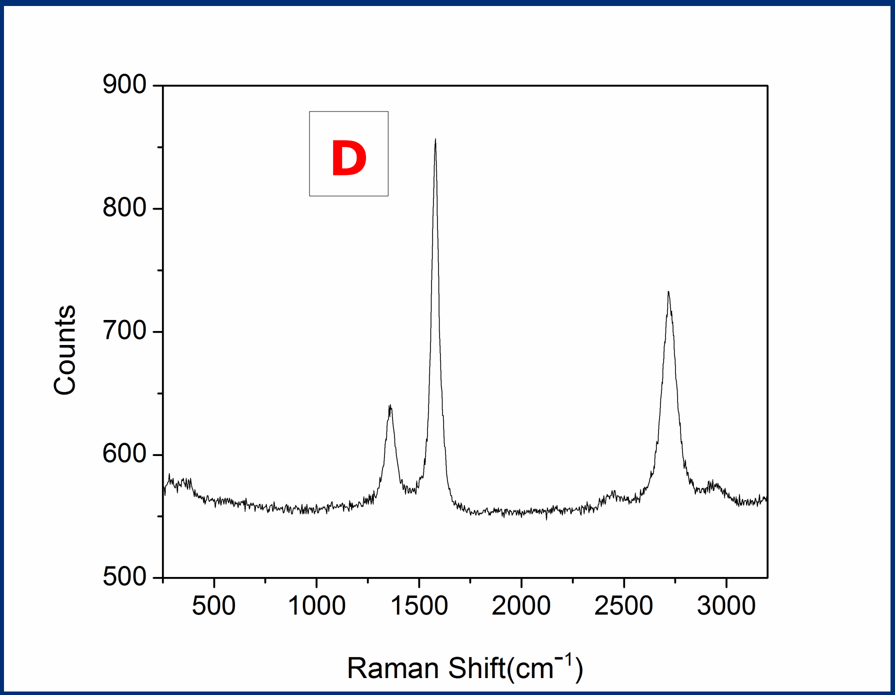


MWCNTs_2.9 wt %
MWCNTs_2.0 wt %
Magnetização (Am²/Kg)
Campo Aplicado (T)
20
10
0
-10
-20
-0.8
-0.4
0.0
0.4
0.8

Fe

G

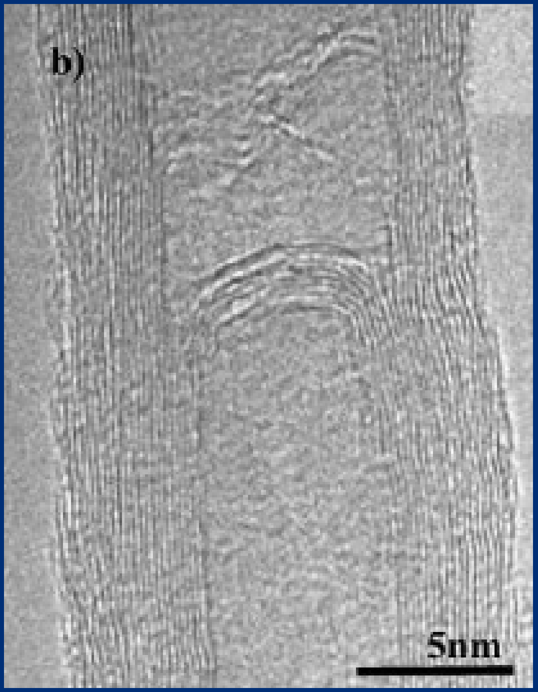




Espectro Raman de um MWNT depositado por spray-pirólise a partir do touleno e obtido no Raman-AFM da NT-MDT

Nanotubos CN –paredes múltiplas

TEM

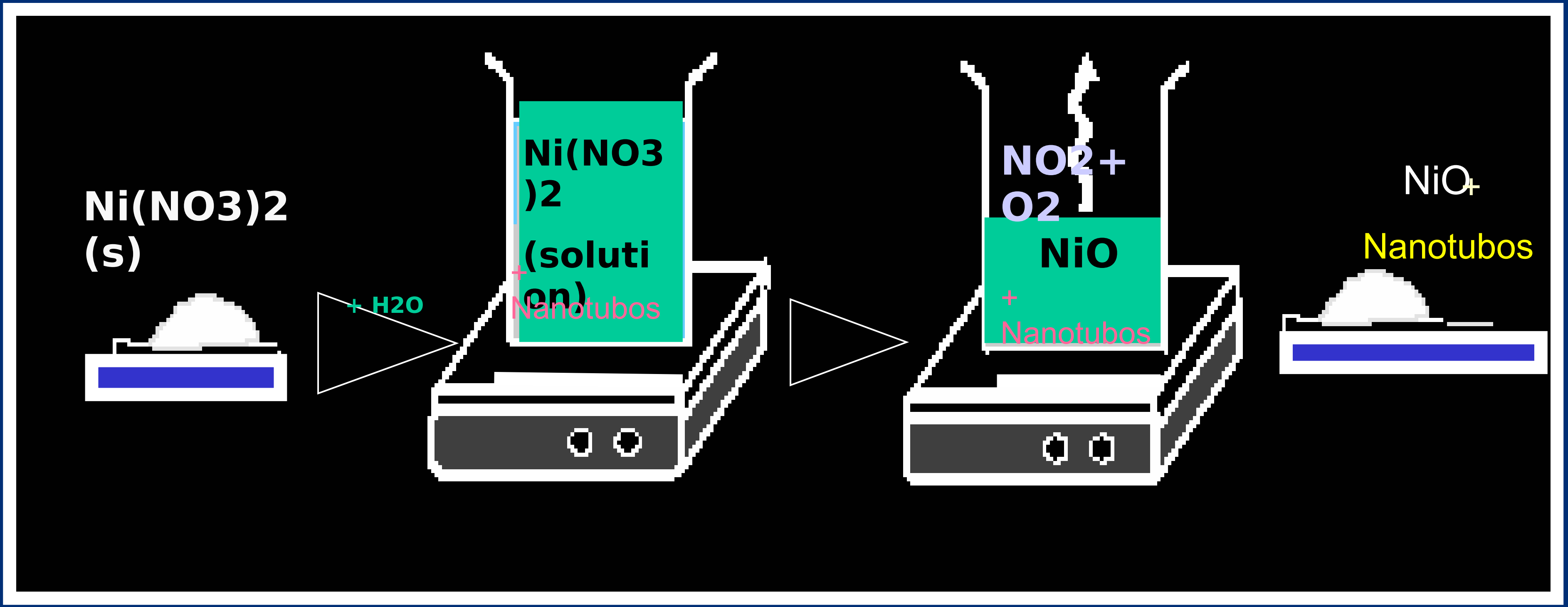


HRTEM

Precursores: ferroceno e benzilamina (C_7H_9N)
Temperatura: 850oC

Decoração com nanopartículas metálicas:

1) dissociação de Ni(NO3)2 na presença de MWNT para a sintese de nanopartículas de NiO.

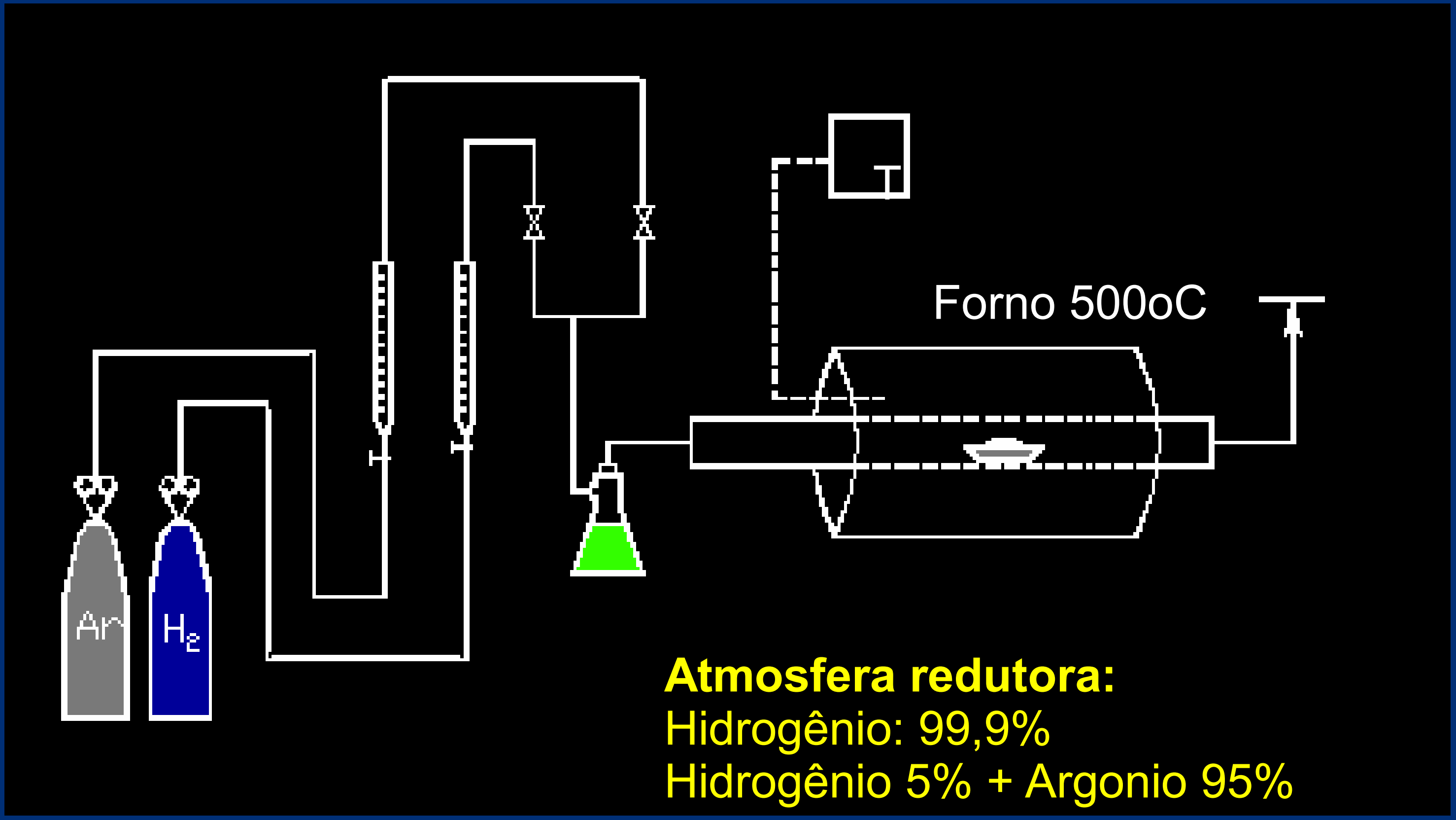


2Ni(NO3)2 (s) 2 NiO(s) + 4 NO2(g) + O2(g)

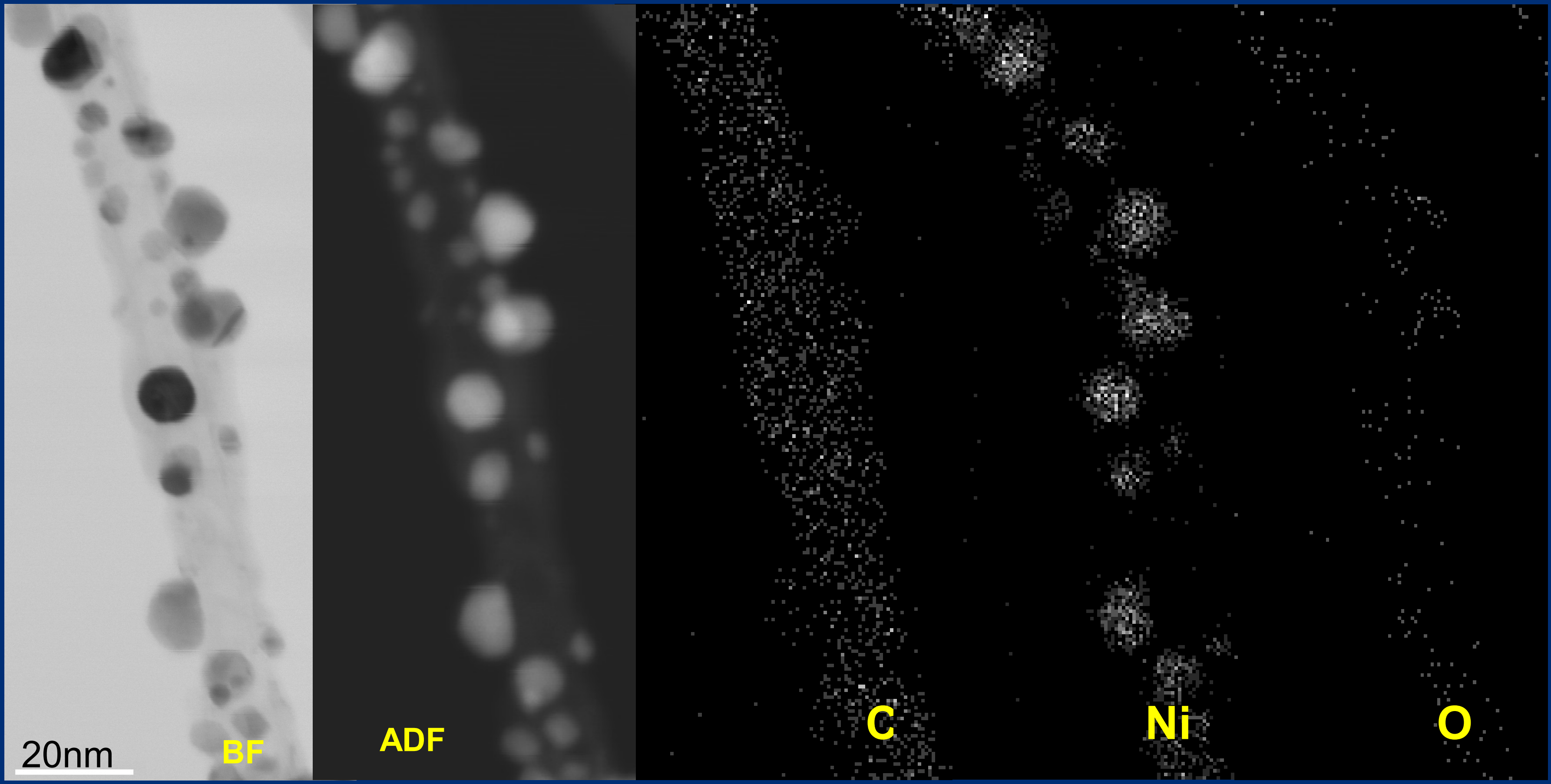
Nanotubos

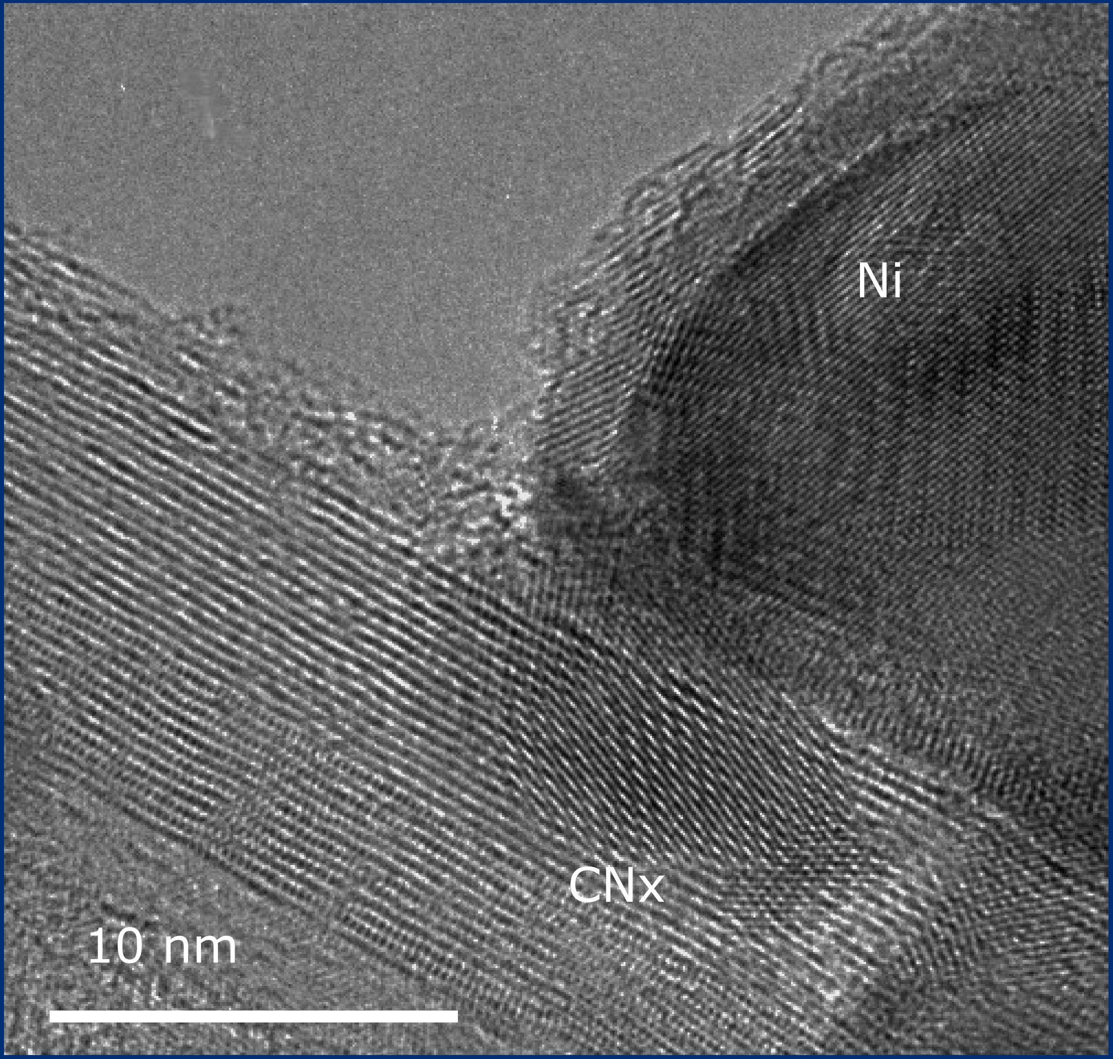
2) Arranjo para redução de óxidos:

$$NiO + H_{2(g)} \longrightarrow Ni + H_2O$$



STEM, medidas feitas no Arizona

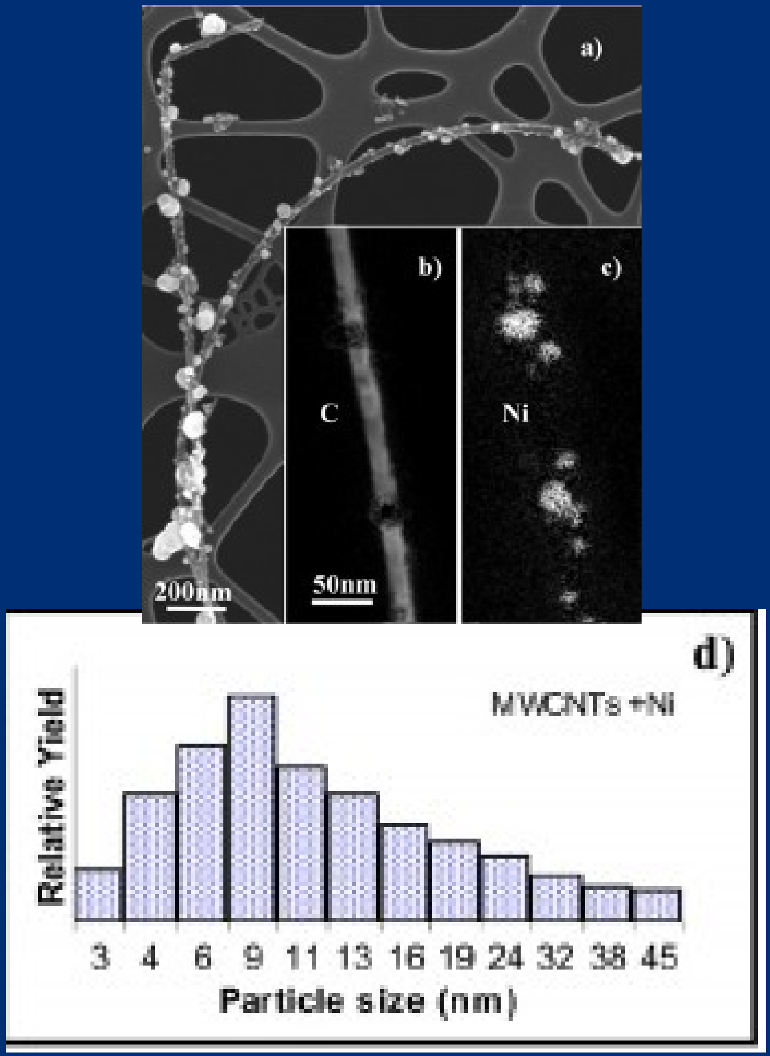




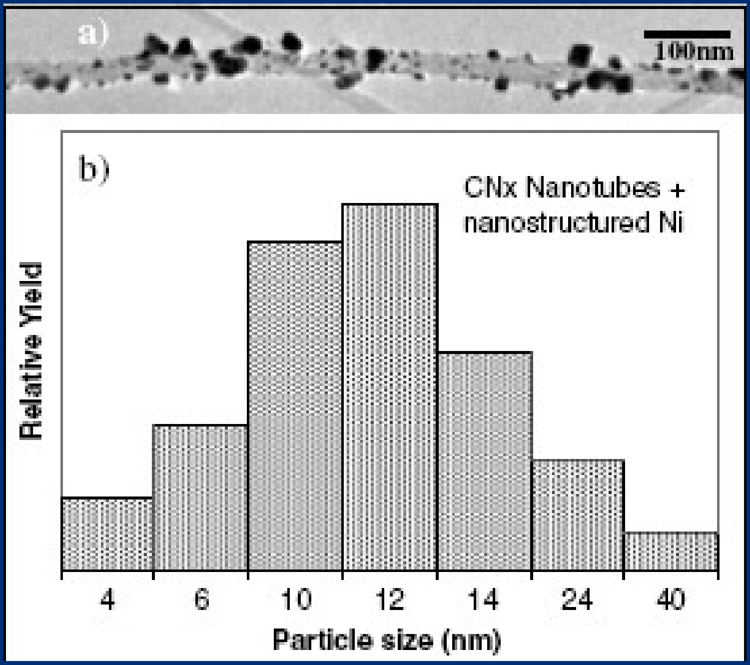
HREM

Imagem obtida em um TEM JEOL 4000EX operando a 400kV.

MWNT

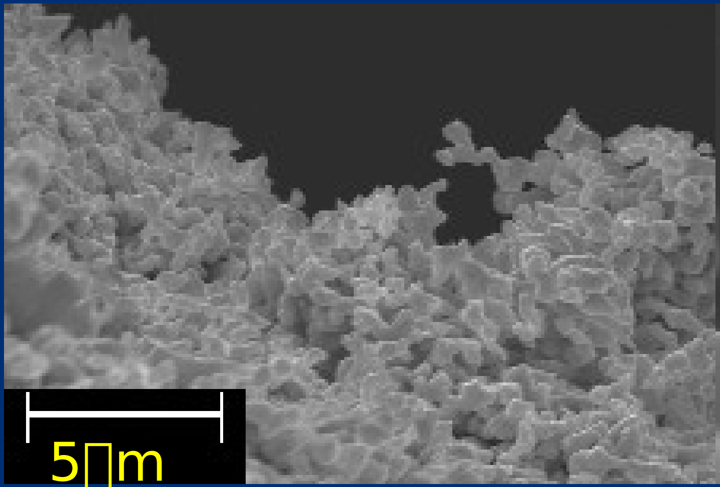


CNx nanotubos



P. Ayala *et al*: Chem. Phys. Lett. **431** (2006) 104

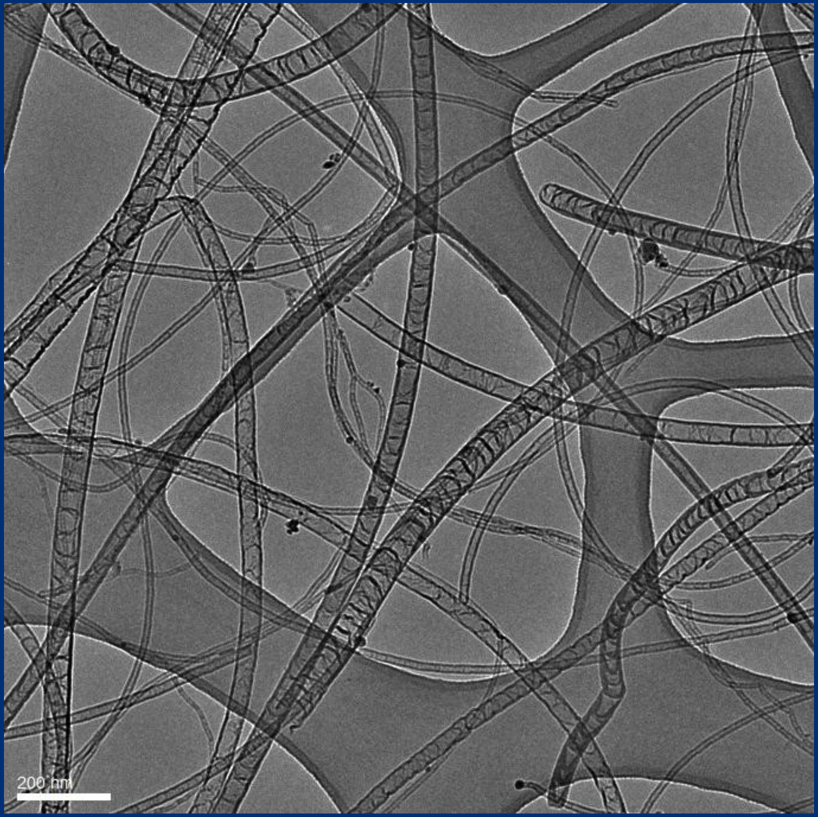
Pastilhas MWNT-Níquel

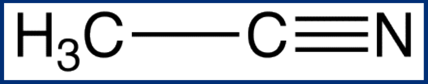


1 □

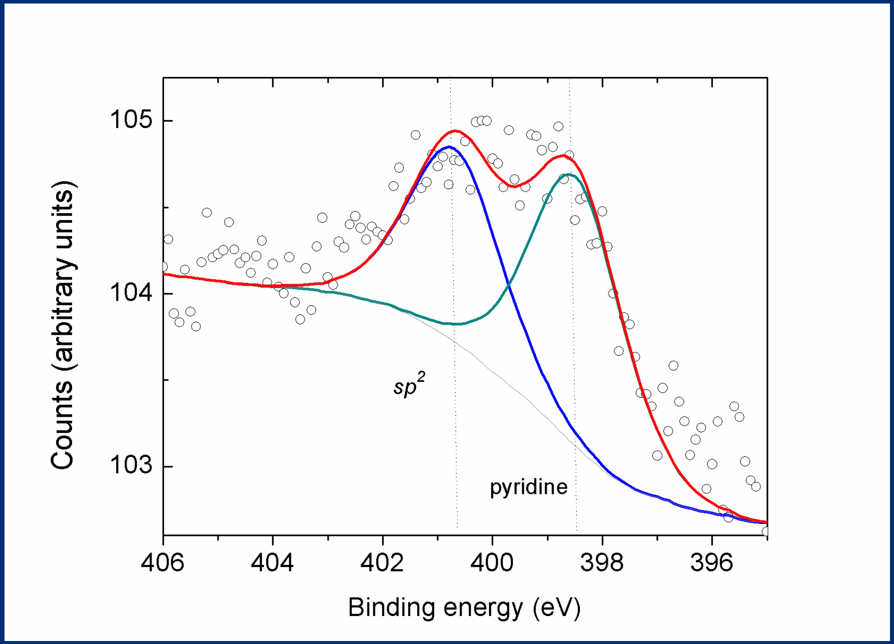
MEV dos pellets de Ni + CNT

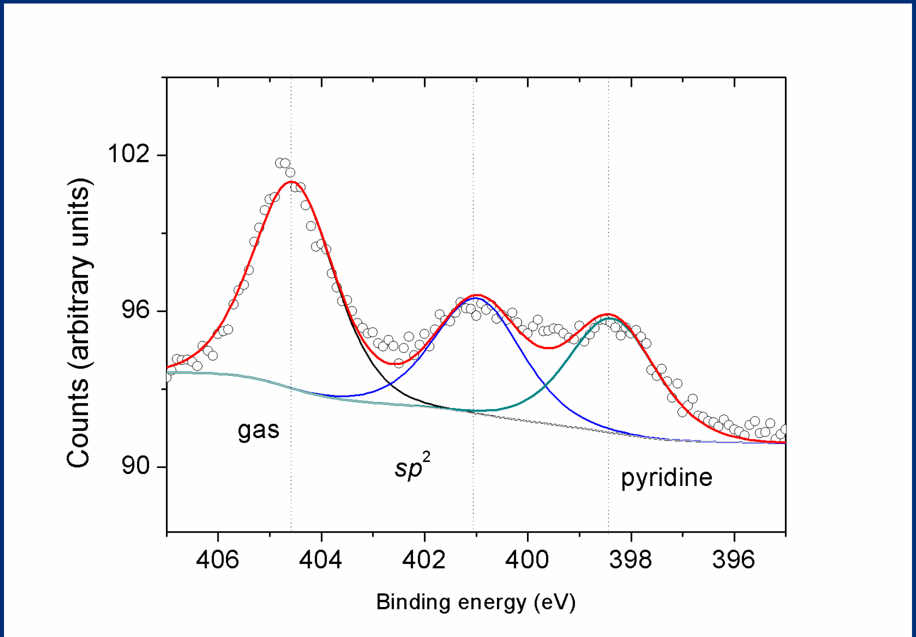
Análise por TEM de MWNT usando acetonitrila como precursor à temperatura de 850∫ C





nálise por XPS de MWNT usando tolueno e acetonitrila como precursore temperatura de 850∫ C

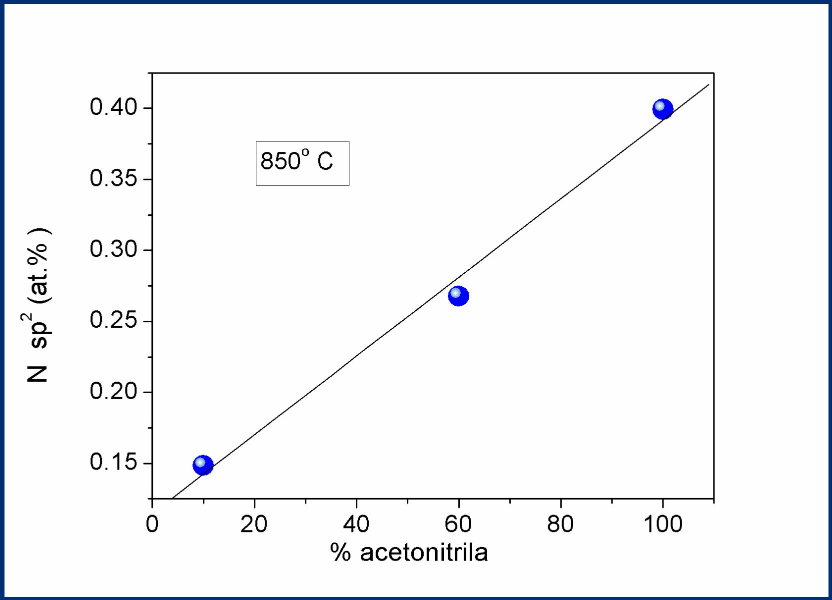


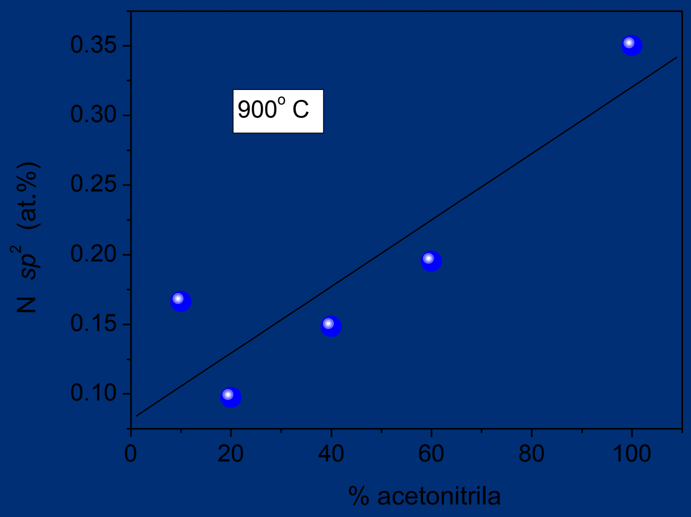


10% acetonitrila

100% acetonitrila

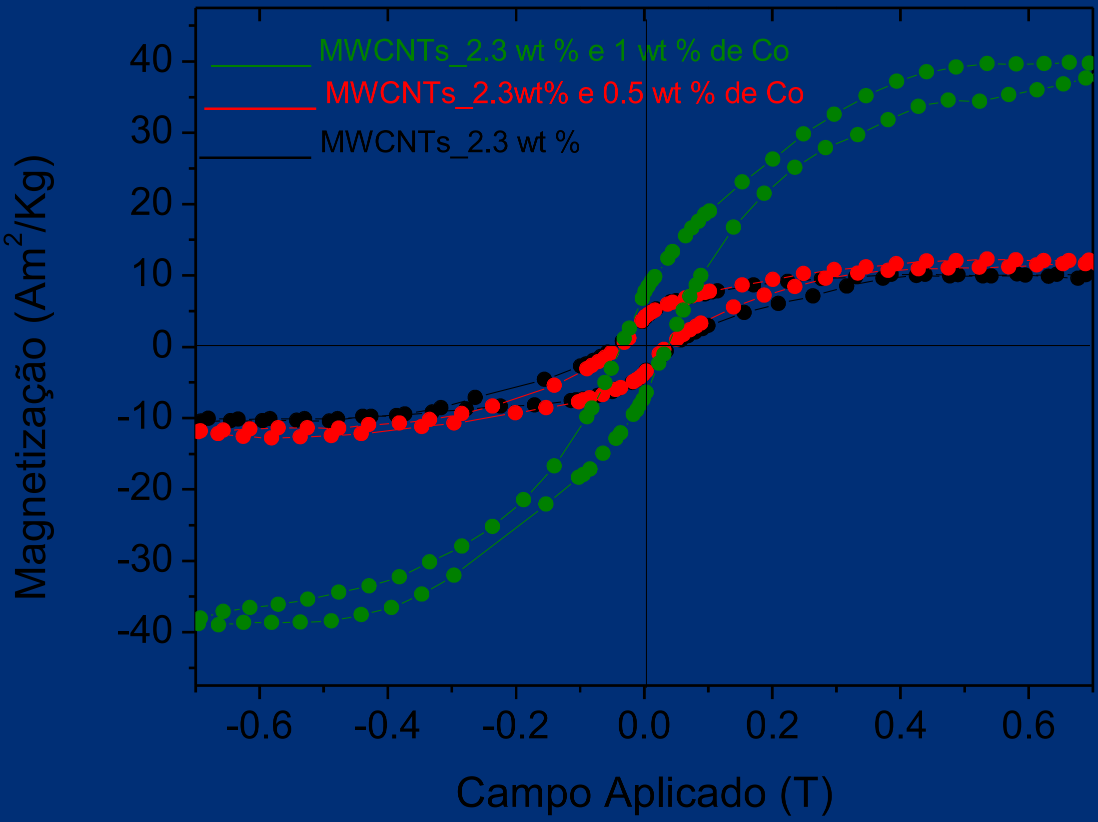
nálise por XPS de MWNT usando tolueno e acetonitrila como precursore

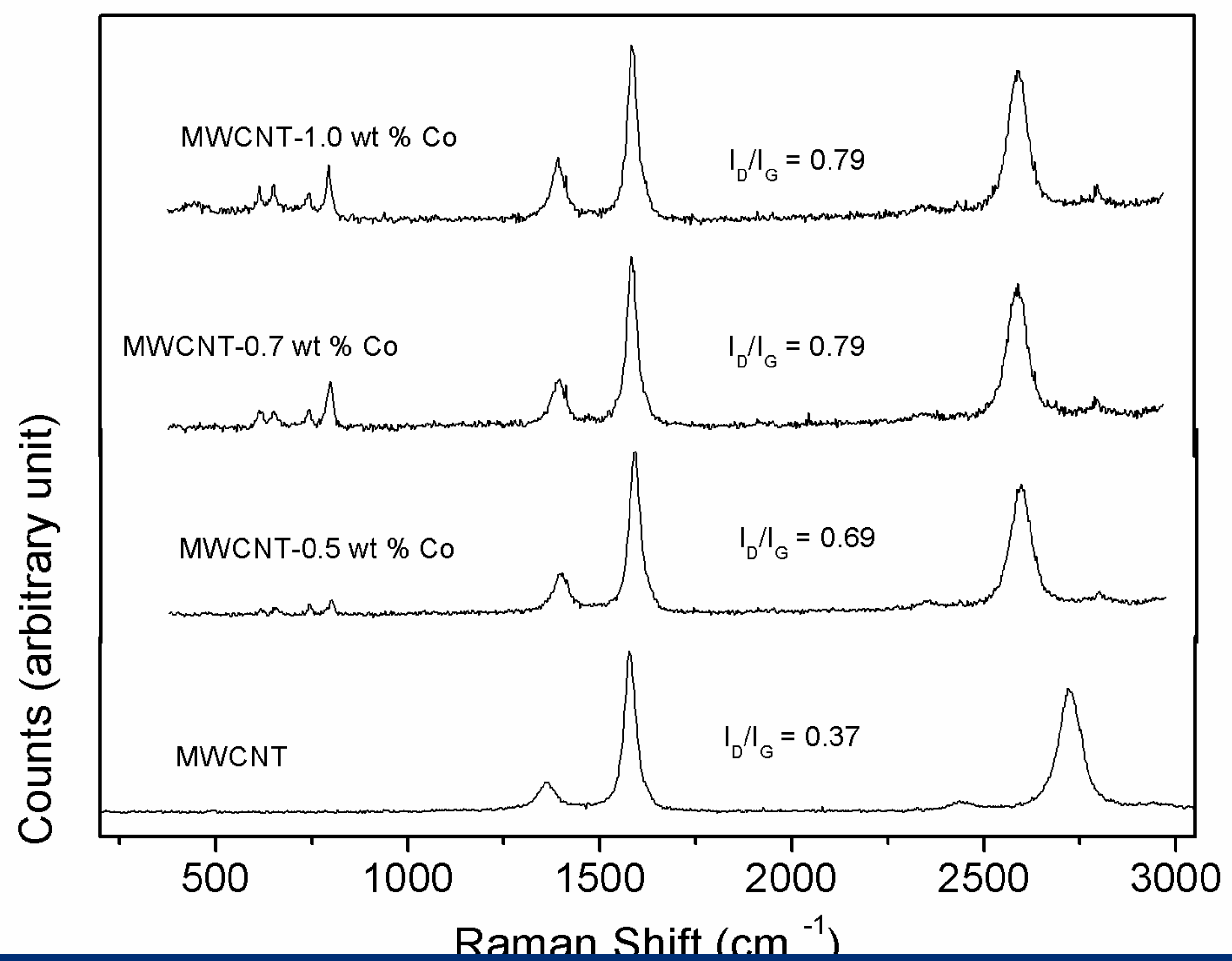


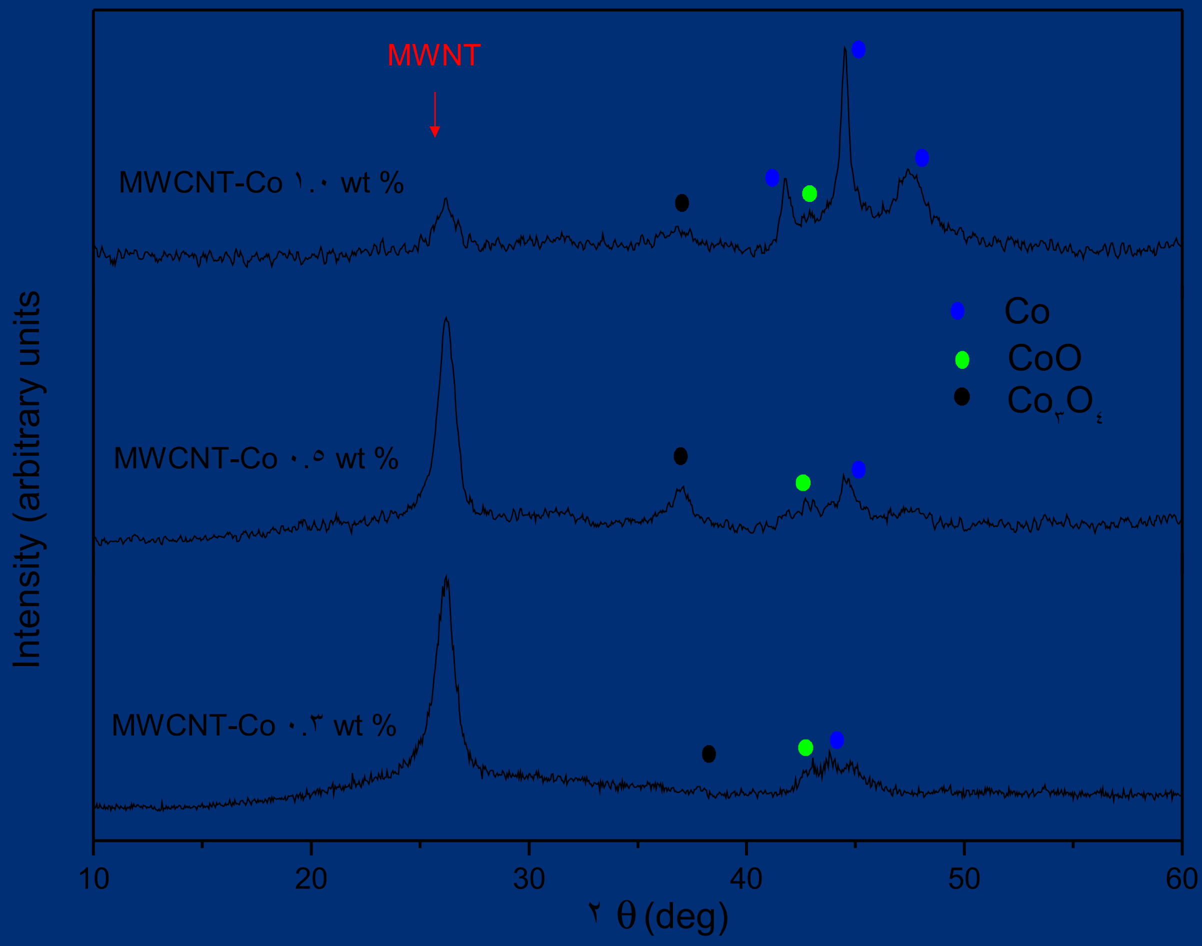


100% acetonitrila

Nanotubos funcionalizados com Cobalto

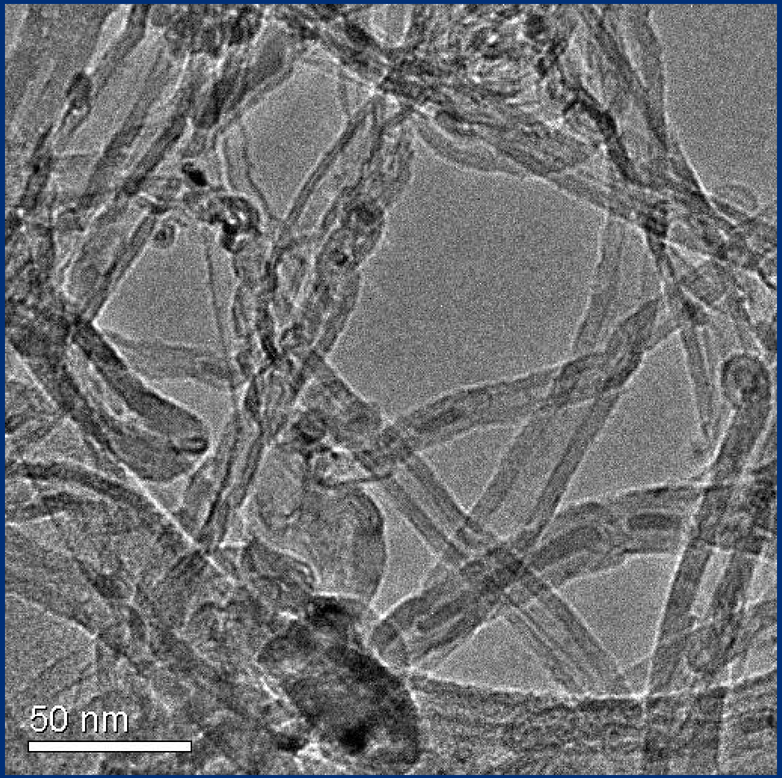


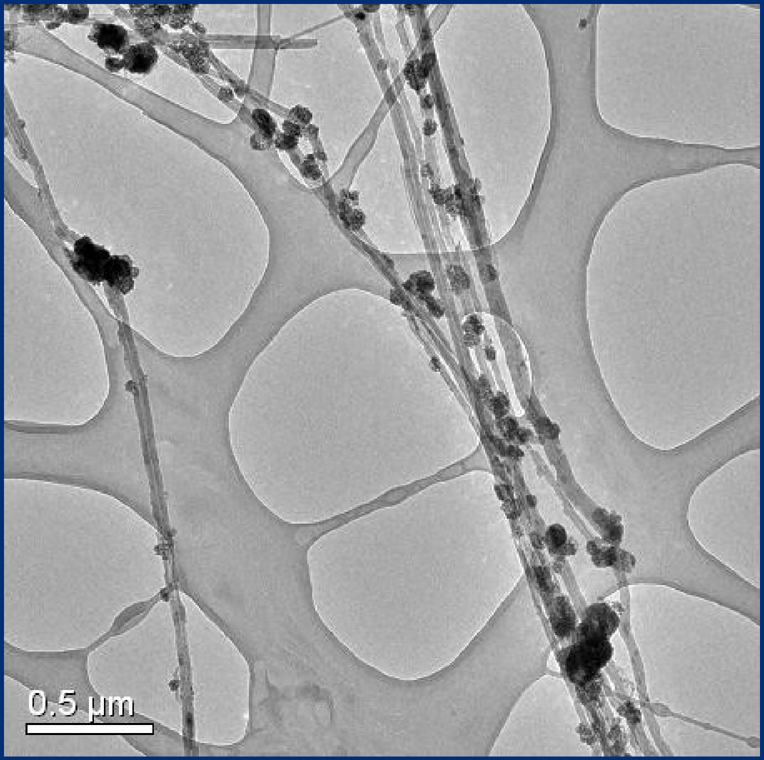

MWCNT-1.0 wt % Co
I_D/I_G = 0.79
MWCNT-0.7 wt % Co
I_D/I_G = 0.79
MWCNT-0.5 wt % Co
I_D/I_G = 0.69
MWCNT
I_D/I_G = 0.37
Counts (arbitrary unit)
500
1000
1500
2000
2500
3000
Raman Shift (cm $^{-1}$)



MWNT
MWCNT-Co ١.٠ wt %
MWCNT-Co ٠.٥ wt %
MWCNT-Co ٠.٣ wt %
Co
CoO
Co٣O٤
Intensity (arbitrary units
10
20
30
40
50
60
٢ θ (deg)

TEM measurements

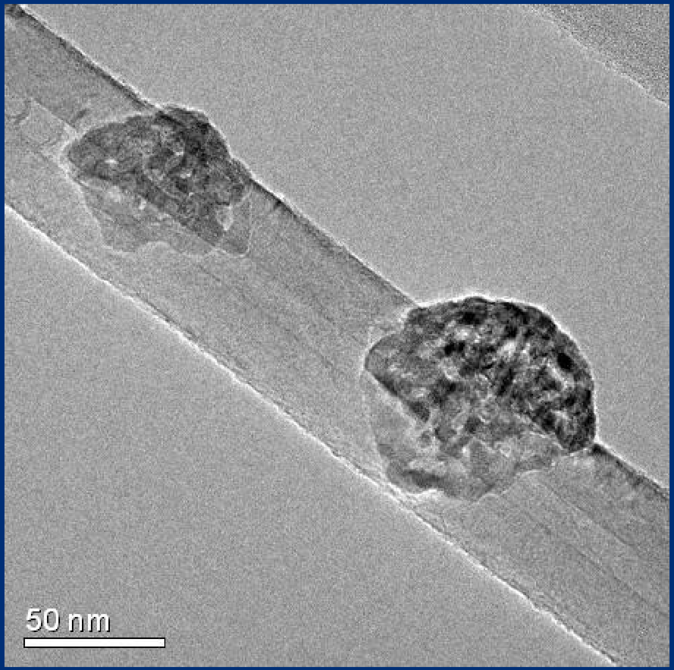


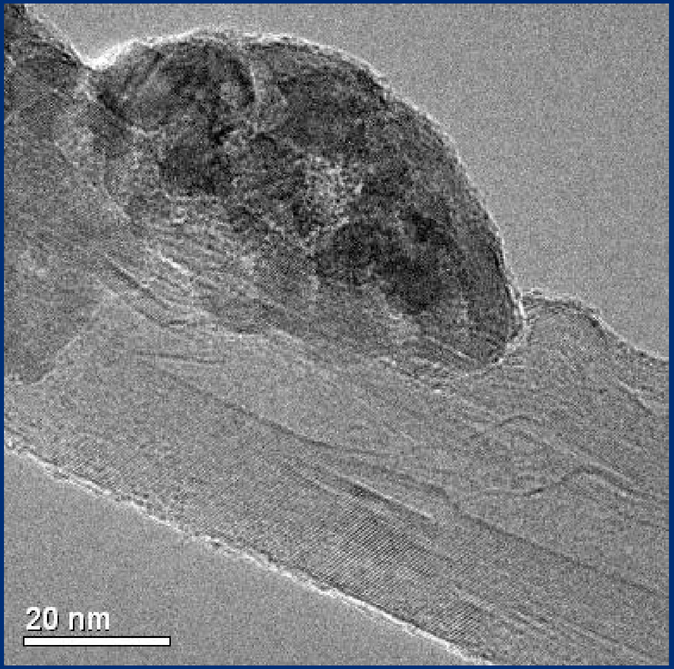


MWNT

MWNT com partículas de Co

damage





MWCNT-Co 0.5 wt %

Perspectivas na PUC-Rio

Com a chegada do FEG-SEM teremos uma boa infra-estrutura para trabalhar com materiais nanoestruturados: XPS-LEIS-Auger, AFM, STM, AFM-Raman, nanoindentador, preparação de amostras.

- Revestimentos superhidrofÛbicos.

- dopagem de nanotubos (sensores ?).

- Funcionalização com nanopartículas metálicas.

Obrigado