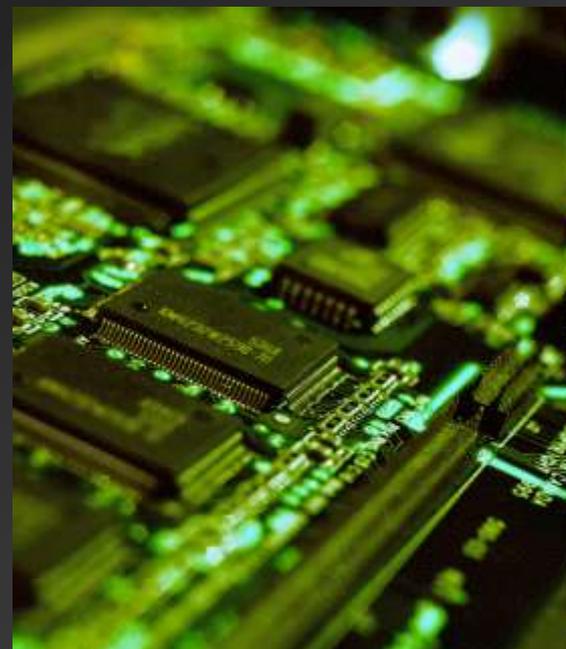


*Dos nanotubos aos  
polímeros condutores*



# Nanotecnologia Orgânica



# Sumário

- Nanotecnologia
- Nanotubos de carbono
- Polímeros Condutores

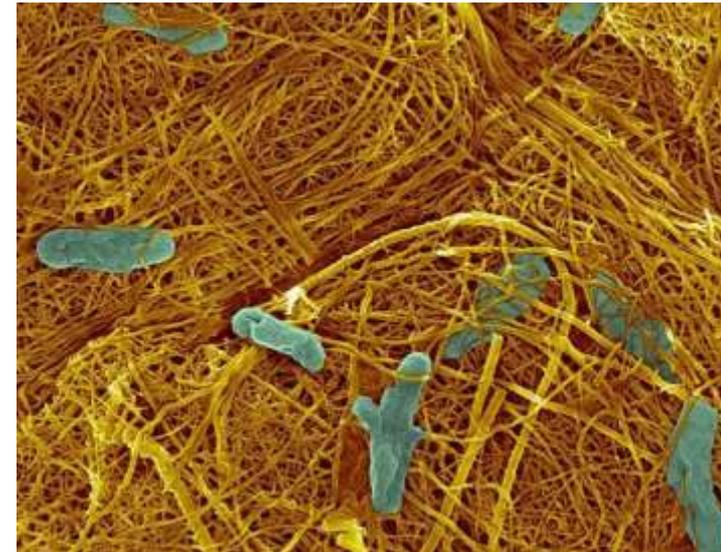


# O “início” da nanotecnologia

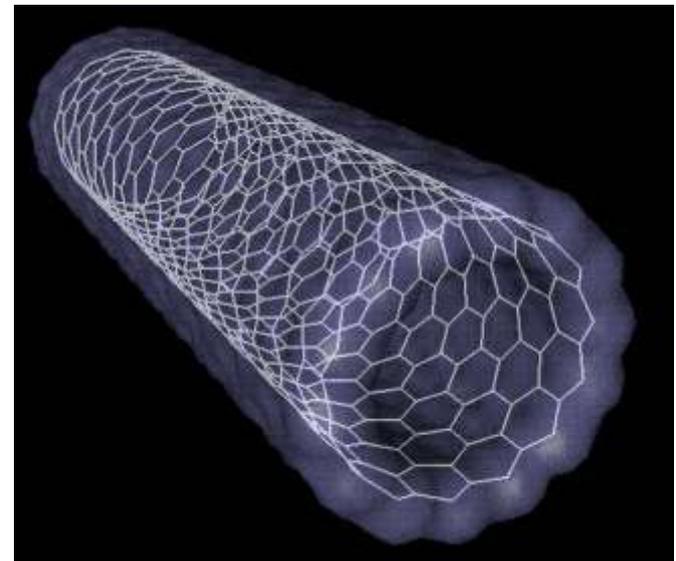
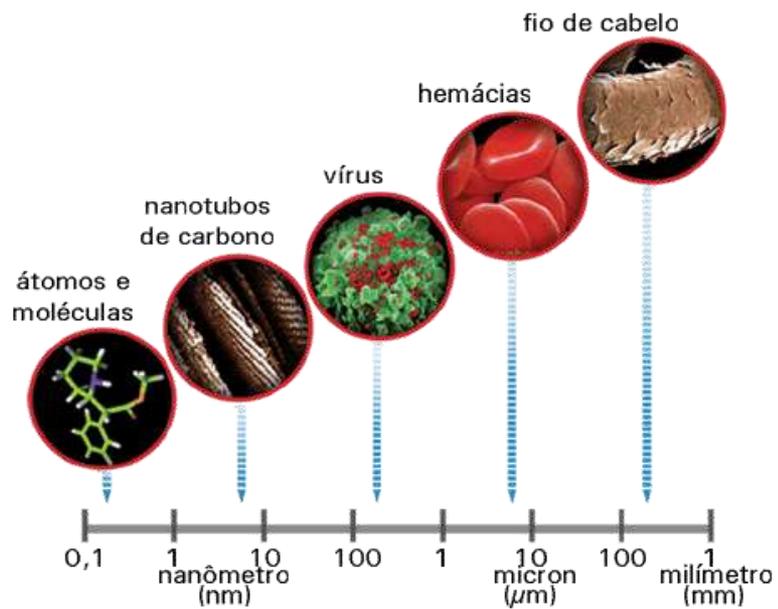
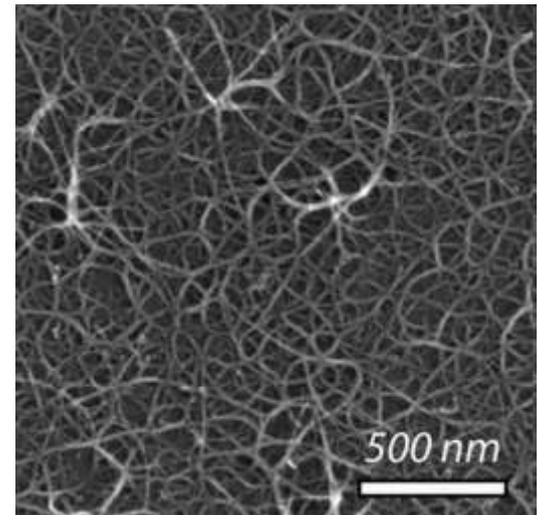
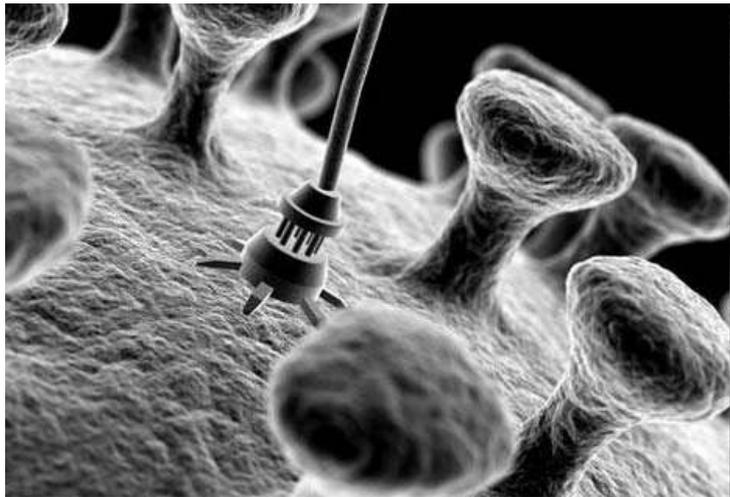
“What I want to talk about is the problem of manipulating and controlling things on a small scale. ...In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction....”

*Palestra proferida por Richard Feynman em 29 de dezembro de 1959 - CALTECH*

Ramo MULTIDISCIPLINAR da ciência que estuda as estruturas, materiais e dispositivos menores que 100 nm com novas propriedades ou propriedades melhoradas



*Shewanella* bacteria (shown in blue) forming nanotubes. (Credit: Hor-Gil Hur, GIST)



# The Scale of Things – Nanometers and More



## Things Natural



Dust mite  
200 μm

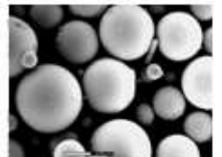


Human hair  
~ 60-120 μm wide

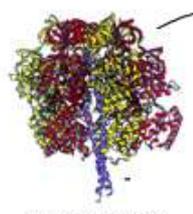
Red blood cells  
(~7-8 μm)



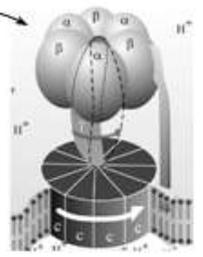
Ant  
~ 5 mm



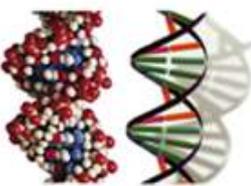
Fly ash  
~ 10-20 μm



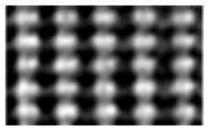
~10 nm diameter



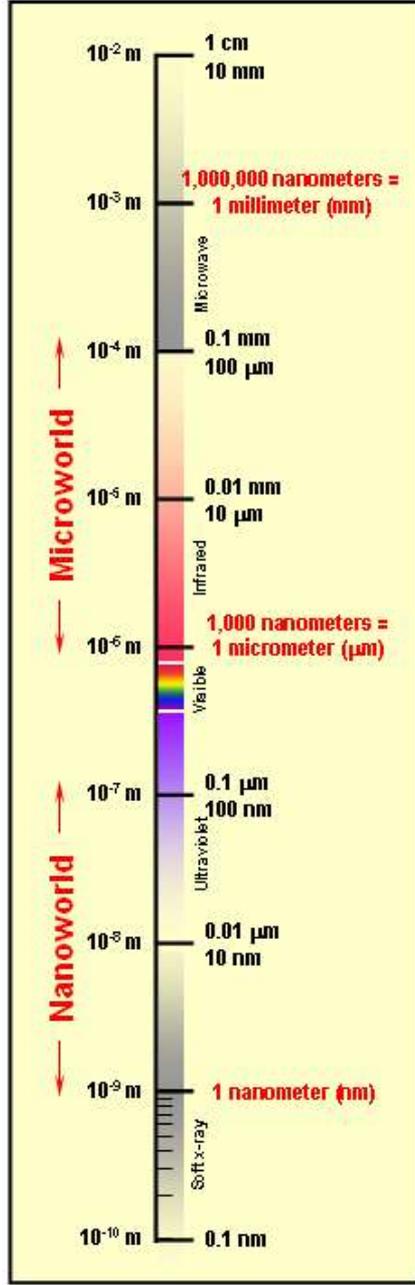
ATP synthase



DNA  
~2-1.2 nm diameter



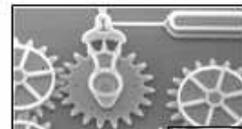
Atoms of silicon  
spacing 0.078 nm



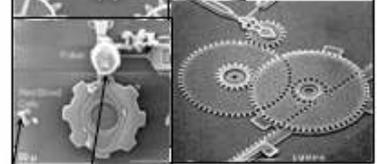
## Things Manmade



Head of a pin  
1-2 mm

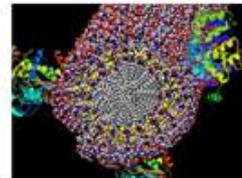
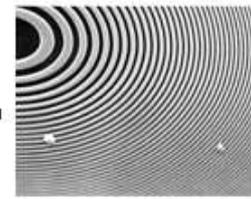


MicroElectroMechanical (MEMS) devices  
10-100 μm wide

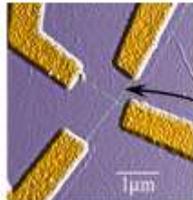


Pollen grain  
Red blood cells

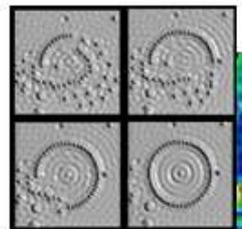
Zone plate x-ray "lens"  
Outer ring spacing ~35 nm



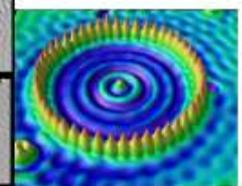
Self-assembled, Nature-inspired structure  
Many 10s of nm



Nanotube electrode

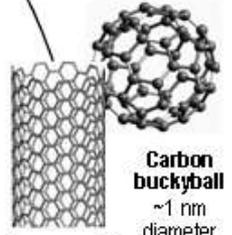


Quantum corral of 48 iron atoms on copper surface  
positioned one at a time with an STM tip  
Corral diameter 14 nm



### The Challenge

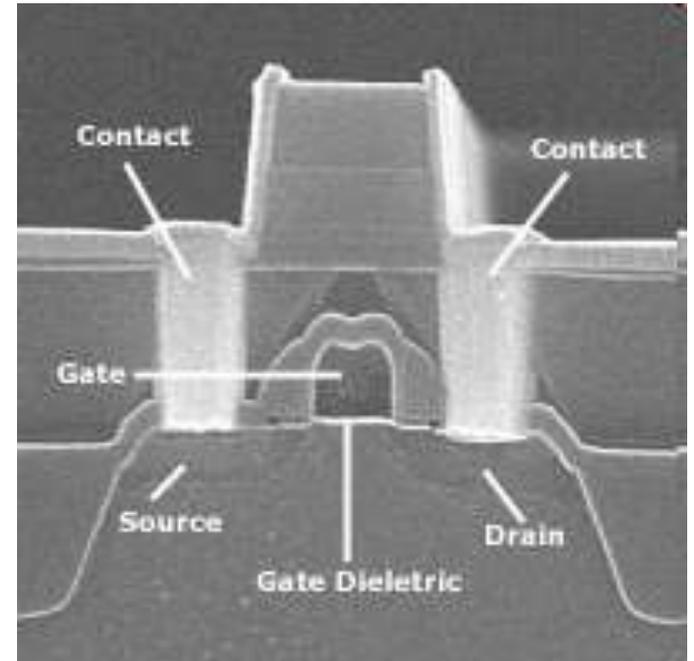
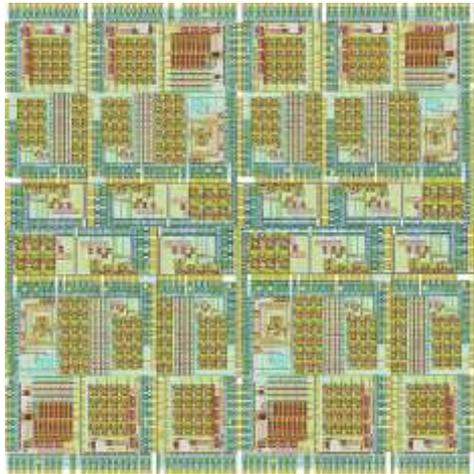
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.



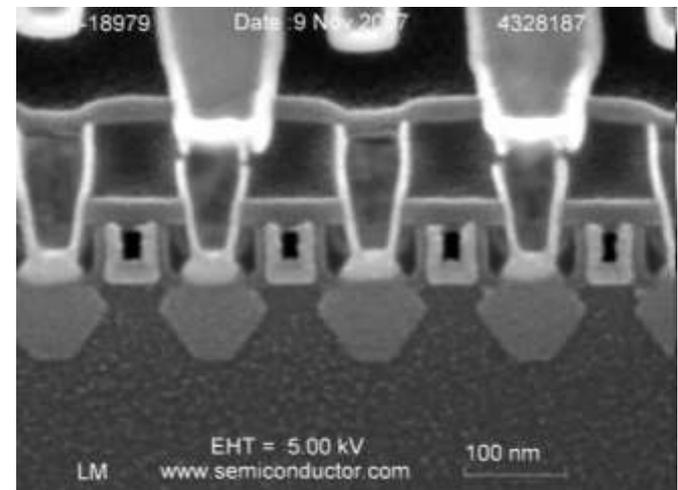
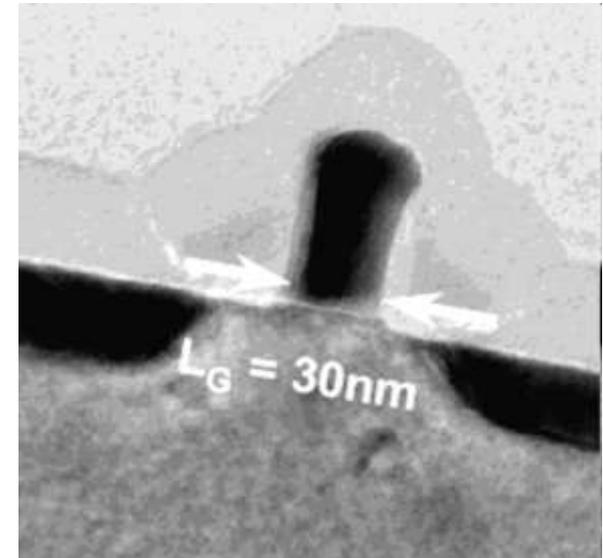
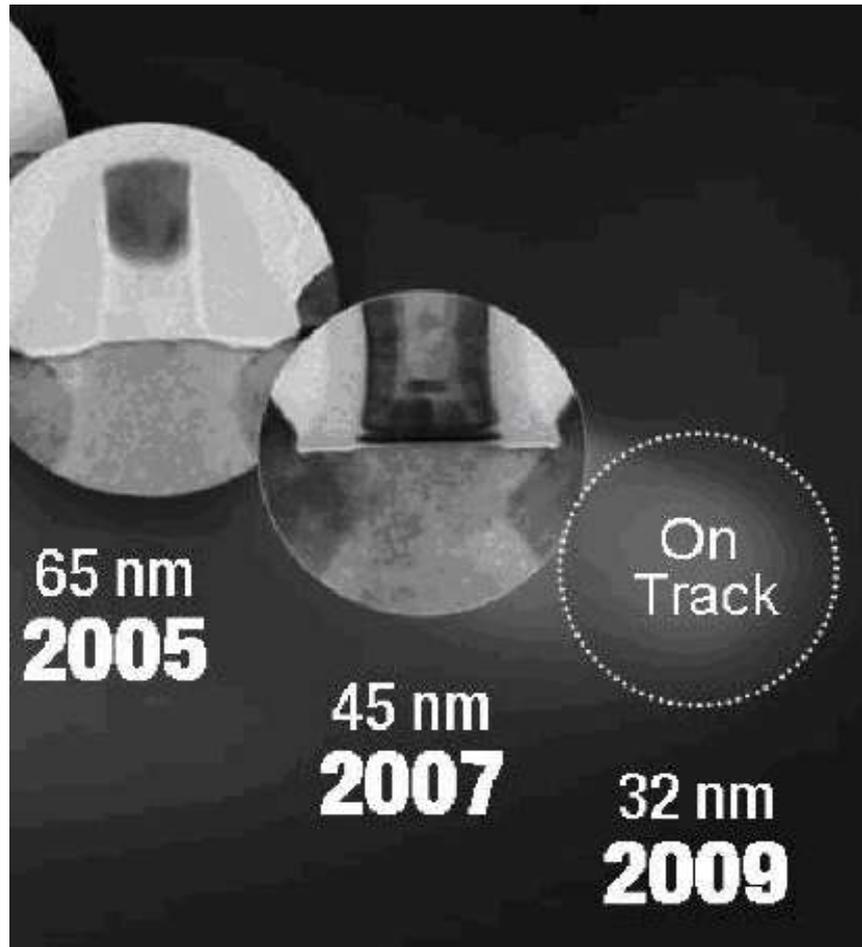
Carbon nanotube  
~1.3 nm diameter

Carbon buckyball  
~1 nm diameter

# Transistores 45 nm



# Continuando a redução...



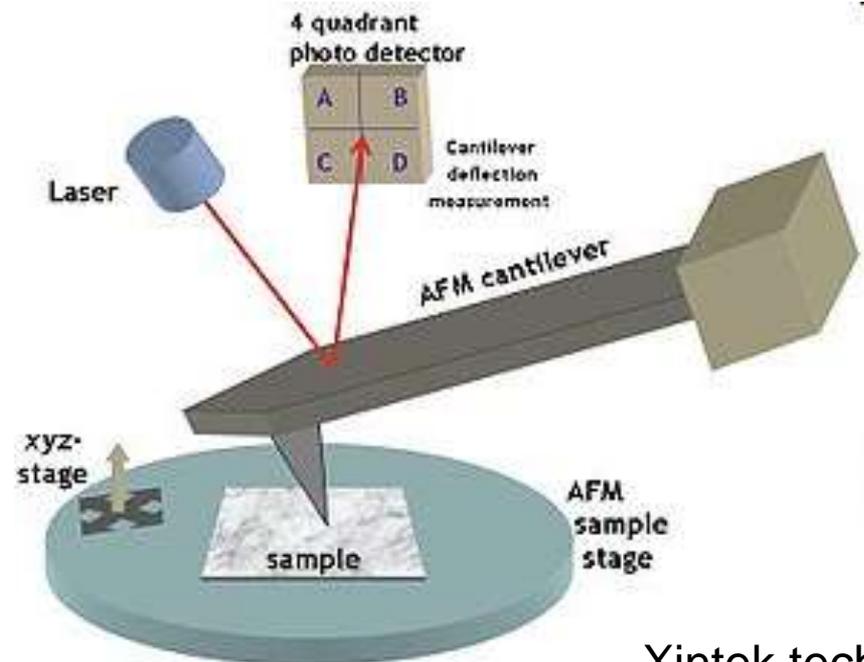
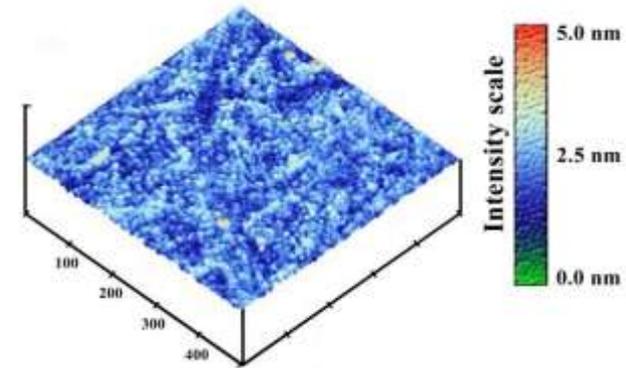
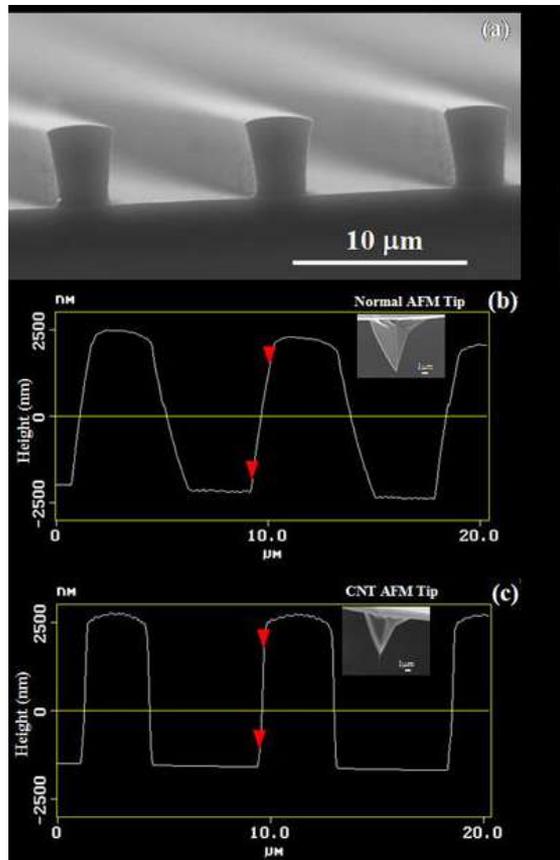
# Abordagens

- Há duas abordagens usadas em nanotecnologia
- “Bottom-up” (de baixo pra cima)
  - Materiais e dispositivos são formados por componentes moleculares que se arranjam quimicamente por princípios de reconhecimento molecular.
- “Top-down” (de cima pra baixo)
  - Nano-objetos são construídos por materiais volumétricos, através de técnicas de redução de tamanho como litografia, corrosão



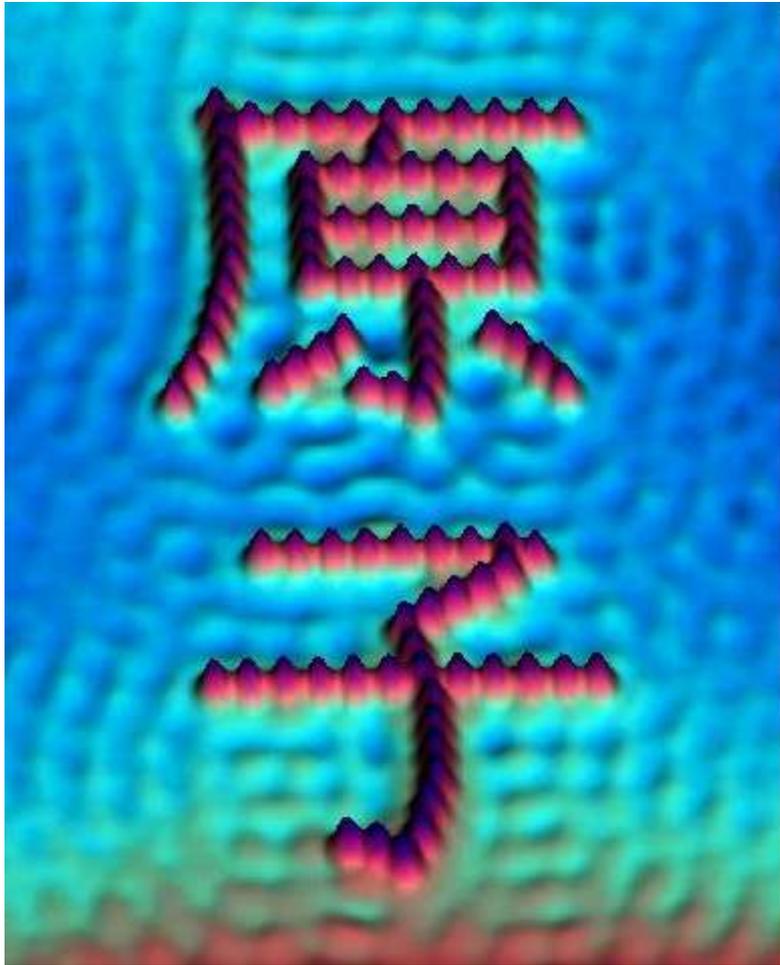
# A tecnologia que realmente permitiu a nanotecnologia

O microscópio de força atômica e o microscópio de varredura por tunelamento foram as ferramentas que permitiram o surgimento da nanotecnologia como ciência “comum”.

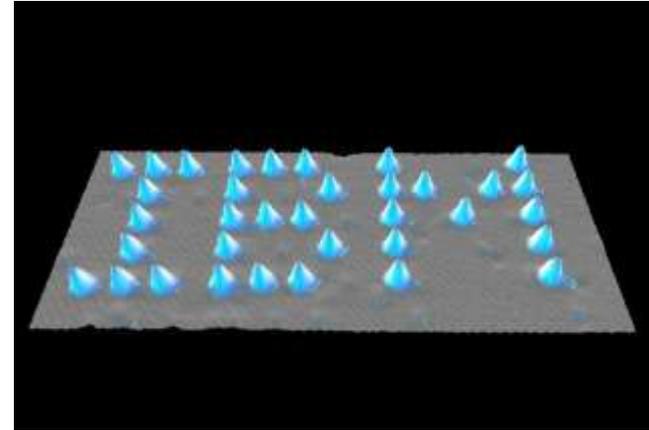


Xintek tech.

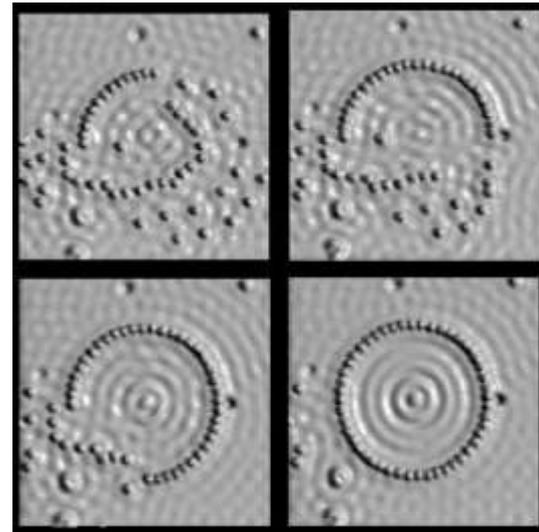
# Manipulando átomos - STM



Lutz e Eigler - Iron on Copper (111)



Eigler (1990) : Xenon on Nickel (110)

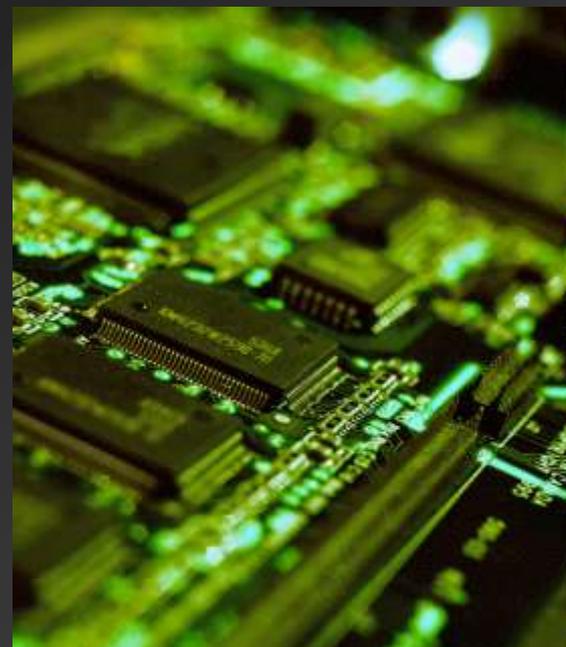
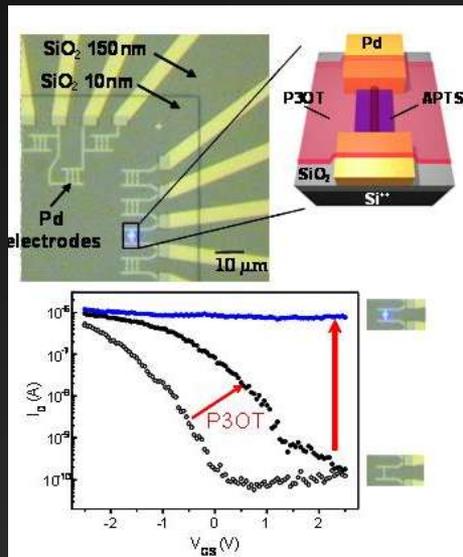
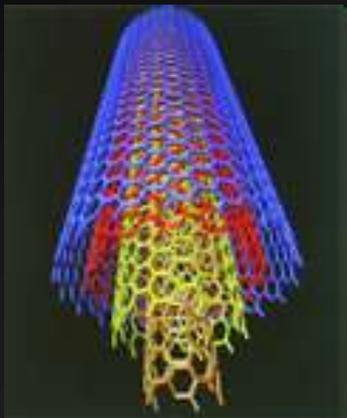


Eigler (1993)

# Algumas aplicações potenciais

- **Deteccção e diagnóstico**
- Algumas doenças não exibem sintomas reconhecíveis até que atinja um nível bem avançado. Habitualmente, quanto mais cedo for detectada a doença, melhores os benefícios do tratamento.
- Cancer de mama
  - Atualmente detectavel (mamografia): tumor maior que um milhão de células.
- Nanosensores ou materiais nanométricos tem o potencial de serem milhões de vezes mais sensíveis que sensores “macros”. Devido a serem bastante reduzidos, também é possível construir detectores com centenas ou milhares de diferentes sensores no tamanho de um “dedo”, possibilitando o diagnóstico de milhares de doenças ao mesmo tempo.
  - Com o uso de nanosensores: deteção de tumor entre 100 a 1000 células.





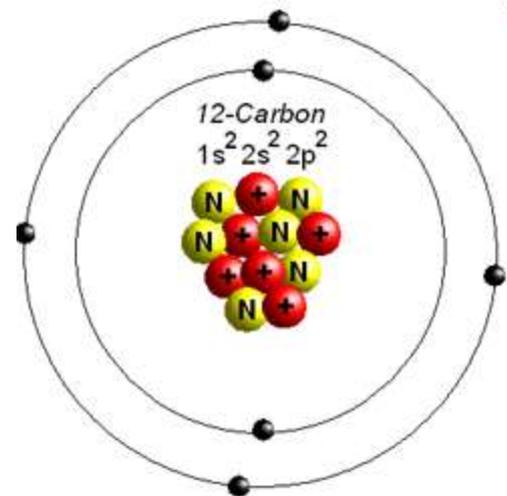
# Nanotubos de carbono



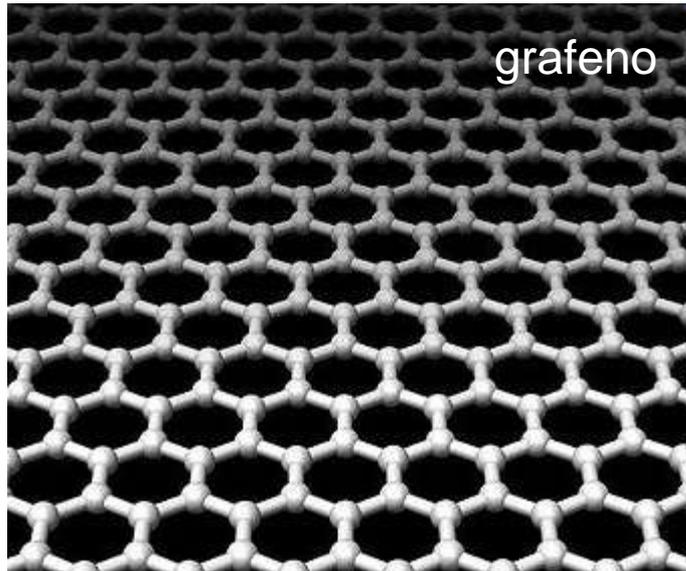
# Um pouco de química orgânica

**Ramo da química que estuda os compostos do carbono**

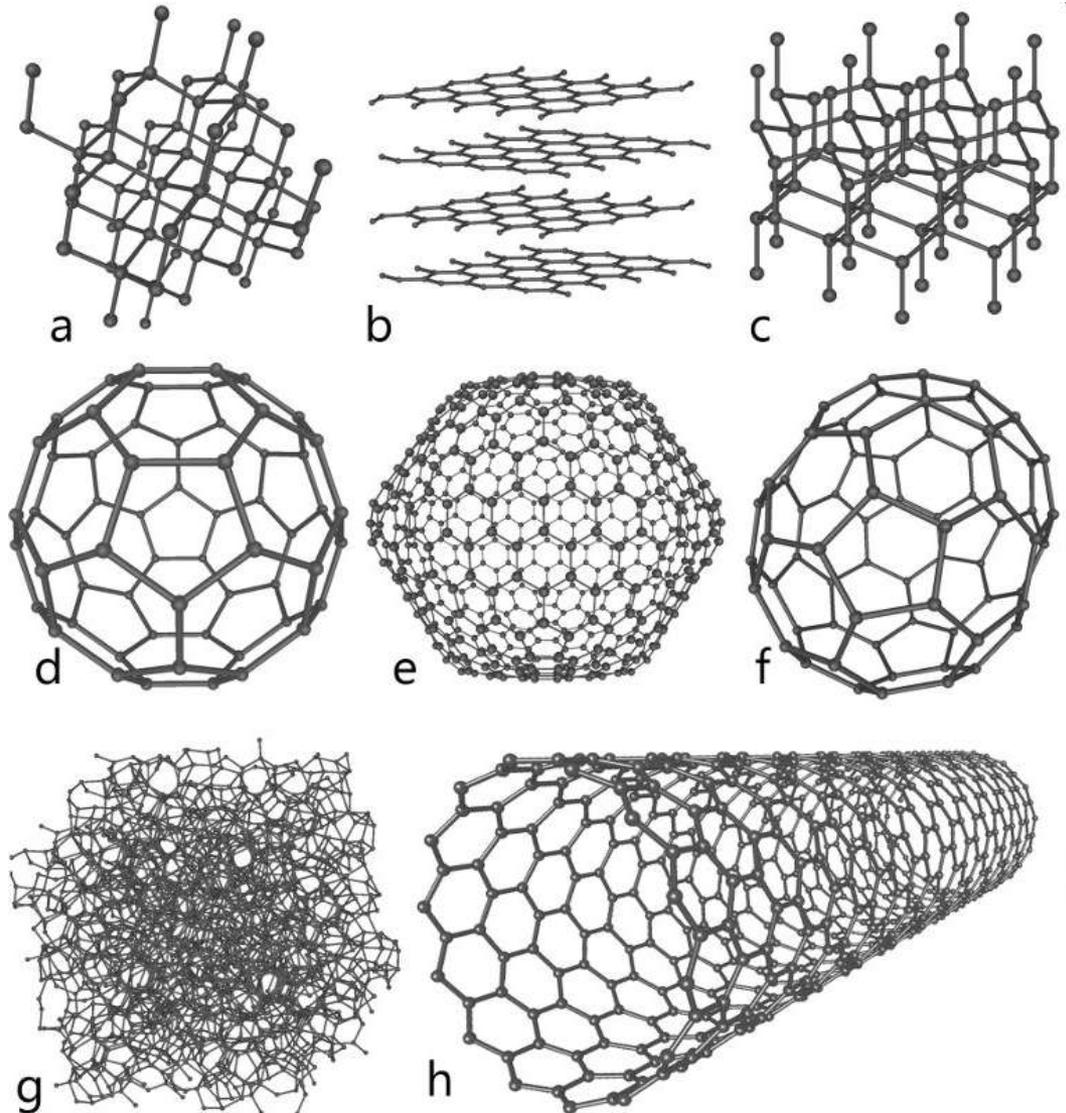
Nem todos os materiais que tem carbono são considerados orgânicos (ex.: dióxido de carbono, o ácido carbônico, Grafite, diamante)



# Formas do carbono



- a) *Diamante*
- b) *Grafite*
- c) *Lonsdalita*
- d) *C60 (Buckminsterfulereno)*
- e) *C540 Fulereno*
- f) *C70 Fulereno*
- g) *Carbono amorfo*
- h) *Nanotubo de carbono de parede única*



# Nanotubos de carbono

## Propriedades

### Resistência a tração (63 GPa)

Um cabo de um milimetro poderia  
Suportar 6,3 toneladas!

### Cinética

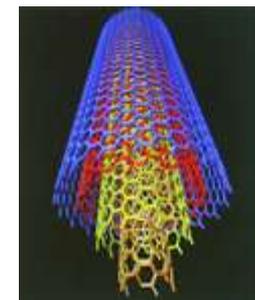
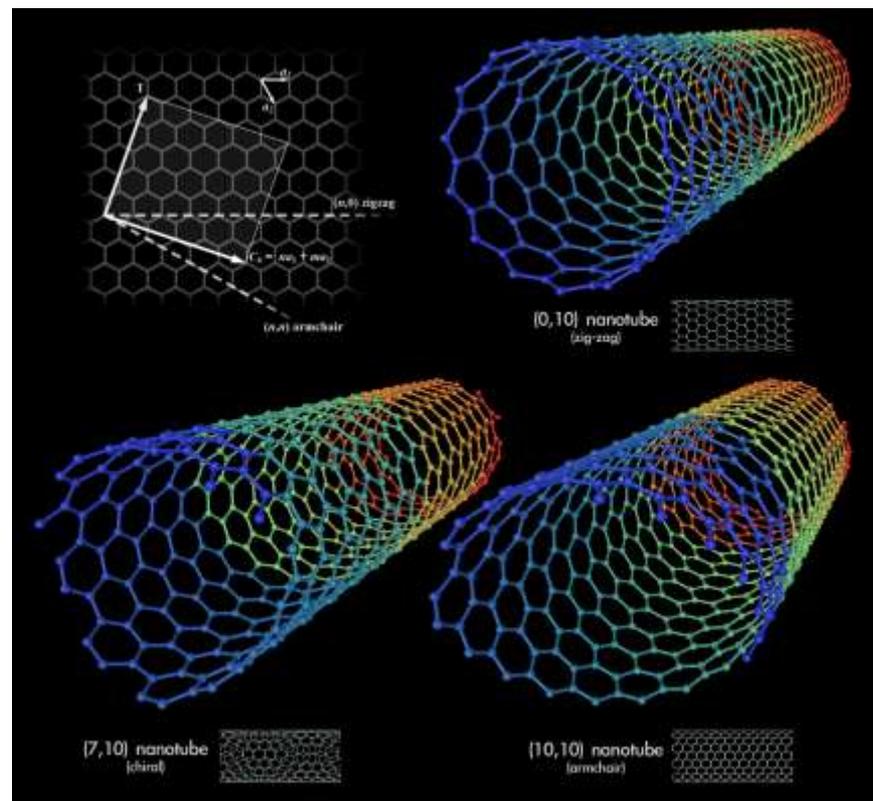
Pode operar como telescópio

### Elétrica

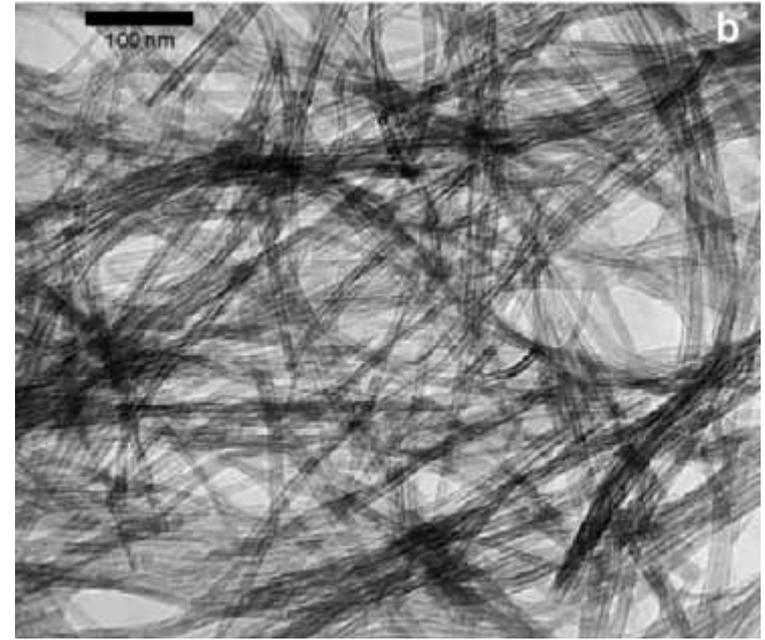
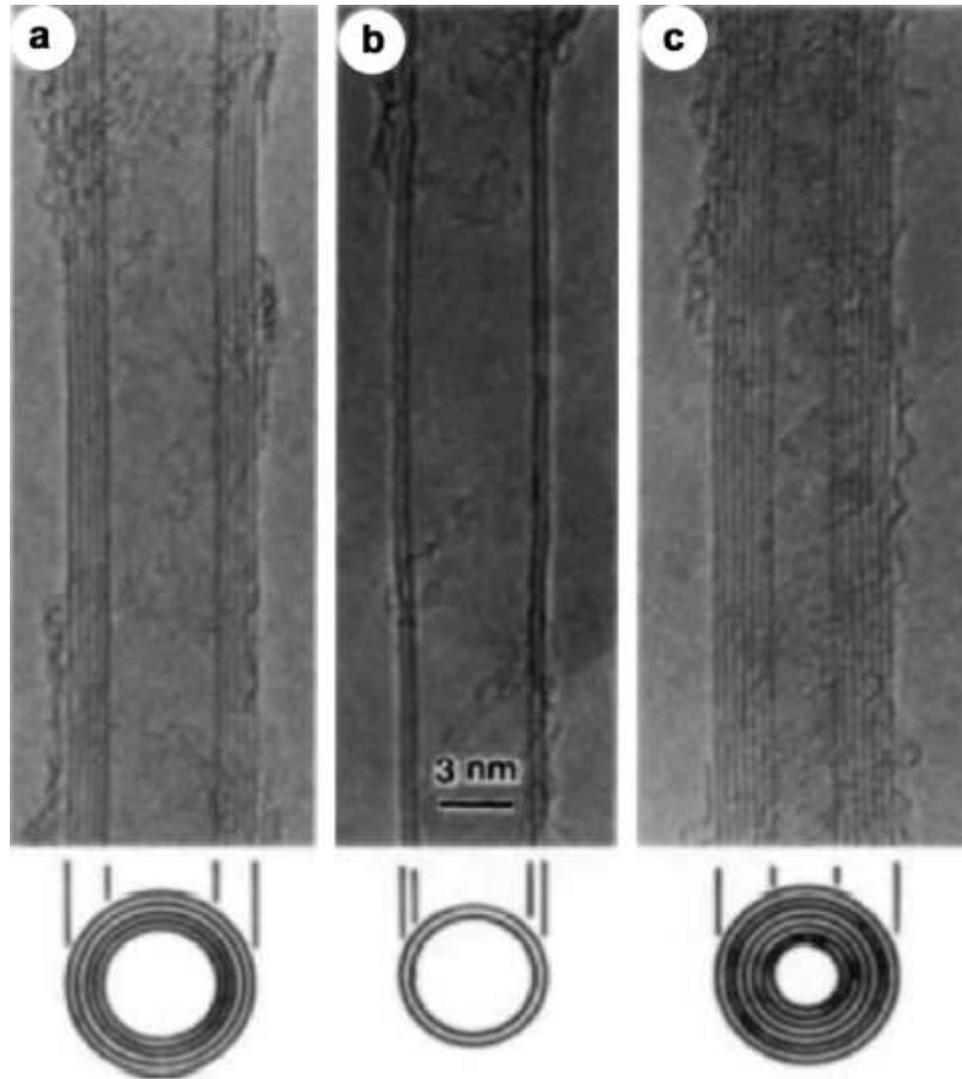
Pode ser condutor, semicondutor  
e isolante (dependendo da orientação)  
teoricamente suporta  $4 \cdot 10^9 \text{A/cm}^2$   
(cobre 1000 vezes menor)

### Térmica (6000 W/mK)

Condução balística ao longo do tubo

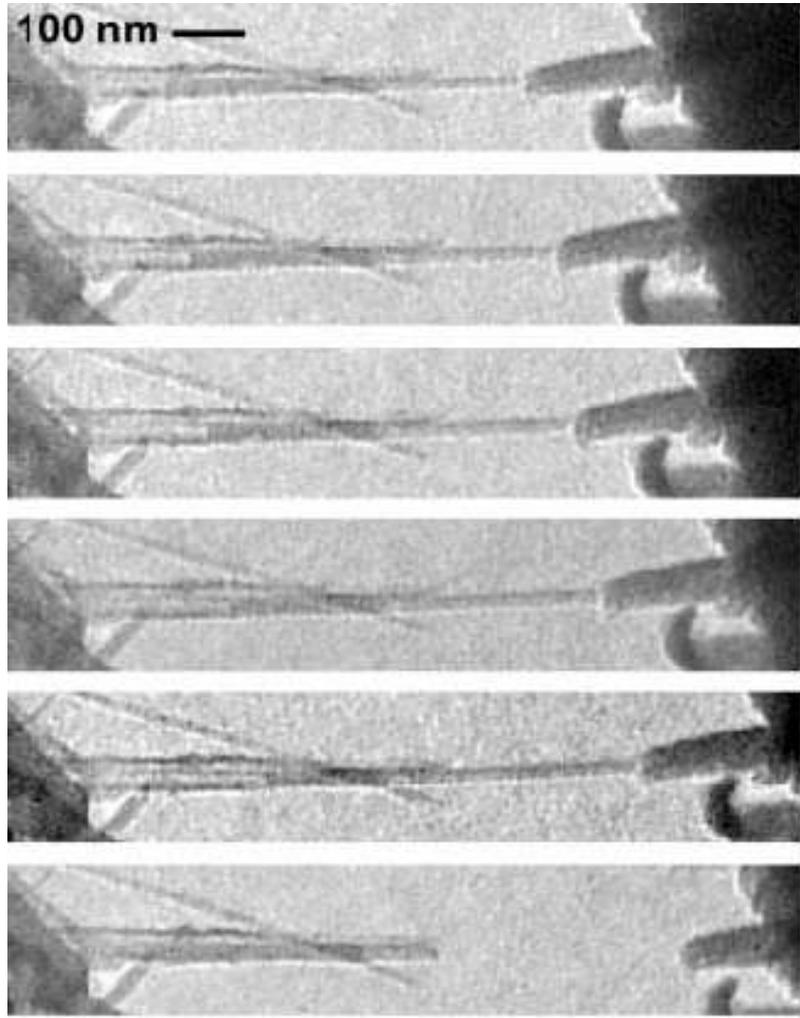


# Nanotubos de carbono - multicamada



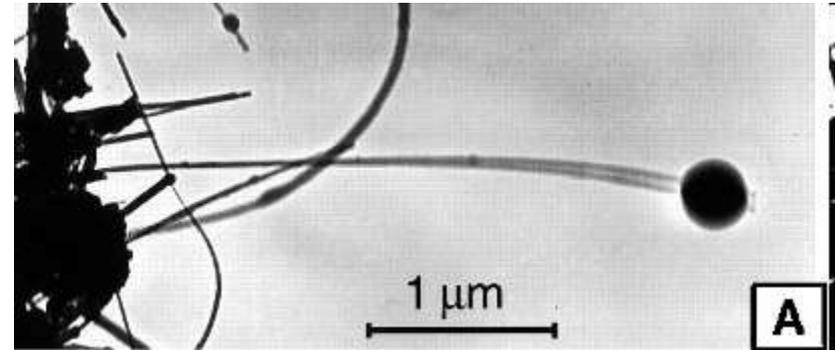
Iijima S. Nature 1991;354:56.

# Telescópio e balança



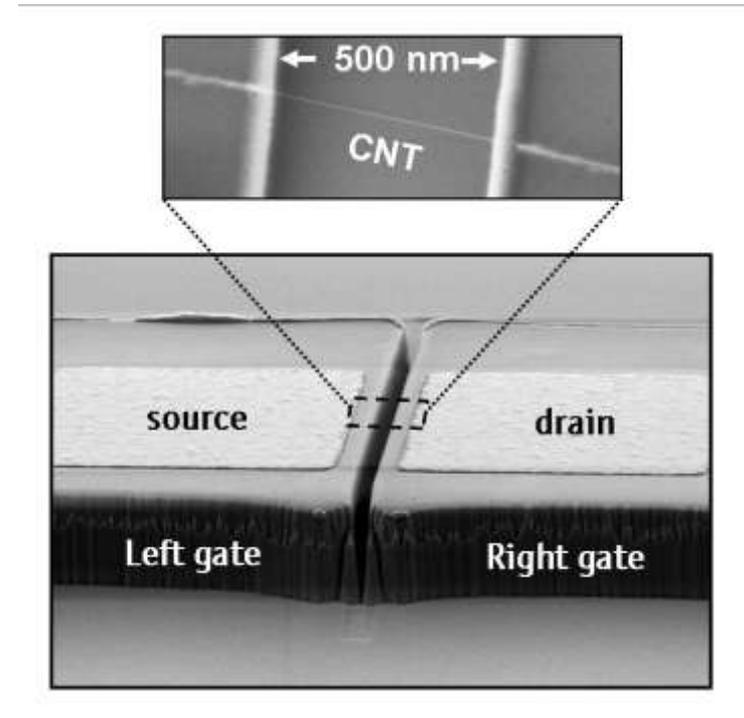
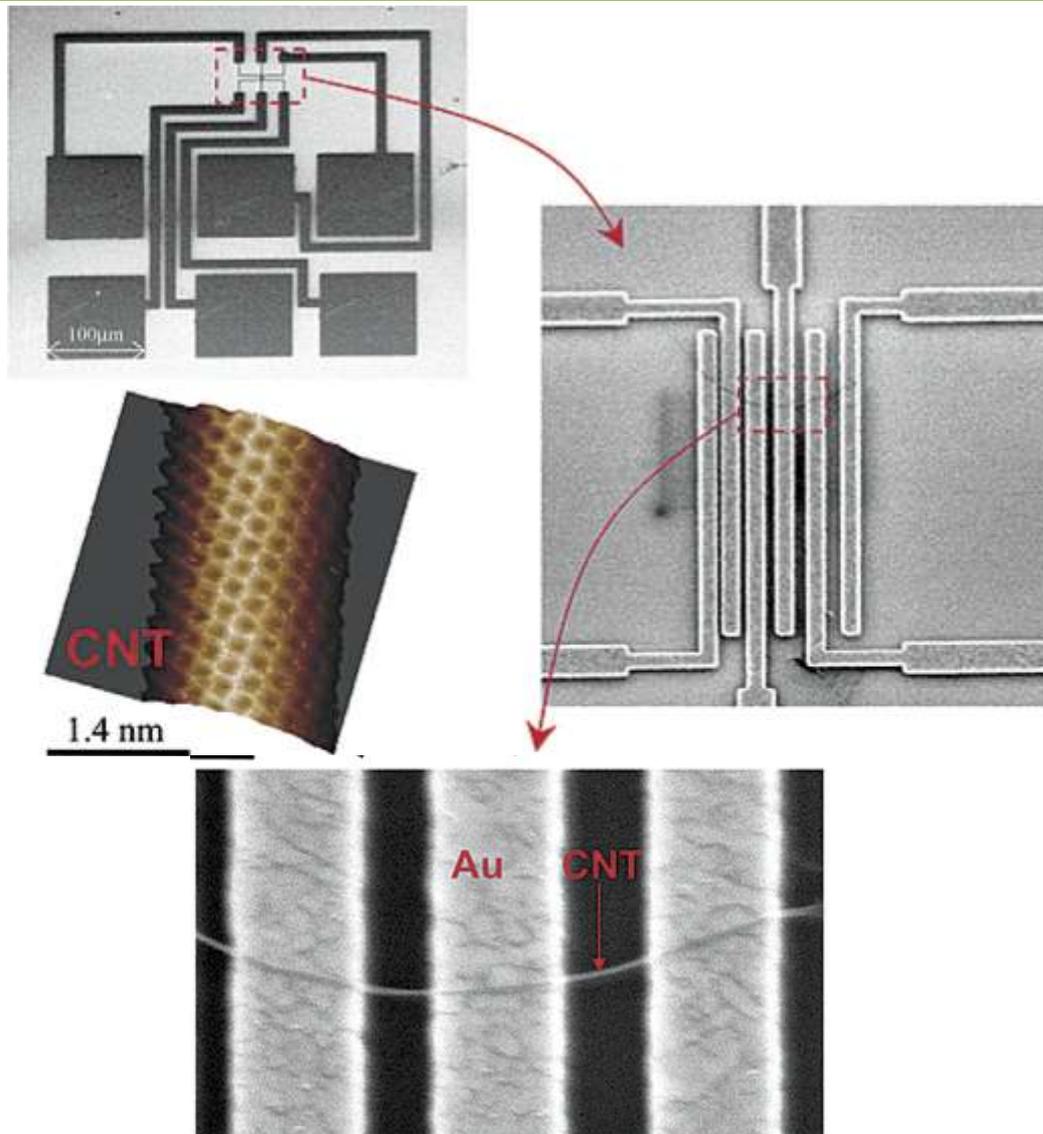
J. Cumings and A. Zettl, Science 289, 602 (2000)

Partícula de 22fg



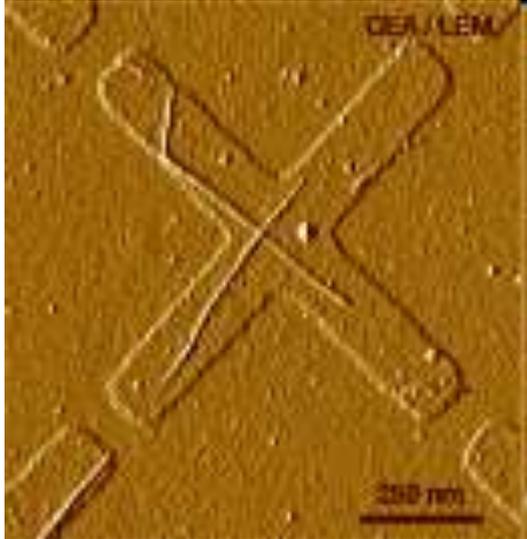
P. Poncharal et al., Science 283, 1513 (1999)

# Dispositivo com nanotubos de carbono

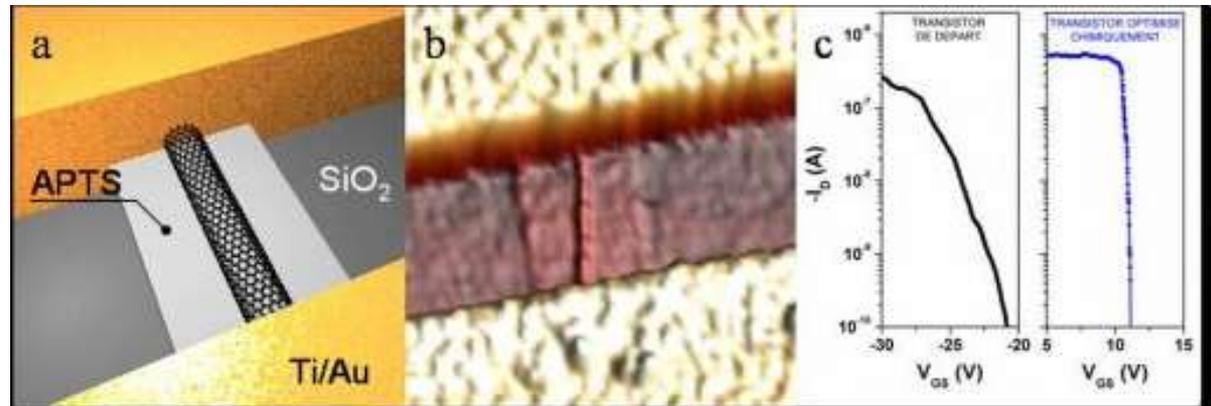


Ralph group – Cornell Univ

# Como alinhar os nanotubos?

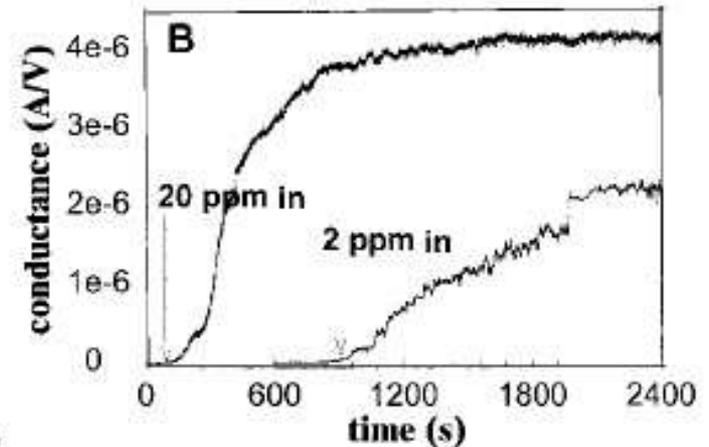
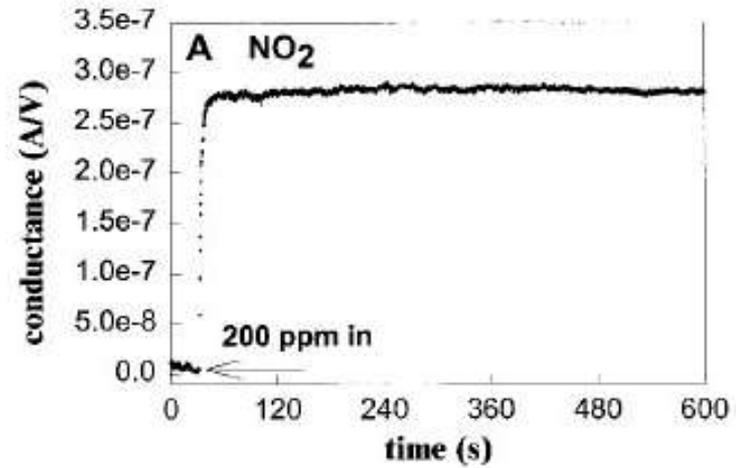
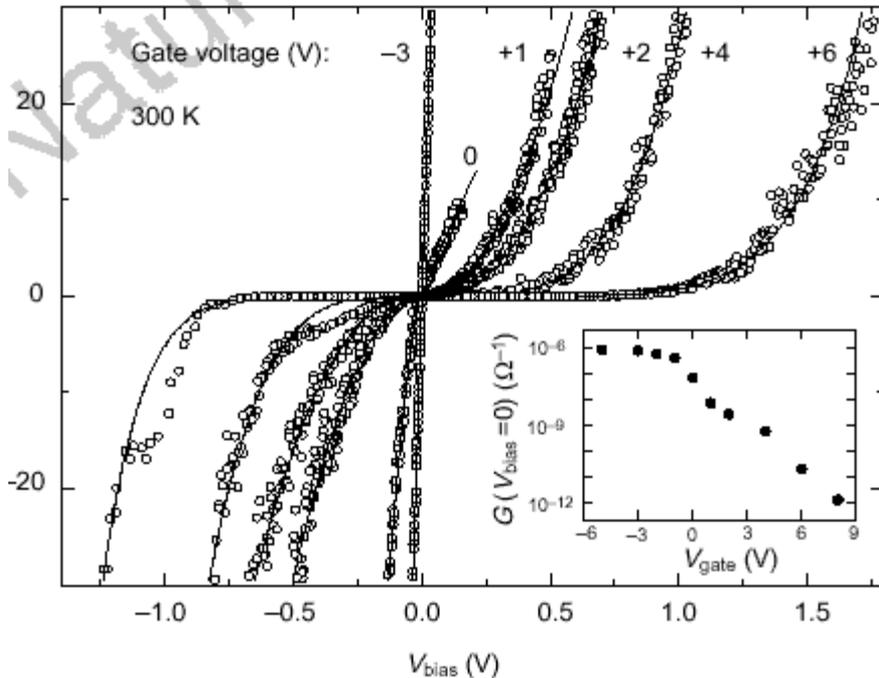
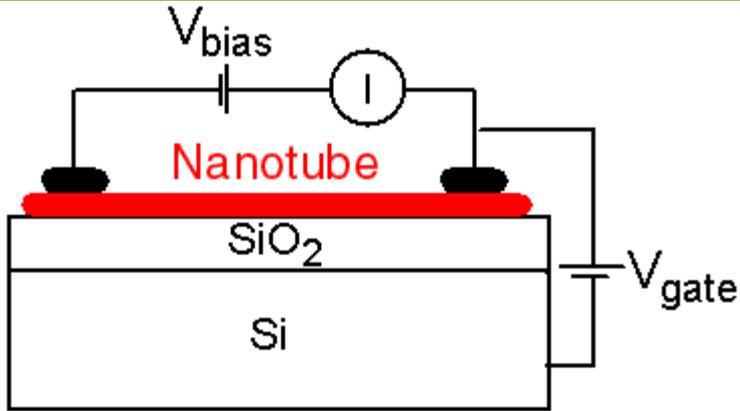


Adsorção seletiva de CNTs sobre APTS(silano)



<http://dx.doi.org/10.1002/adma.200601138>

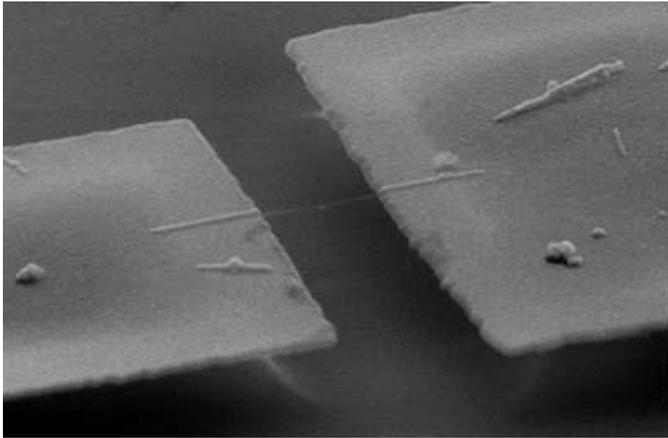
# Transistores e sensores



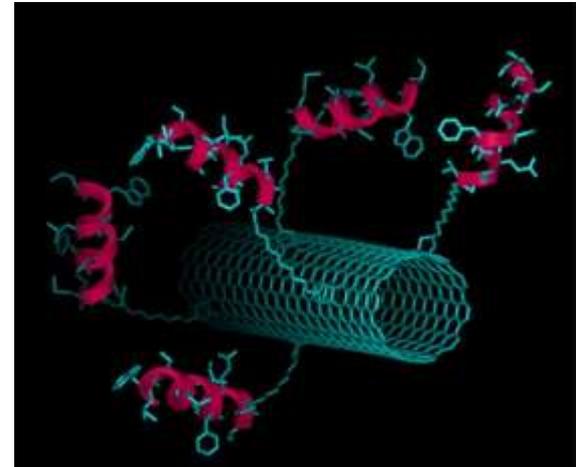
S.J. Tans et al., Nature 393, 49 (1998)

J. Kong et al., Science 287, 622 (2000)

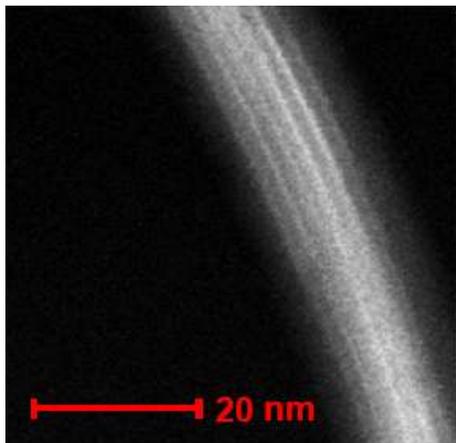
# Outras aplicações



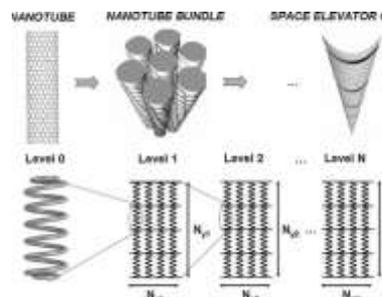
Nano ressoador



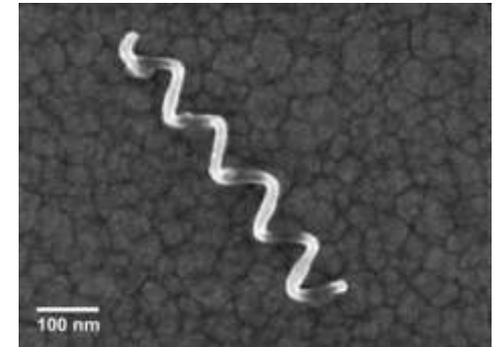
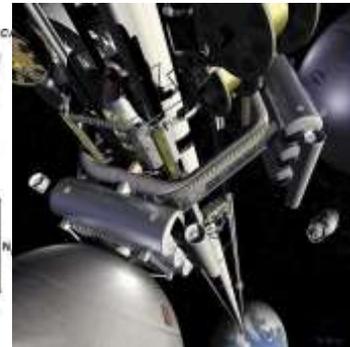
Drug Delivery



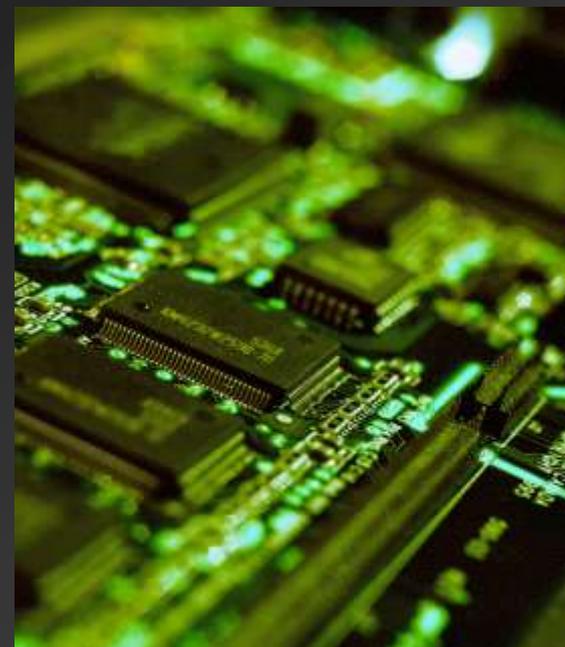
Nanoheater (Fe)



Elevador espacial



Nanomola



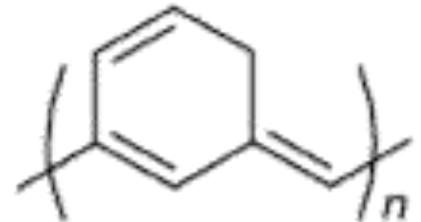
# Polímeros Condutores



# O que é um polímero?

- Poli-muitos; mero – unidade
- Muitas unidades!
- Material cujas cadeias são formadas por unidades repetidas

Polyheptadiyne  
(PHT)



Pergunta:

Os polímeros são materiais isolantes?

Depende....

# Dopagem!

Conductivity increases with increased doping

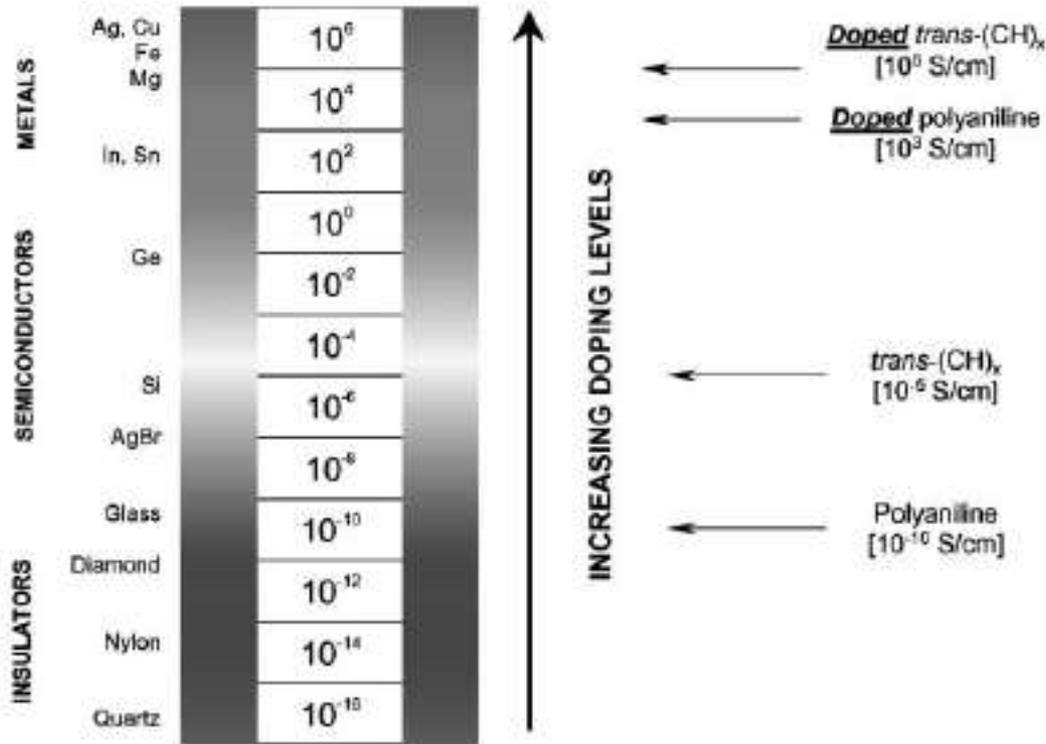


Fig. 1. Conductivity of electronic polymers.

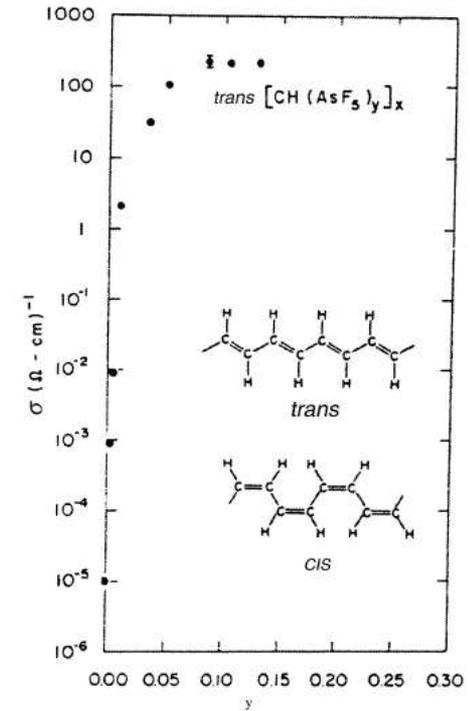


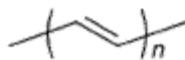
Fig. 2. Electrical conductivity of  $trans-(CH)_x$  as a function of  $(AsF_5)$  dopant concentration. The *trans* and *cis* polymer structures are also shown.



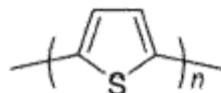
Figura 2.3: Da esquerda para a direita - MacDiarmid, Shirakawa e Heeger.

# Polímeros Conjugados (1)

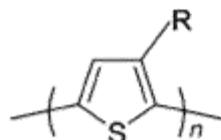
Polyacetylene  
(PA)



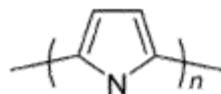
Polythiophene  
(PT)



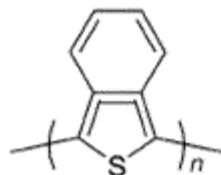
Poly (3-alkyl)  
thiophene  
(P3AT)  
(R-methyl, butyl, etc.)



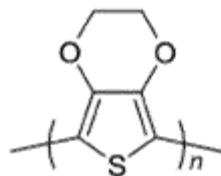
Polypyrrole  
(PPy)



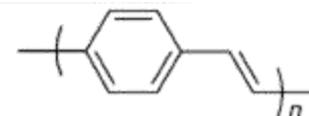
Poly  
isothianaphthene  
(PITN)



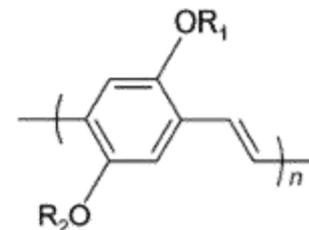
Polyethylene  
dioxathiophene  
(PEDOT)



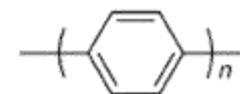
Polyparaphenylene  
vinylene  
(PPV)



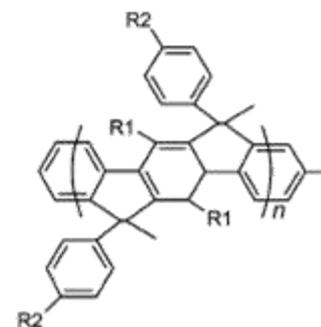
Poly (2,5 dialkoxy)  
paraphenylene  
vinylene  
(e.g. MEH-PPV)



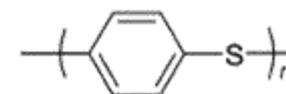
Polyparaphenylene  
(PPP)



Ladder-type  
polyparaphenylene  
(LPPP)

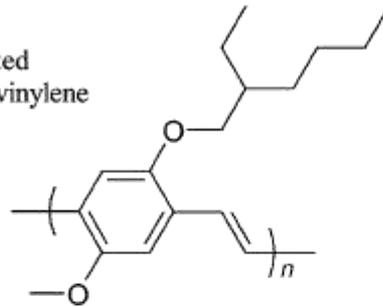


Polyparaphenylene  
sulphide  
(PPS)

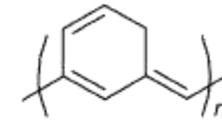


# Polímeros Conjugados (2)

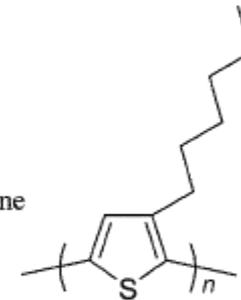
Alkoxy-substituted  
poly *para*-phenylene vinylene  
(MEH-PPV)



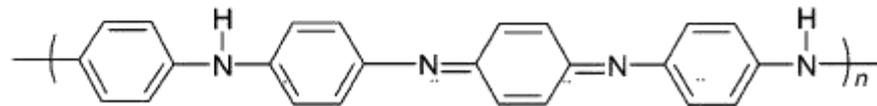
Polyheptadiyne  
(PHT)



Poly (3-hexyl) thiophene  
(P3HT)



Polyaniline, PANI

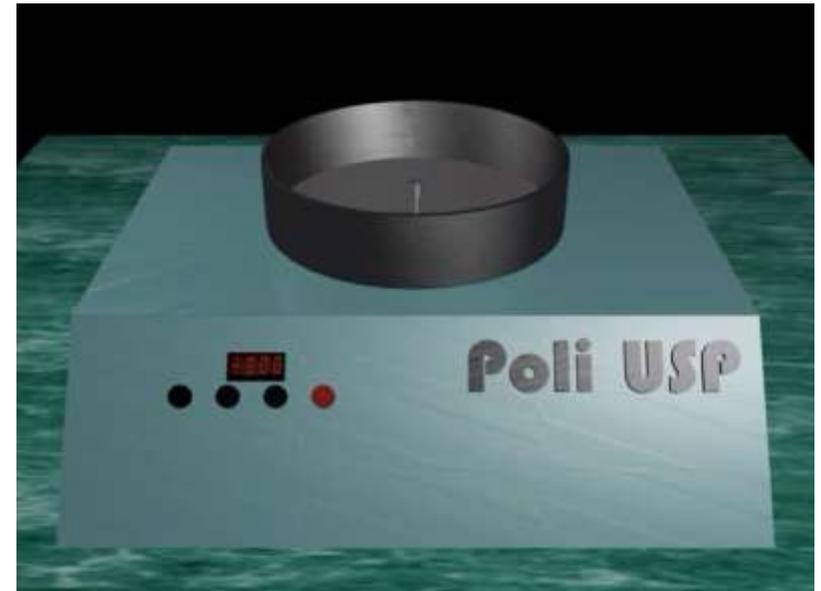


# Métodos

- Casting;
- Spin casting;
- Langmuir-Blodegett (LB);
- Ink-jet;
- Self-assembly;
- In situ

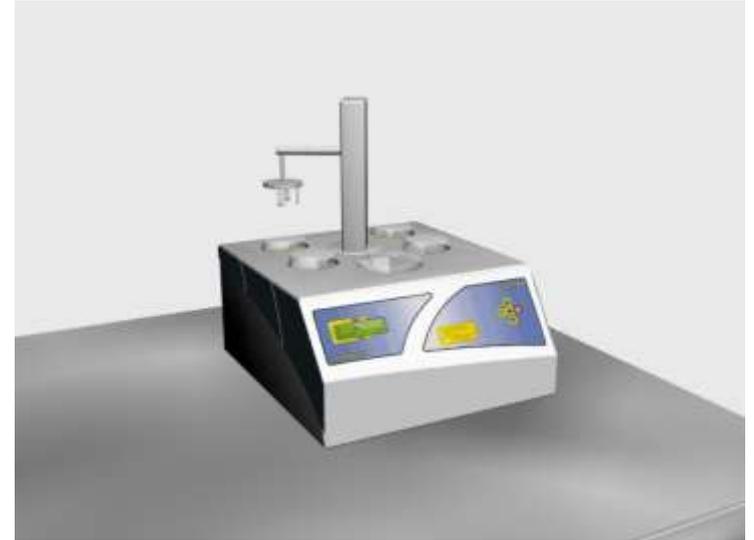
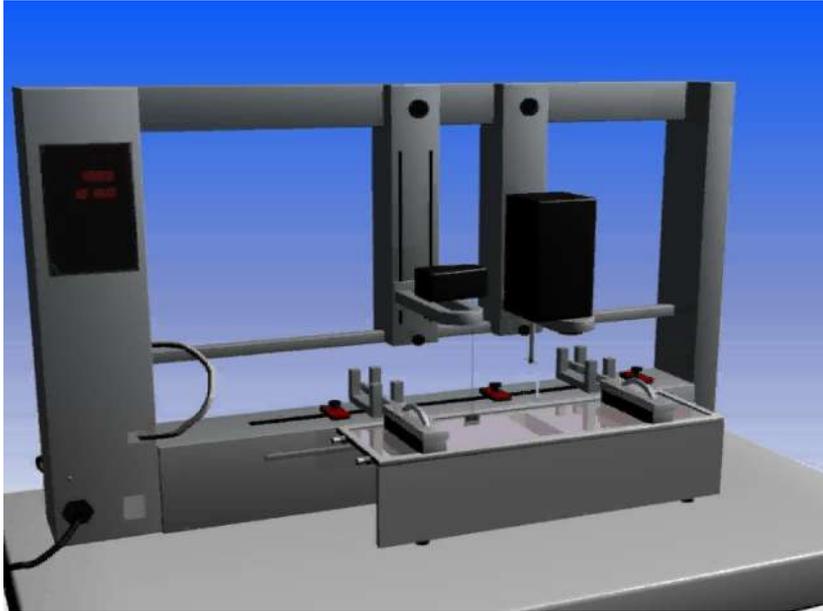
# Processamento

## Spin Coating

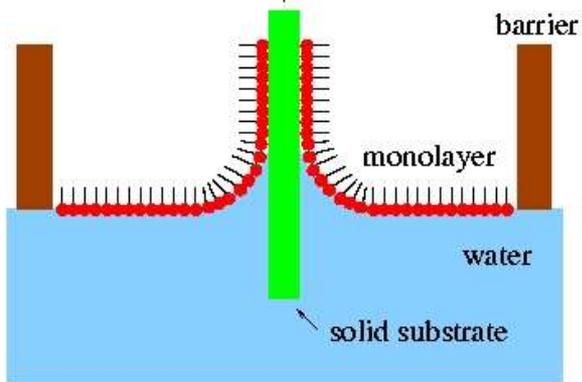


Glove box

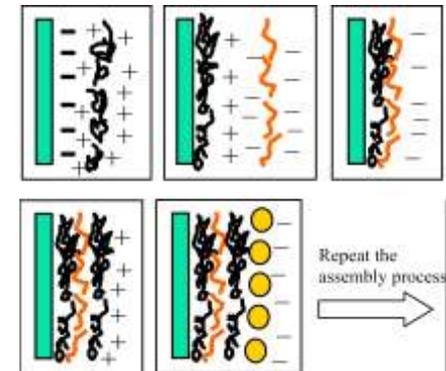
# Processamento



Langmuir – Blodgett (LB)



Automontagem



# Eletropolimerização

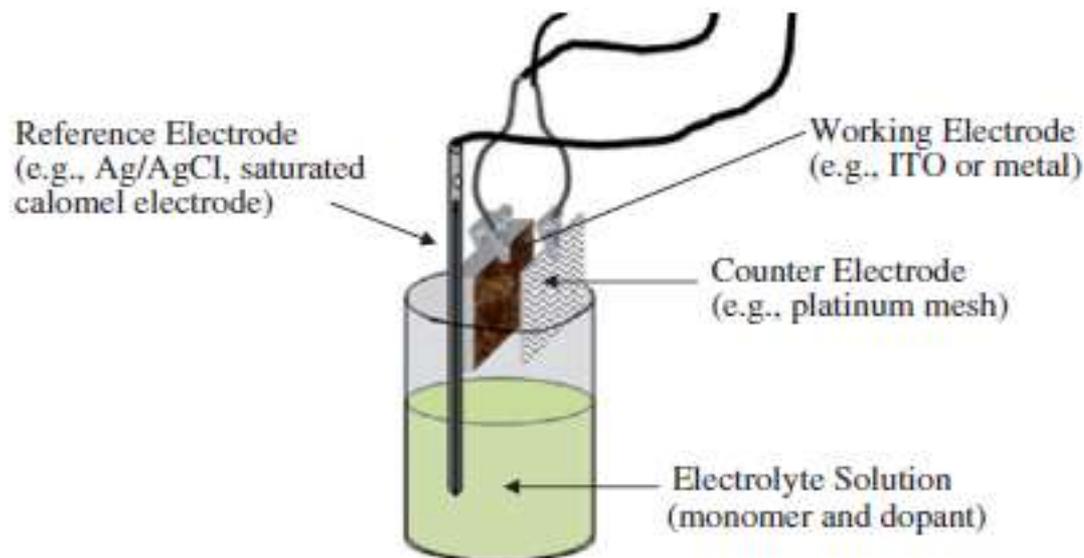


Fig. 2. Three electrode setup for electrochemical synthesis: reference electrode, working electrode (where polymerization occurs), and counter electrode all submersed in a monomer and electrolyte solution.

*N.K. Guimard et al. / Prog. Polym. Sci. 32 (2007) 876–921*

# Principais áreas de aplicação - GEM

- Polímeros condutores
- Equipamentos
- Sensores

## Sensores químicos

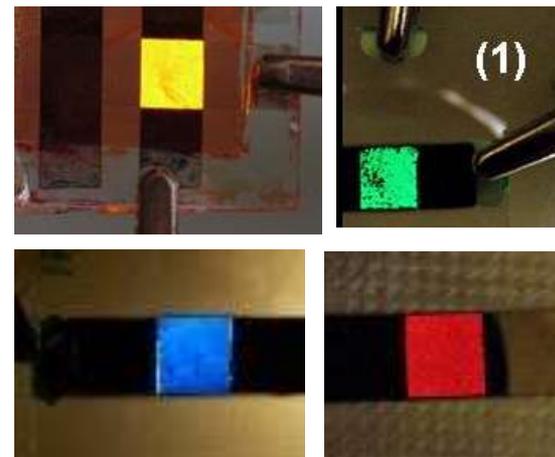


- Detecção de amônia em fazendas
- Nariz e língua eletrônica para:

- Análise de alimentos
- (café, suco de frutas, vinho)
- Perfumes e aromas
- Qualidade
- Análise de água
- Análise de combustíveis



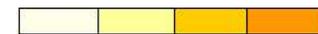
## Organic light emitting diodes - OLEDs



## Outros dispositivos

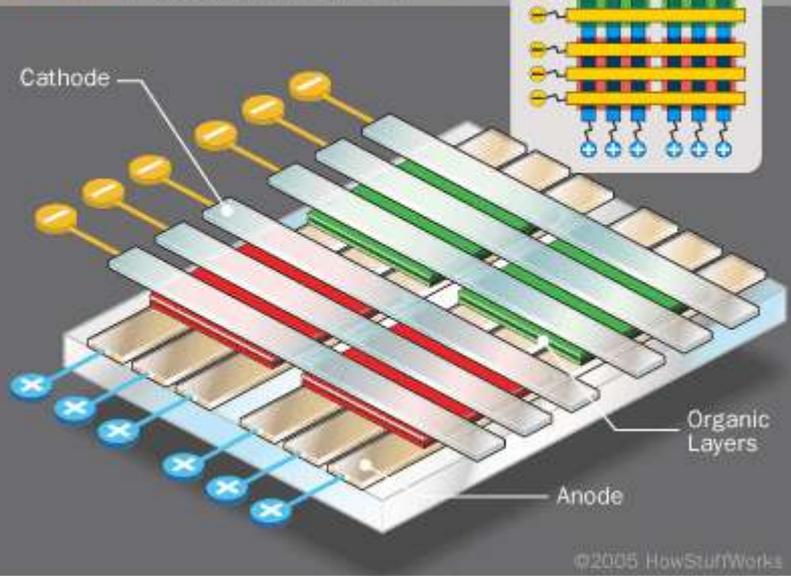
- Sensores de pressão
- Transistores de filmes finos
- Sensores fotoelétricos
- Células solares

Dosímetros de Radiação Gama

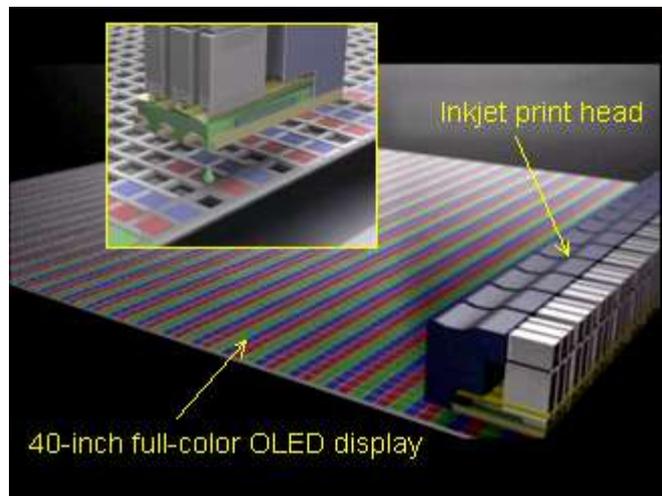
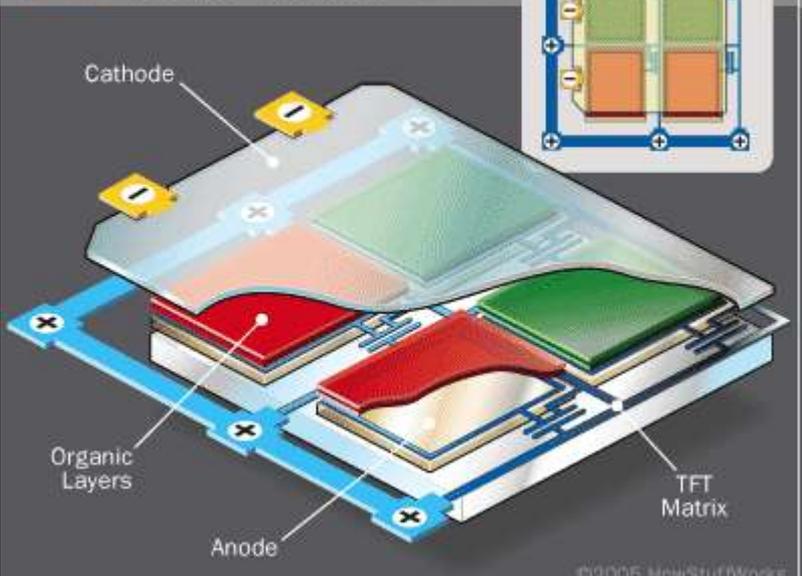


# Tipos de OLEDs

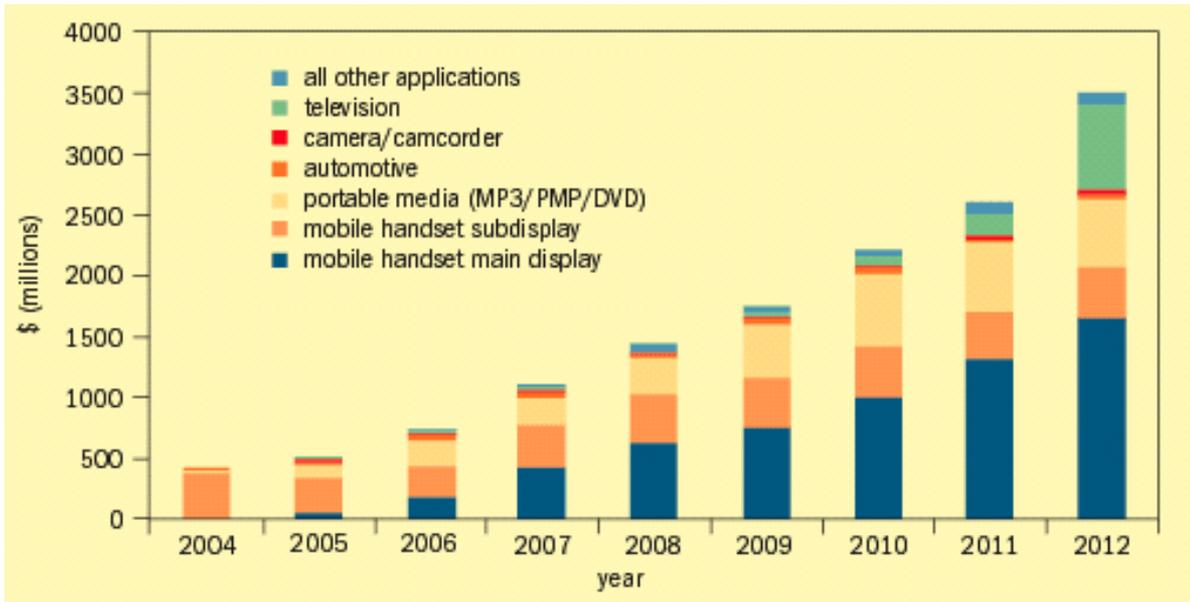
## OLED Passive Matrix



## OLED Active Matrix

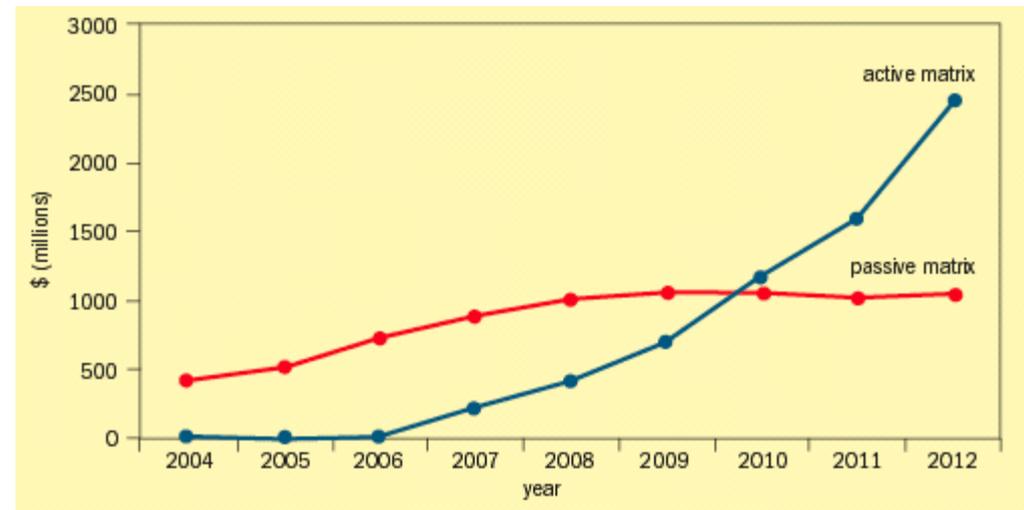


# Mercado para OLEDs

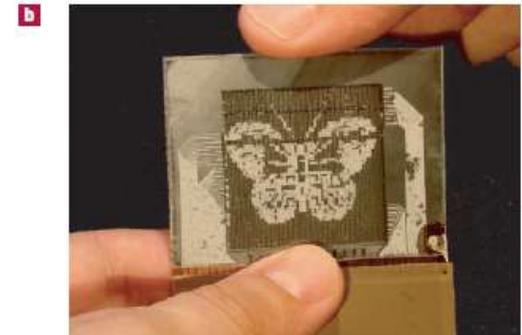
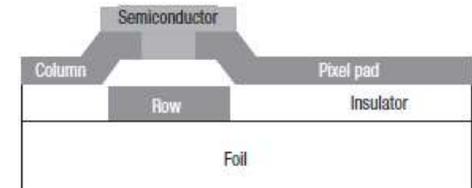
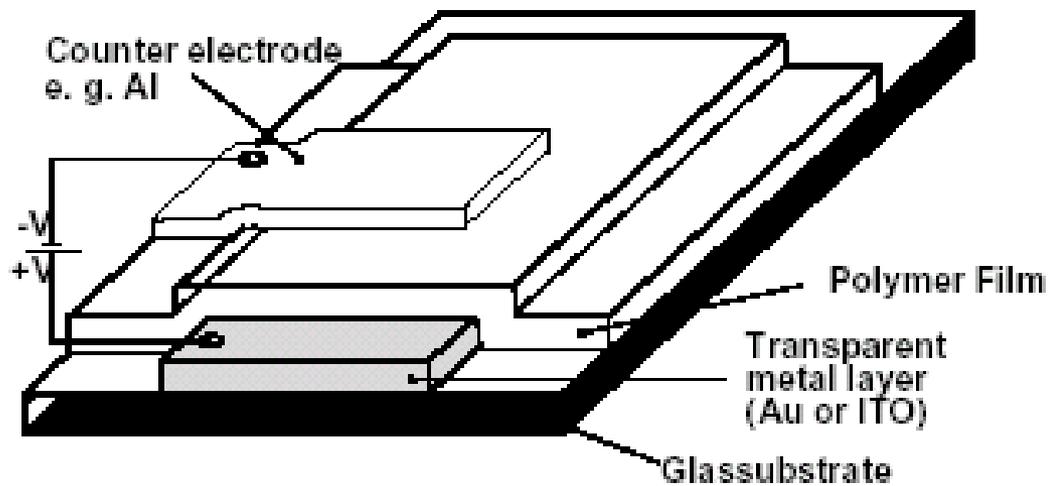


Worldwide OLED panel market, 2004-2012  
Image: iSuppli Corp, Organic Light-Emitting Diode Displays, 1H 2006

Image: iSuppli Corp, Organic Light-Emitting Diode Displays, 1H 2006



## Estrutura Típica

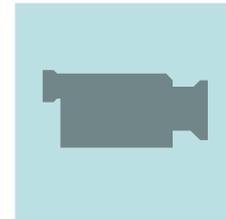


# Aplicações OLEDs



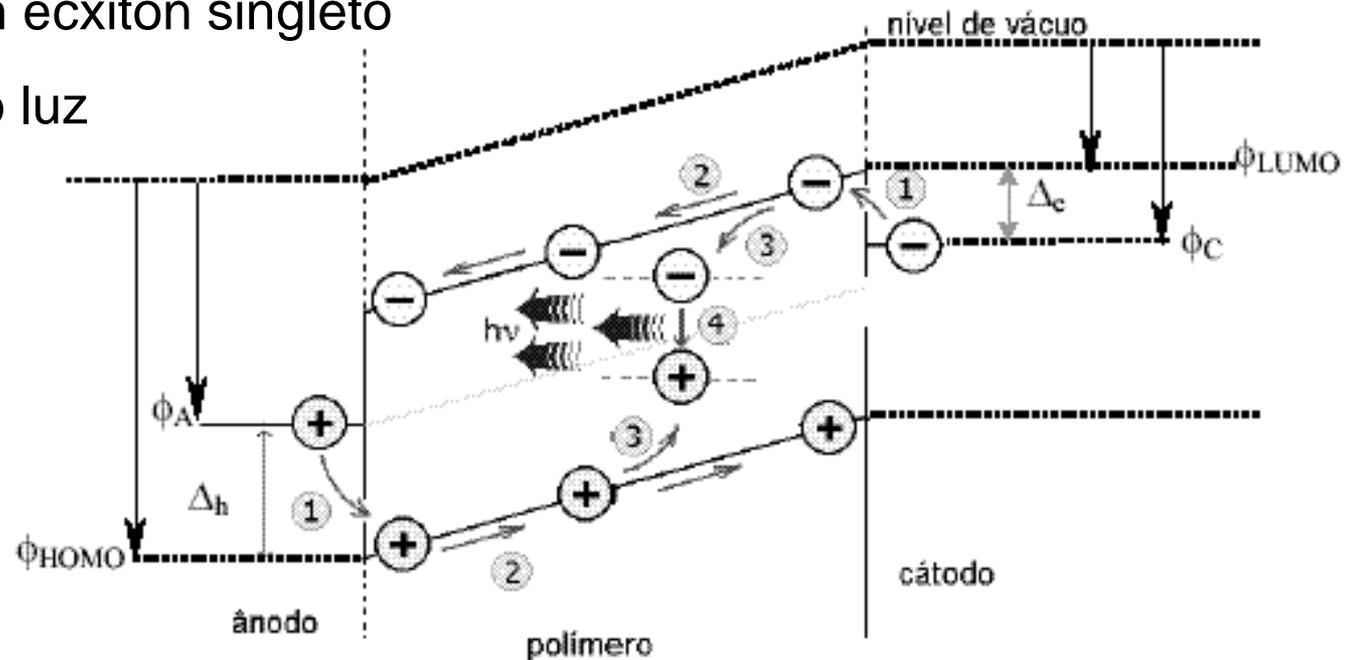
Figura 1.4 - Primeiro visor monocromático de polímero luminescente (1", ano 1995) [20] e TV policromático (2001) usando tecnologia ink-jet. Ambos ainda estão em fase de protótipo.

# OLEDs

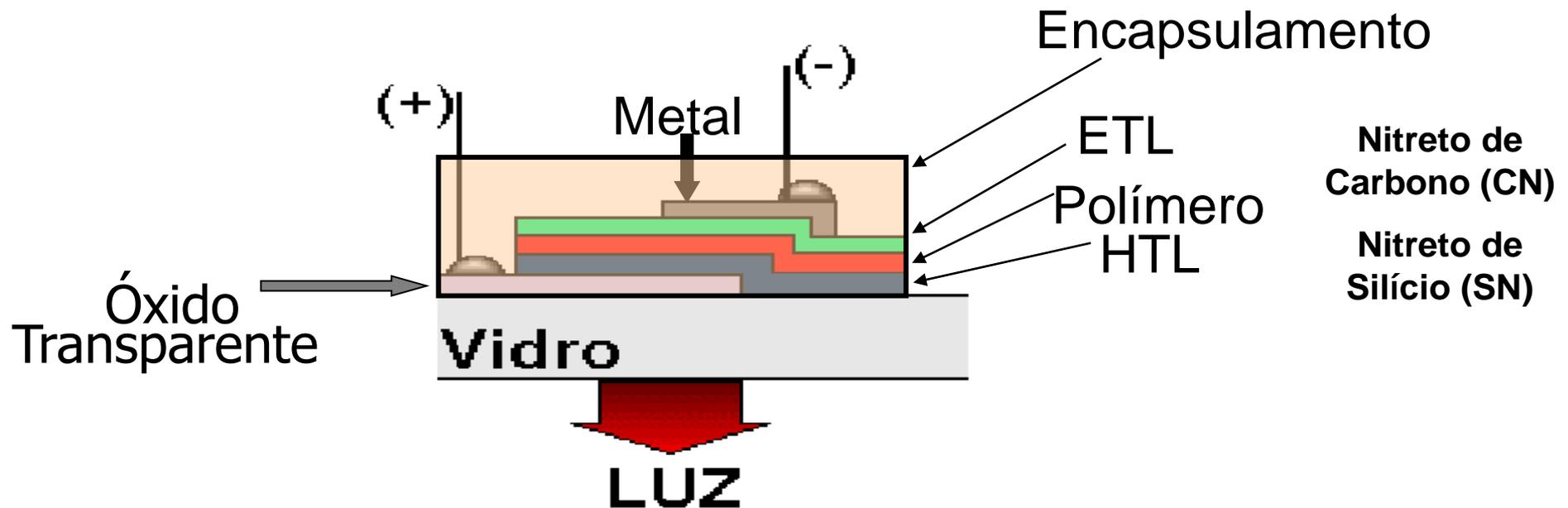


## Injeção e Transporte de Portadores

- (1) - Injeção de portadores negativos pelo catodo
- (2) - Geração de pólarons + e - (Campo Elétrico)
- (3) - Geração de um écxiton singleto
- (4) - Decai emitindo luz (Fóton)

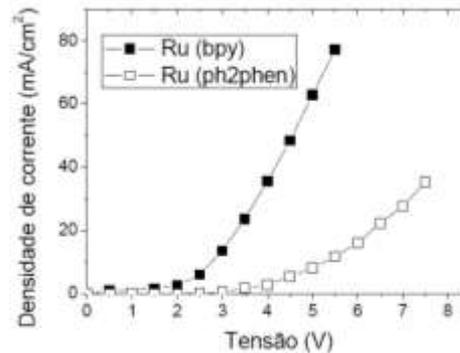
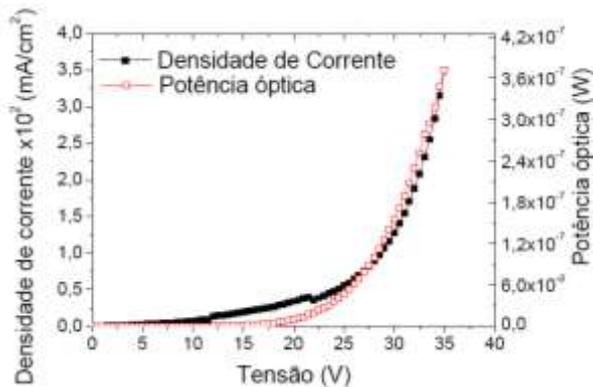
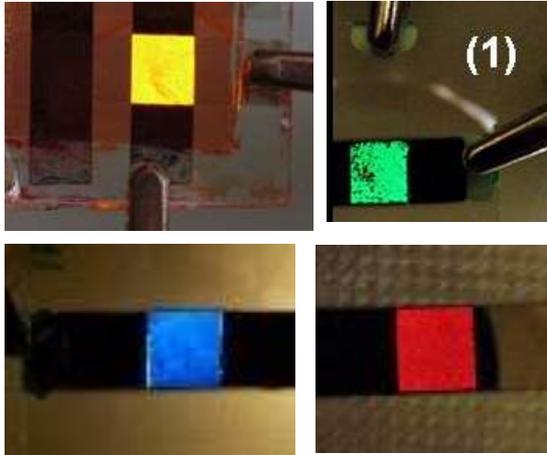


## Estrutura Melhorada



Visa obter uma maior eficiência do dispositivo (PLED)

# Diodos emissores de luz orgânicos - OLEDs



- Substratos flexíveis
- Diferentes cores
- Baixa tensão de operação

# Células Solares

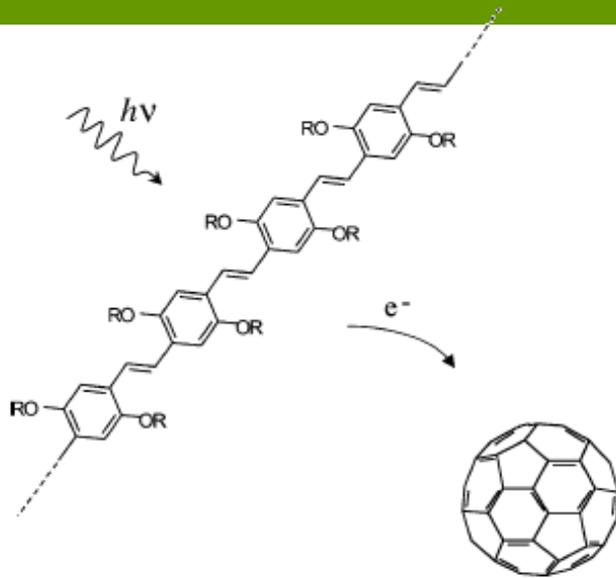
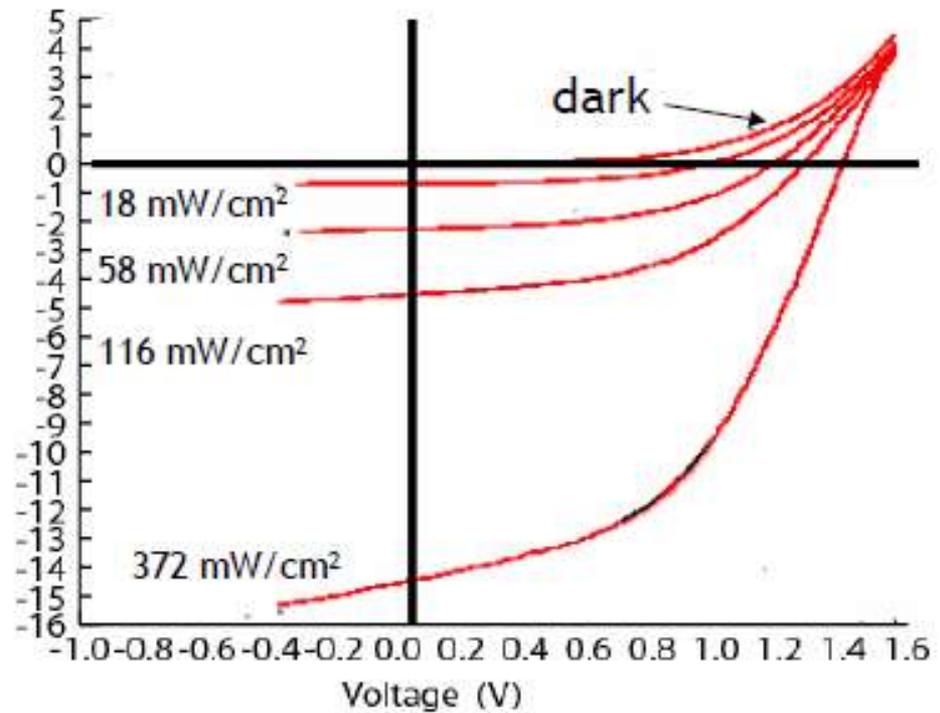
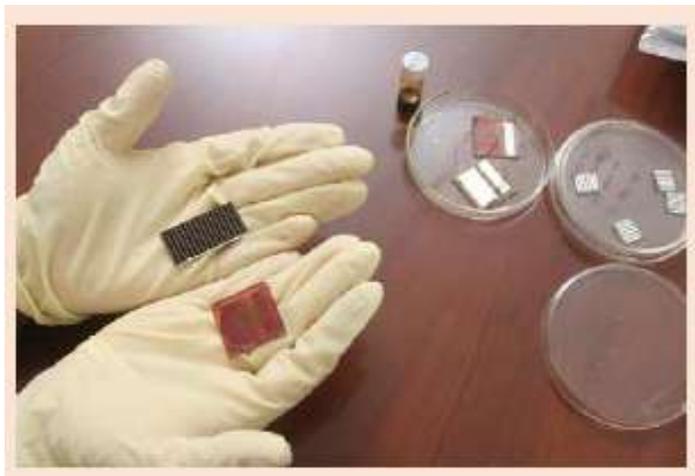
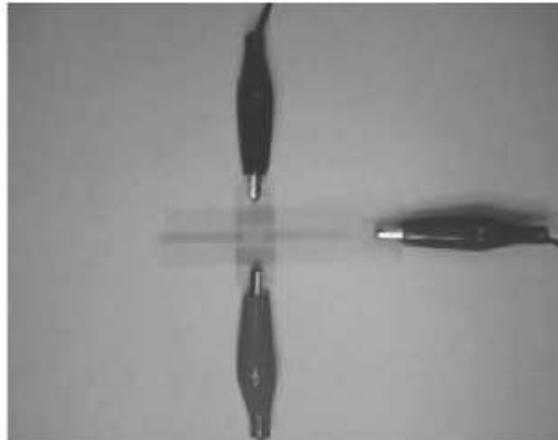


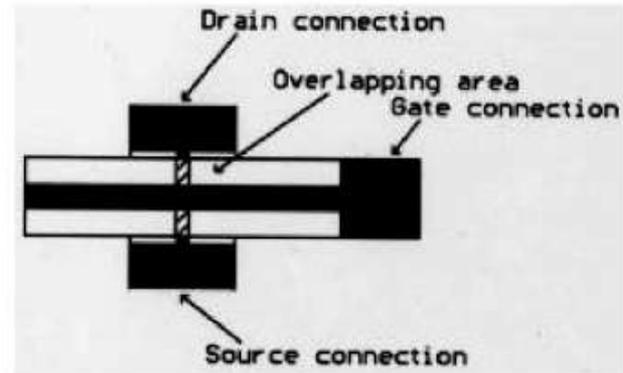
Fig. 12. Illustration of photo-induced electron transfer from a conjugated semiconducting polymer to C<sub>60</sub>.



# Transistores



FET-type device



Field effect configuration

Fig. 13. Field effect doped "PEDOT".

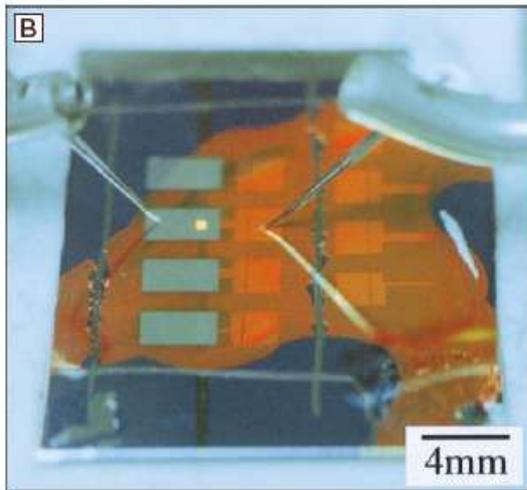
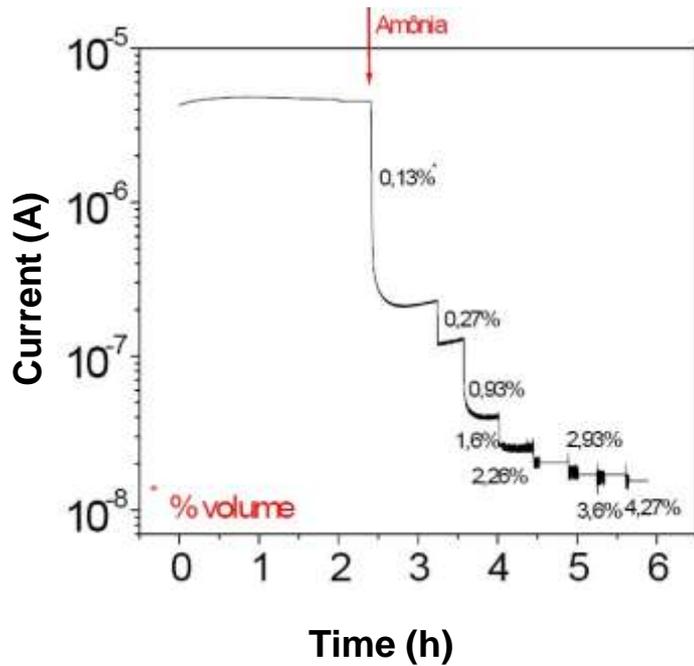
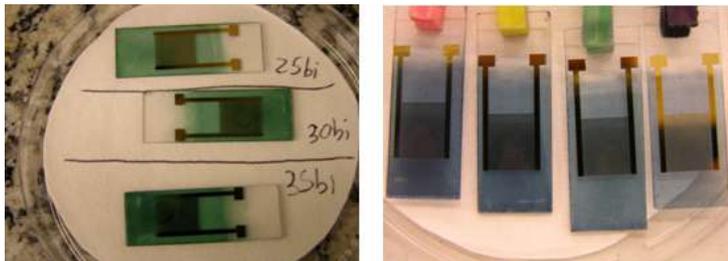
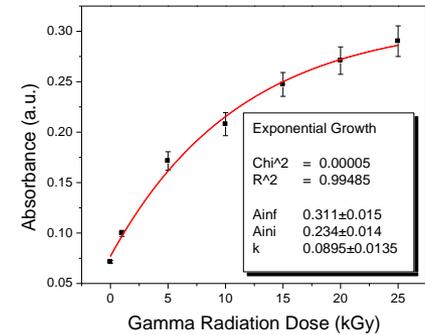
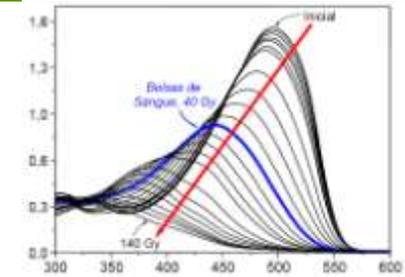
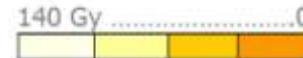


Fig. 14. FET-type device.

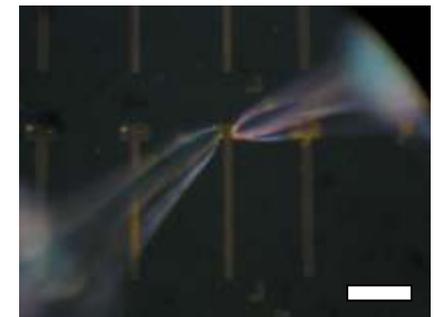
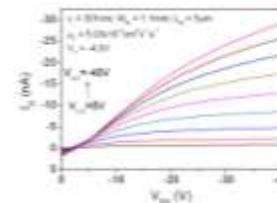
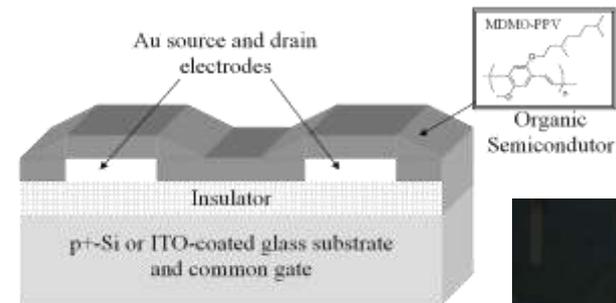
# Sensores



## Dosímetros de radiação gama



## Sensores de amônia



# Propriedades

## Materiais

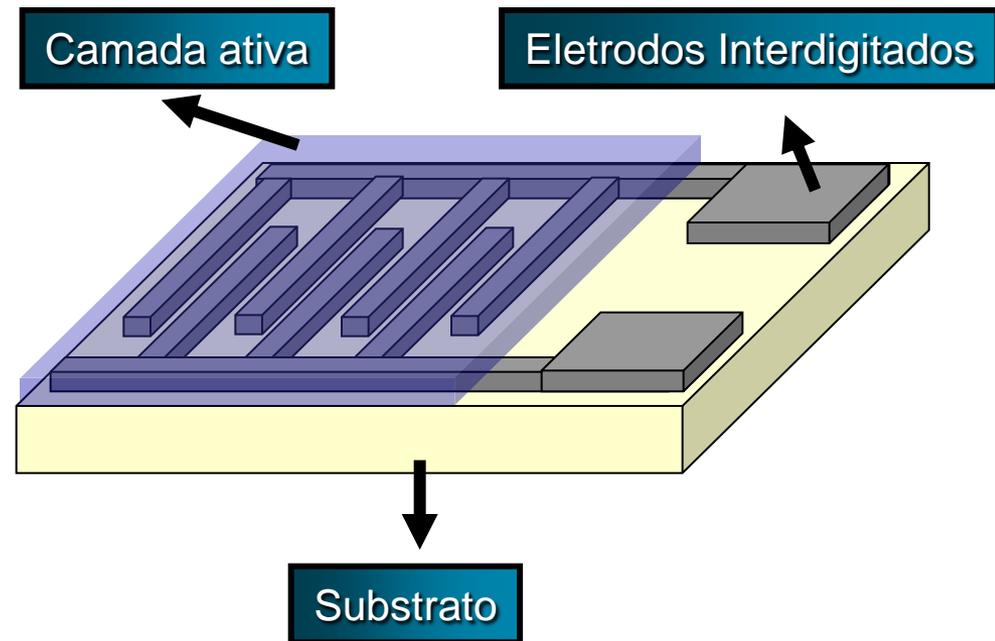
- espessura
- rugosidade
- condutividade

## Ambiente

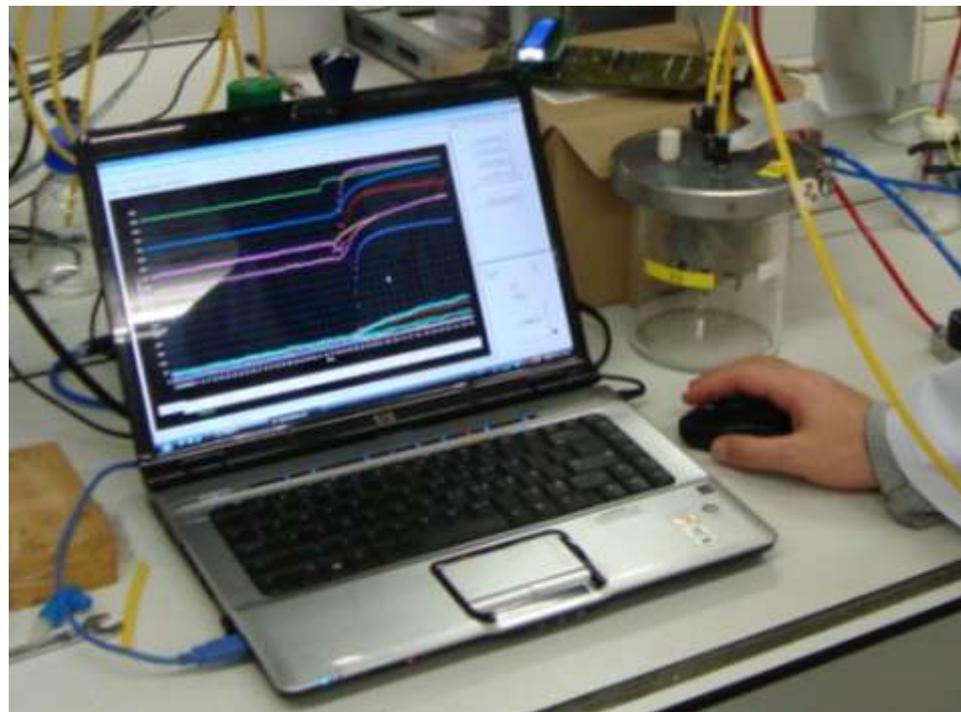
- pressão
- fluxo
- umidade
- temperatura

## Sensores

- Controle de processos
- sinais eletricos
- reprodutibilidade
- sensibilidade

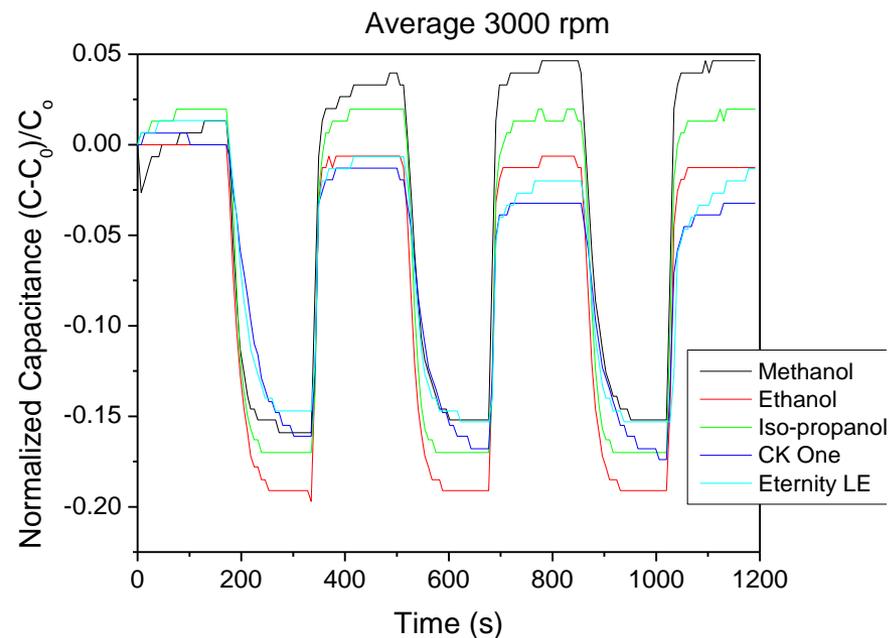
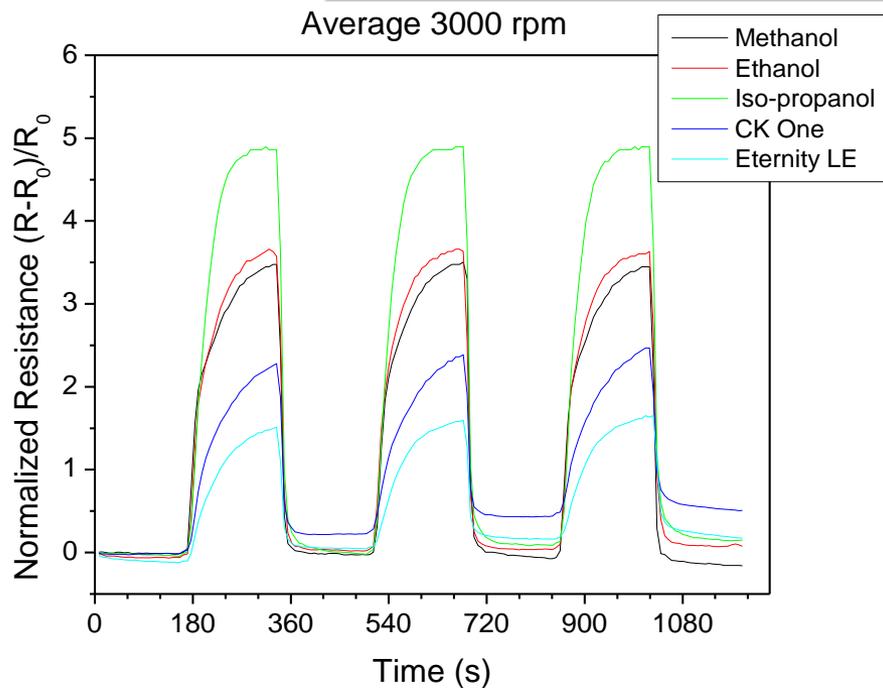


# E-Nose setup



# Diferentes analitos – PEDOT:PSS 3000 rpm films

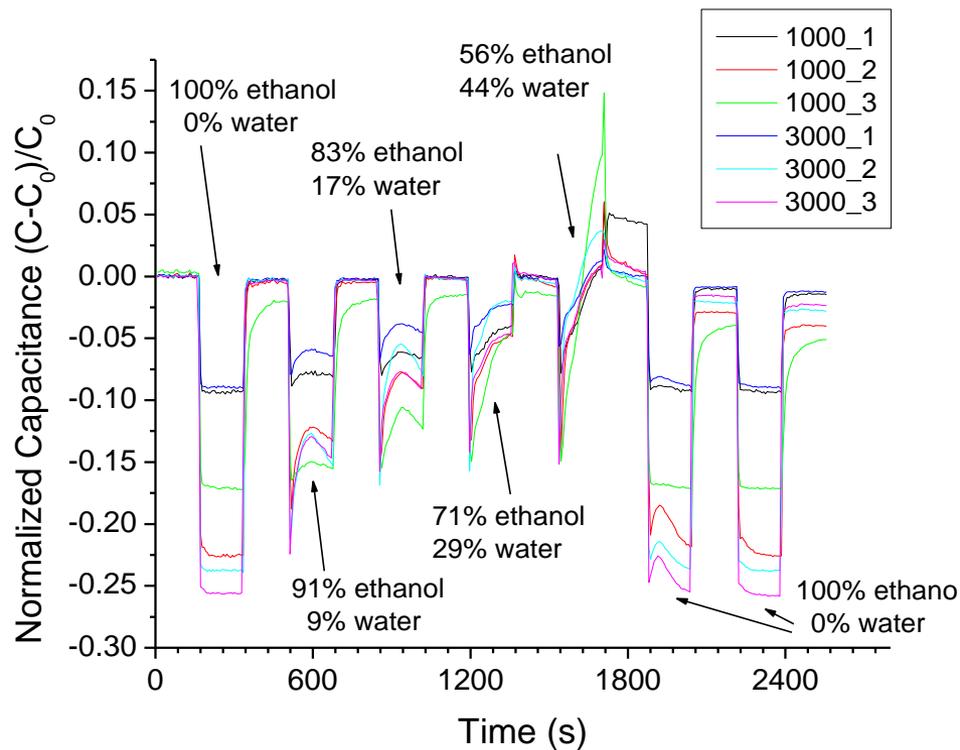
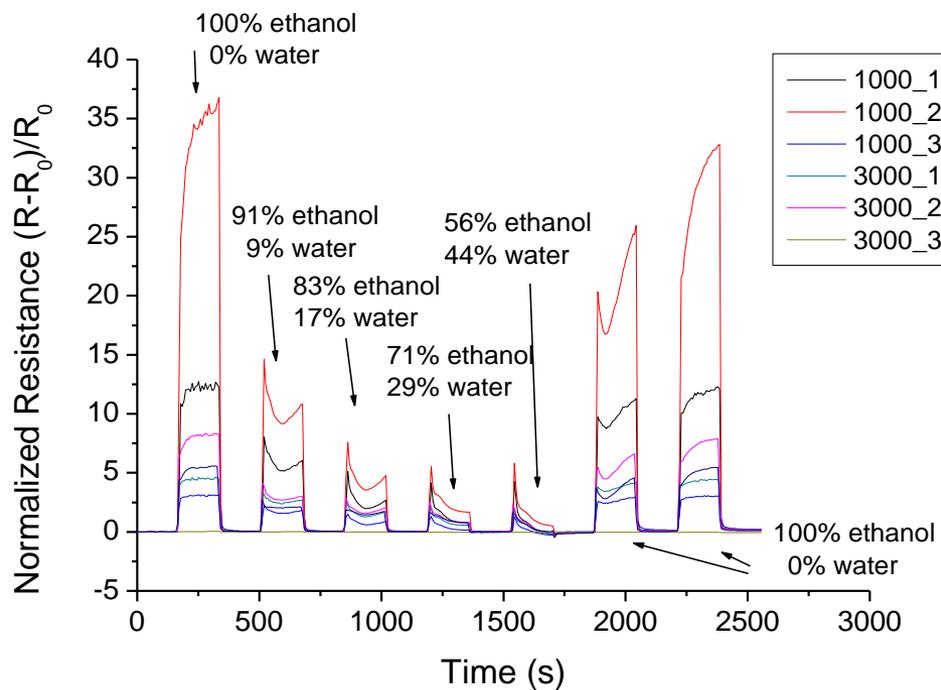
## Ar e ar com analitos



- diferentes analitos: diferentes intensidades de sinais
- Resistência tem maiores variações do que capacitância

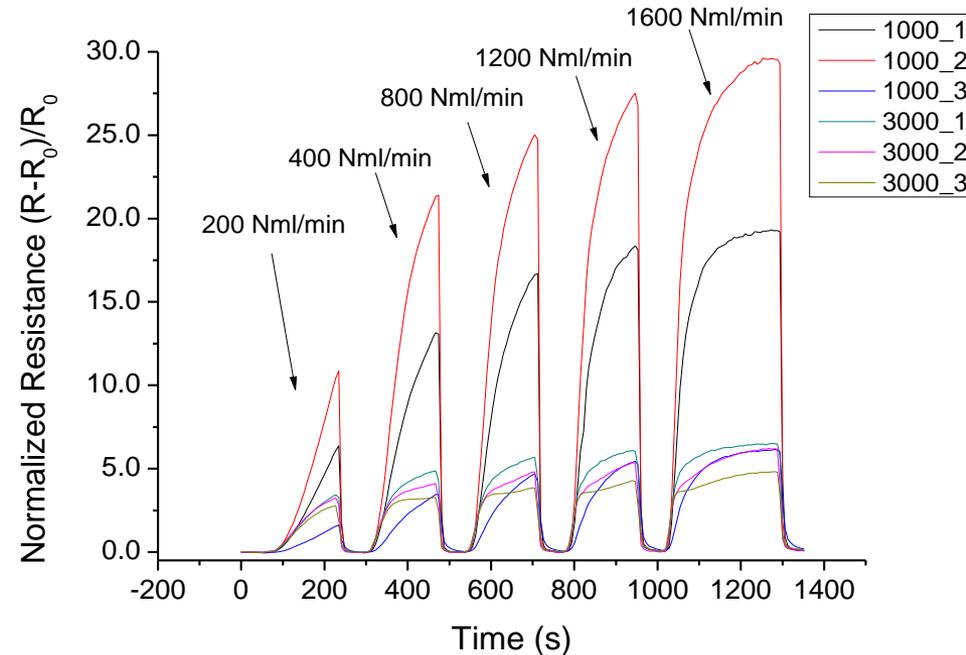
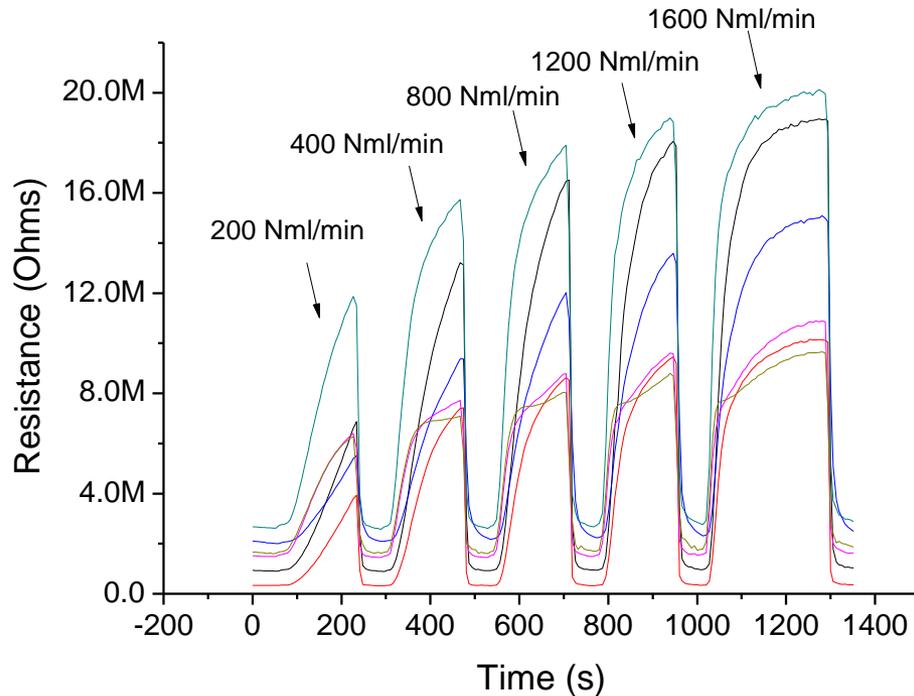
# Detecção de etanol e adulteração de combustível

Ar, Ar com etanol e ar com etanol e água



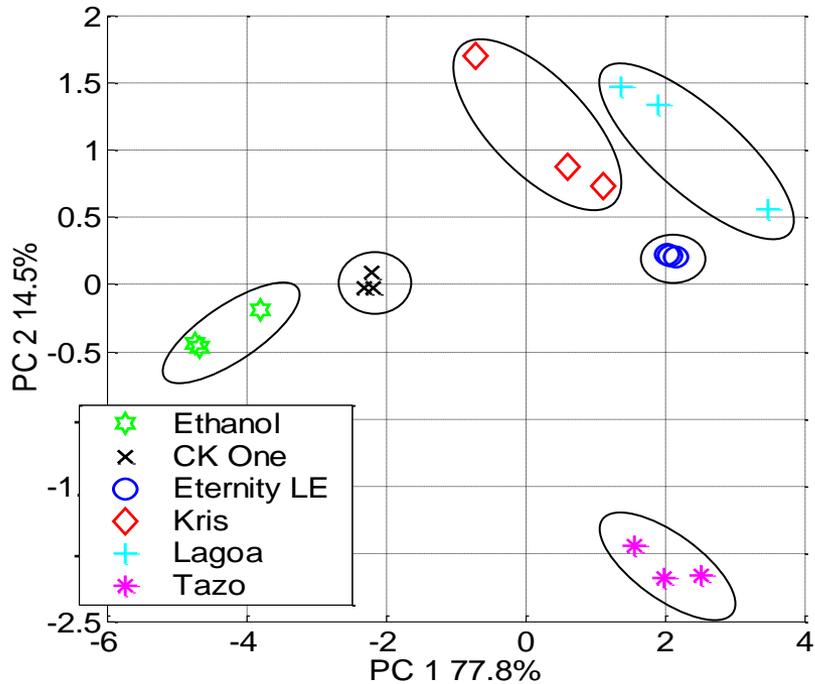
# Influência da vazão – medidas de resistência

Ar e ar com metanol

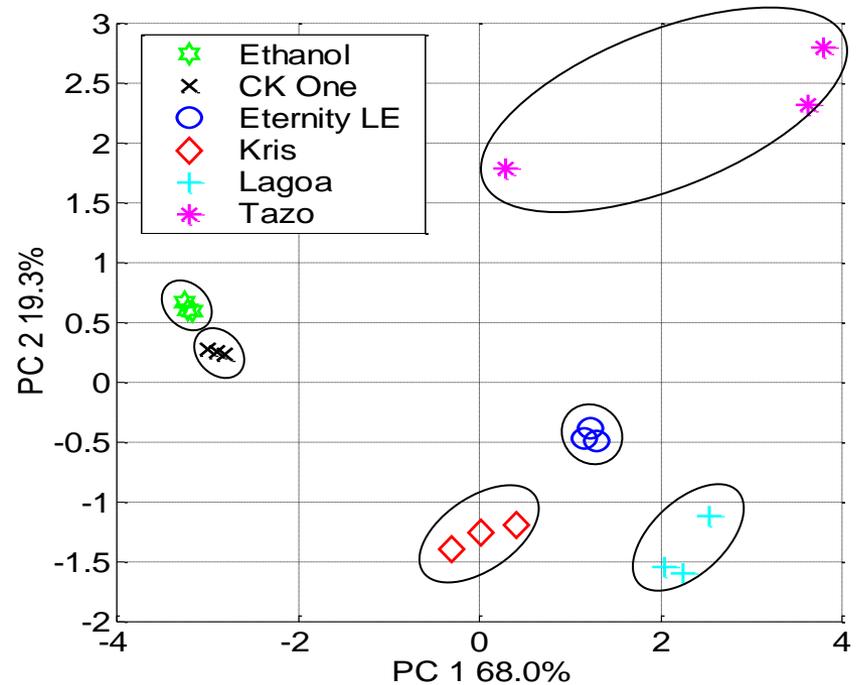


A vazão influencia fortemente a constante de tempo do sinal e não necessariamente a intensidade máxima

# Discriminação de perfumes

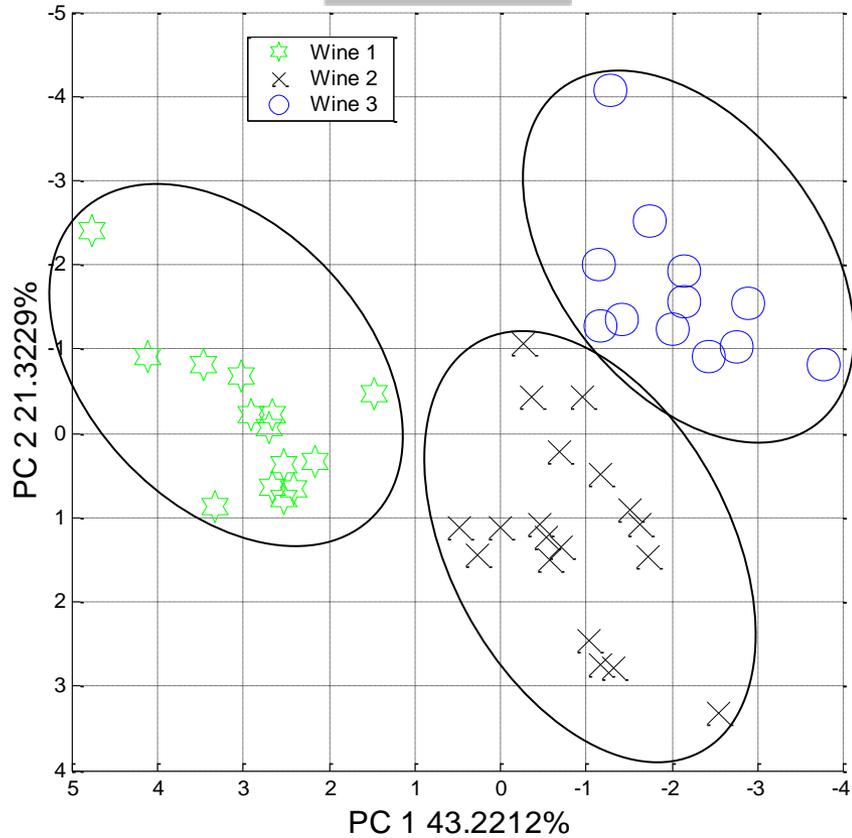


Resistência

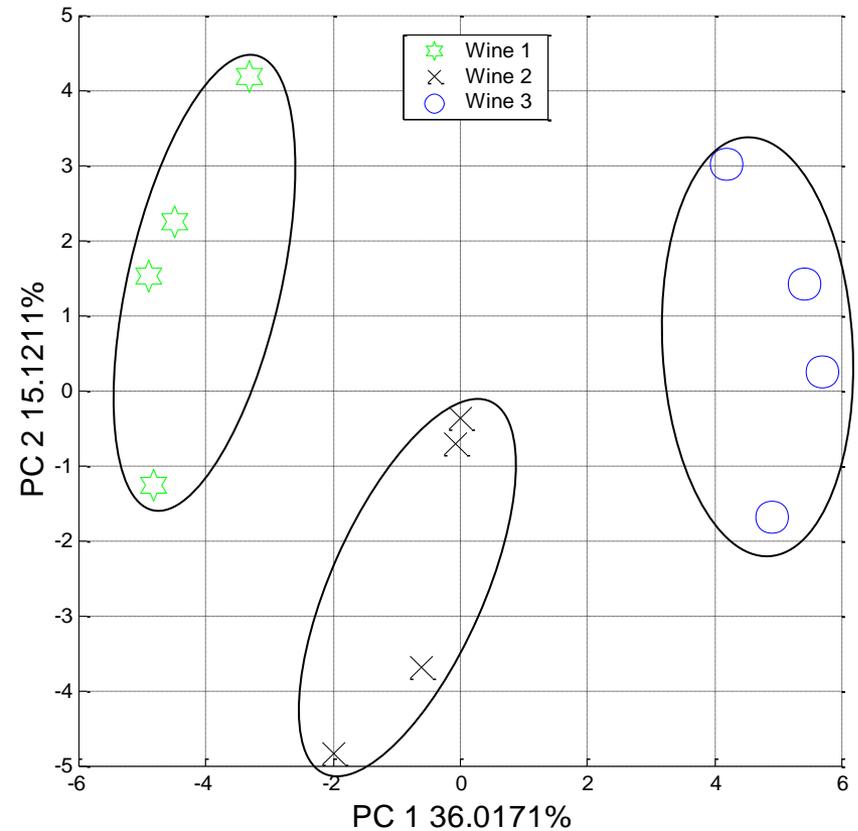


Capacitância

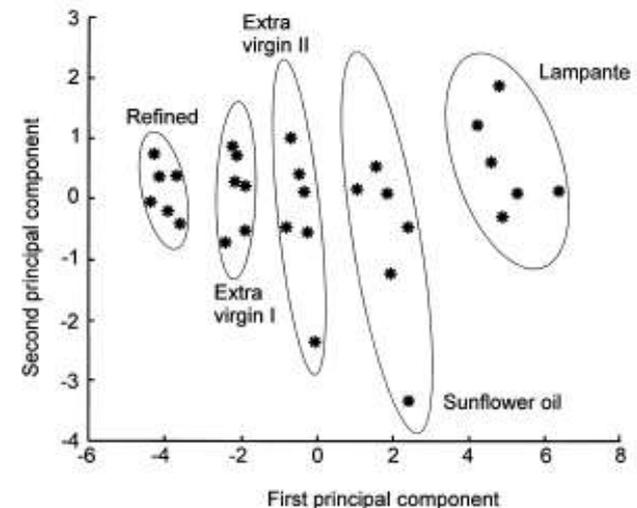
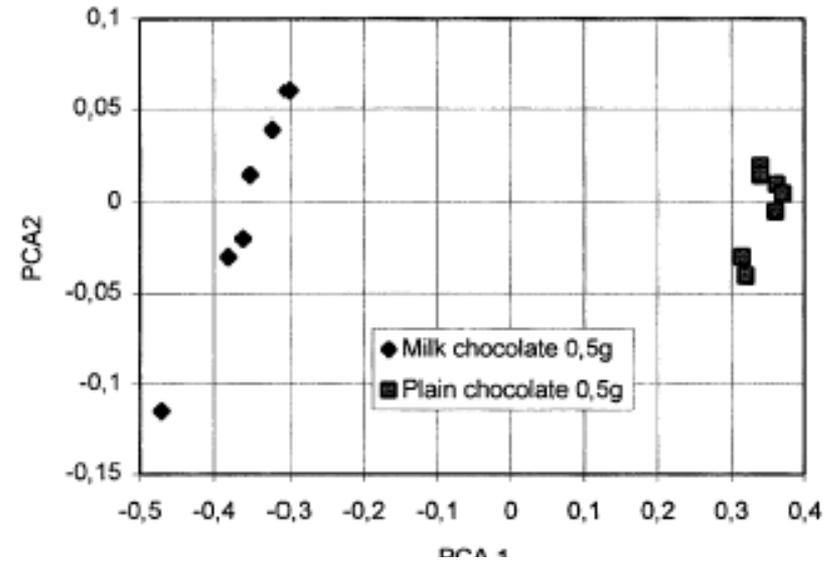
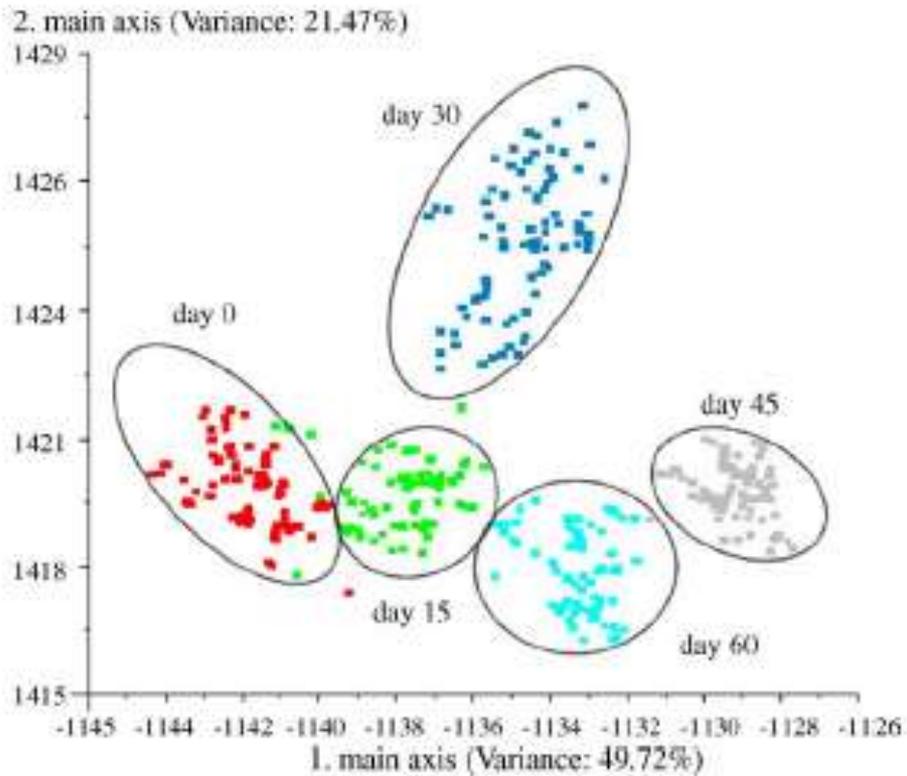
## E-NOSE



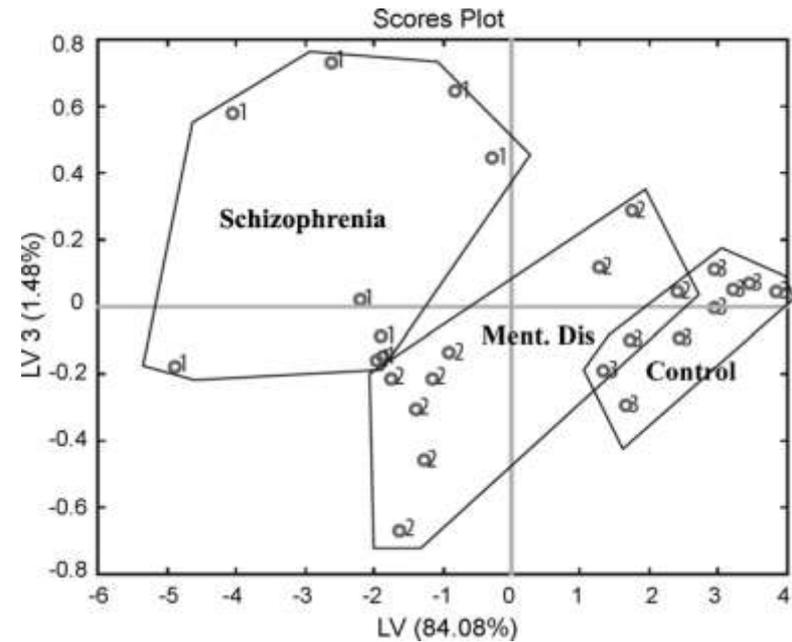
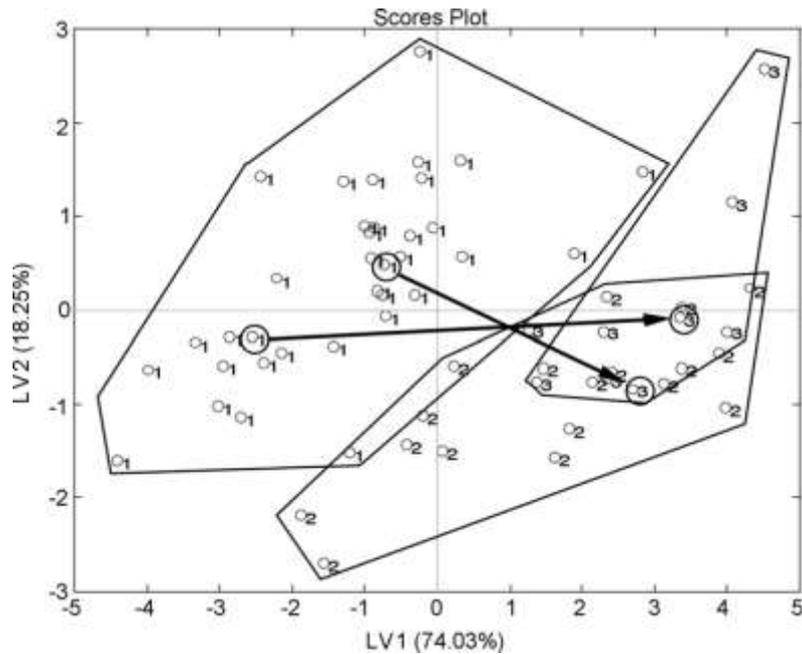
## GC-MS



# Discriminação: leite, azeite e chocolate



# Cancer de pulmão e doenças mentais



# Conclusões

A nanotecnologia é o ramo da ciência que mais cresce, fruto das “menores” descobertas!!!!

O carbono, tão essencial para a vida na Terra, agora mostra-se essencial para o progresso tecnológico

**O futuro é flexível!**

**Obrigado!**