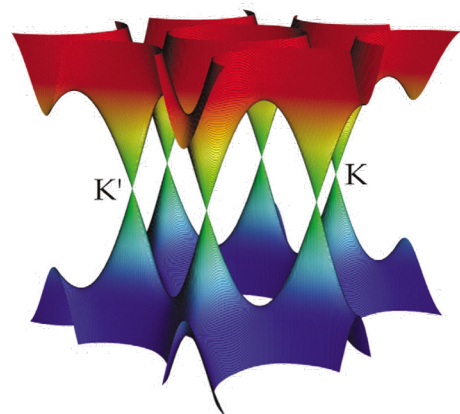


Nanotecnología: Estudiando el Comportamiento de la Materia



Dr. Ricardo Faccio

rfaccio@fq.edu.uy

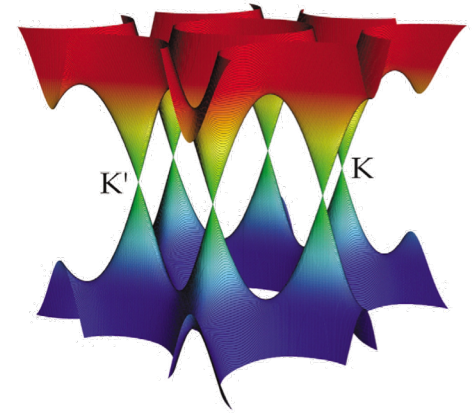
Facultad de Química, UdelaR



Charlas Académicas

Temario

1. ¿Qué es la Nanotecnología?
 1. Ejemplos
 2. Un poco de historia
 3. Aplicaciones y Conceptos
2. Nanomateriales:
 - Carbono: Fullerenos, Nanotubos, Grafeno.
 - Nanotubos inorgánicos y celdas colares
3. Conclusiones



1. ¿Qué es la Nanotecnología?

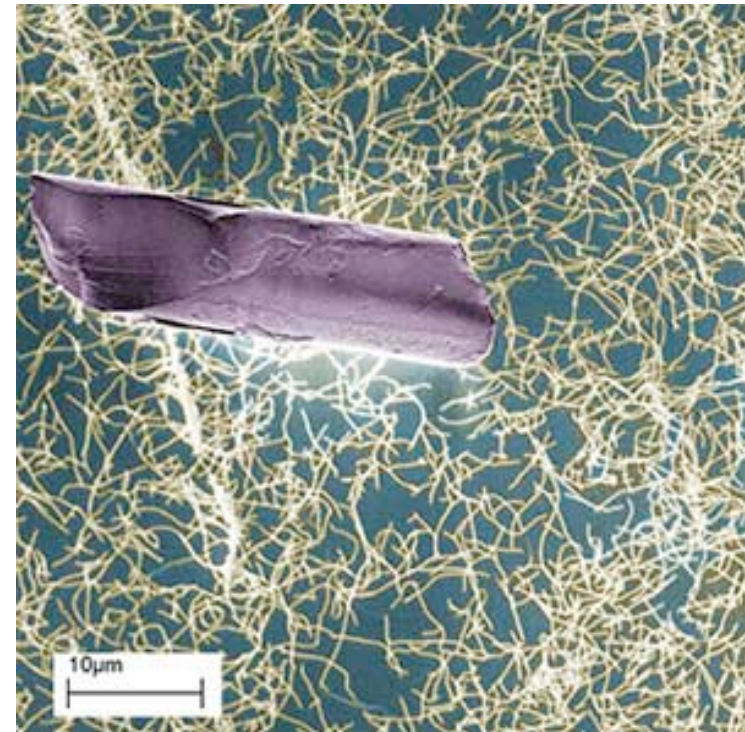
- Es el estudio y control de la materia, a una escala entre 1 y 100 nm

1 nm = 1/1 000 000 000 m

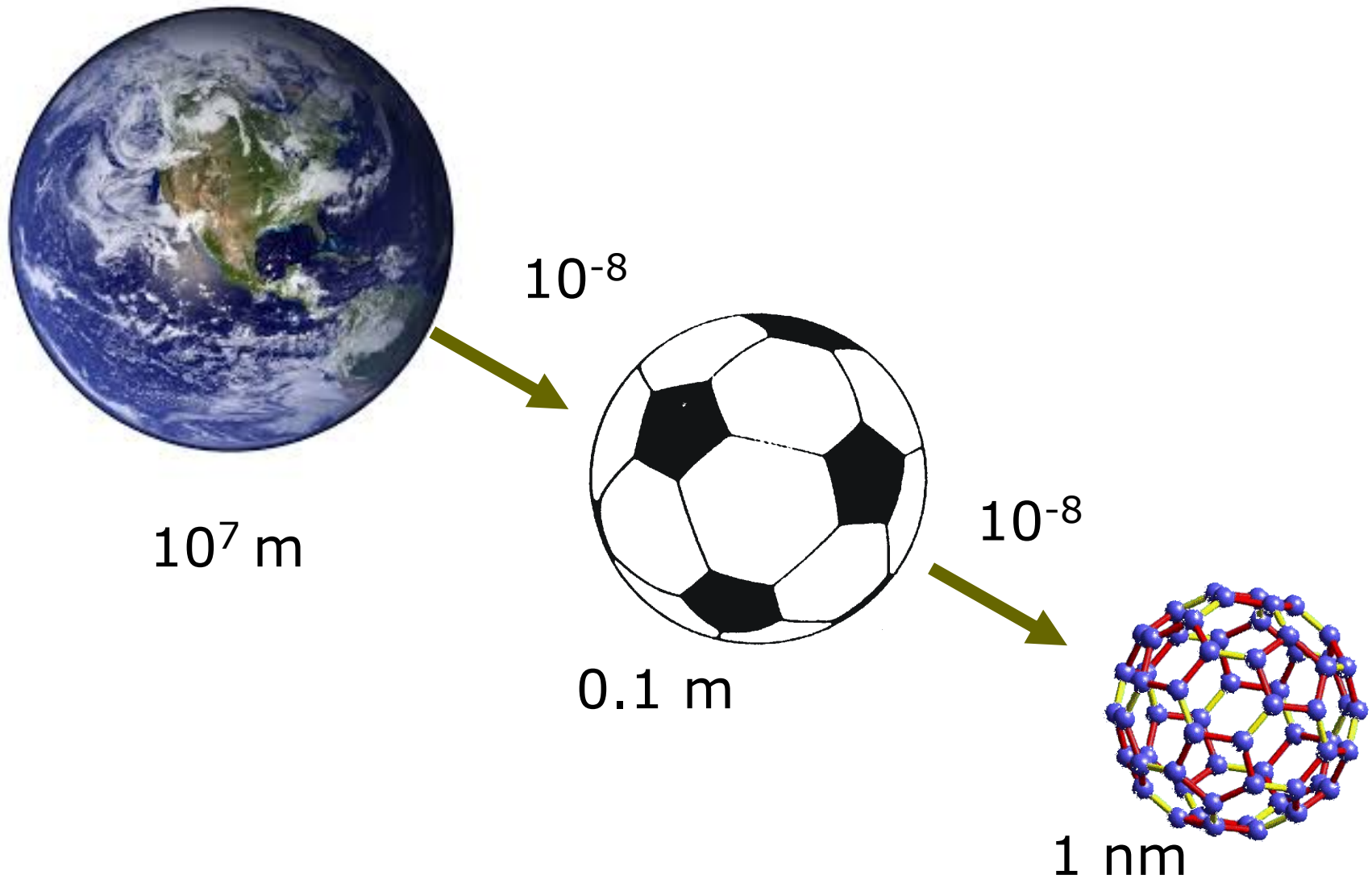
1 nm = 1×10^{-9} m

La nanociencia es el estudio de fenómenos y manipulación de materiales a escalas atómica, molecular y macromolecular; dónde las propiedades difieren significativamente de aquellas a gran escala.

La nanotecnología es el diseño, la caracterización, la producción y la aplicación de estructuras, dispositivos y sistemas para controlar la forma y tamaño a escala nanométrica.



1. Dimensiones

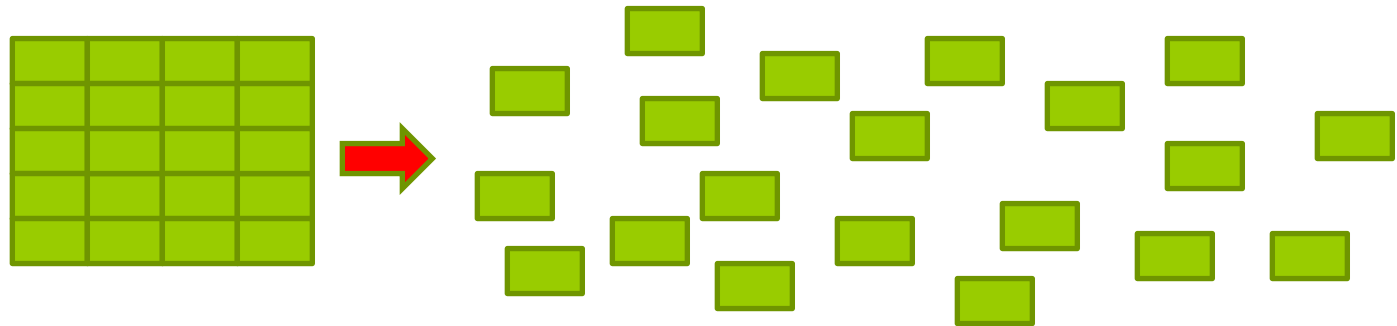


1.1 Conceptos: ¡Las propiedades dependen del tamaño!

Un material nanométrico podrá tener propiedades físicas y químicas diferentes a las que tiene en volumen.

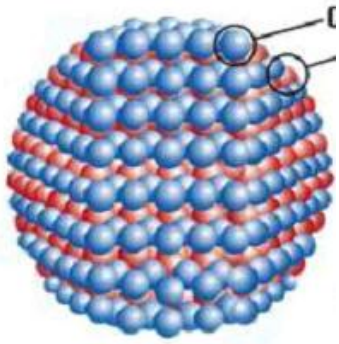
Fenómenos de superficie:

Ej. Catálisis

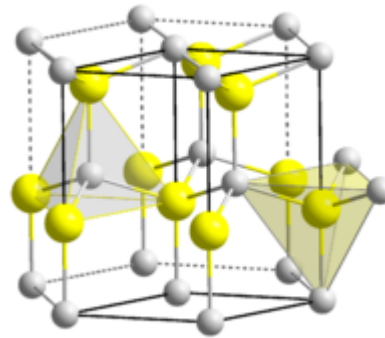


1.1 Conceptos: Confinamiento cuántico

Confinamiento cuántico
Propiedades ópticas

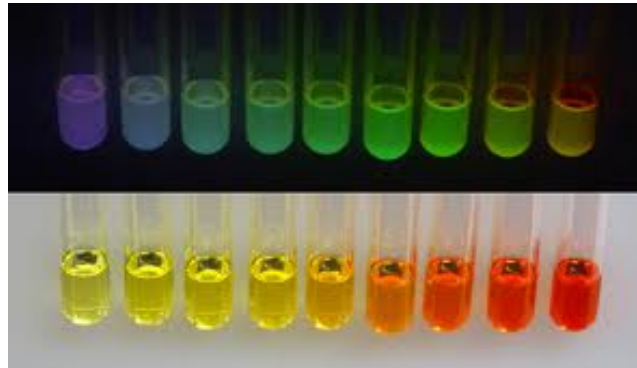
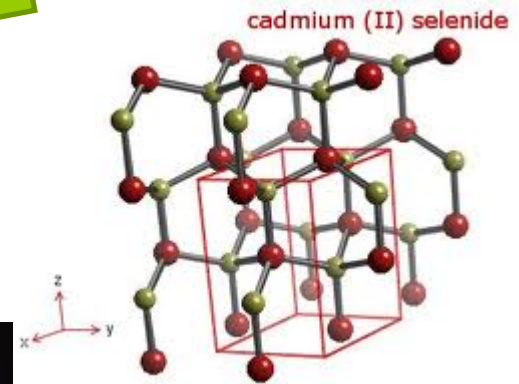


Nanocrystal



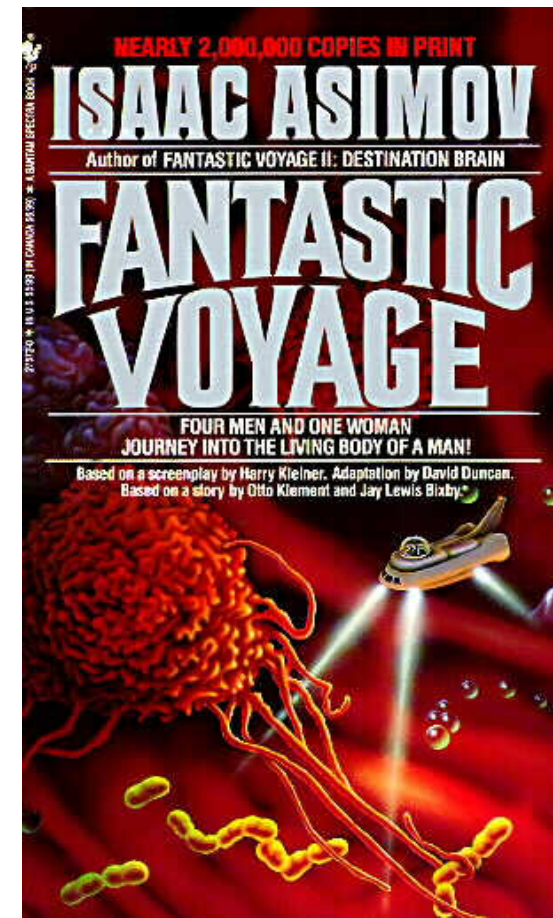
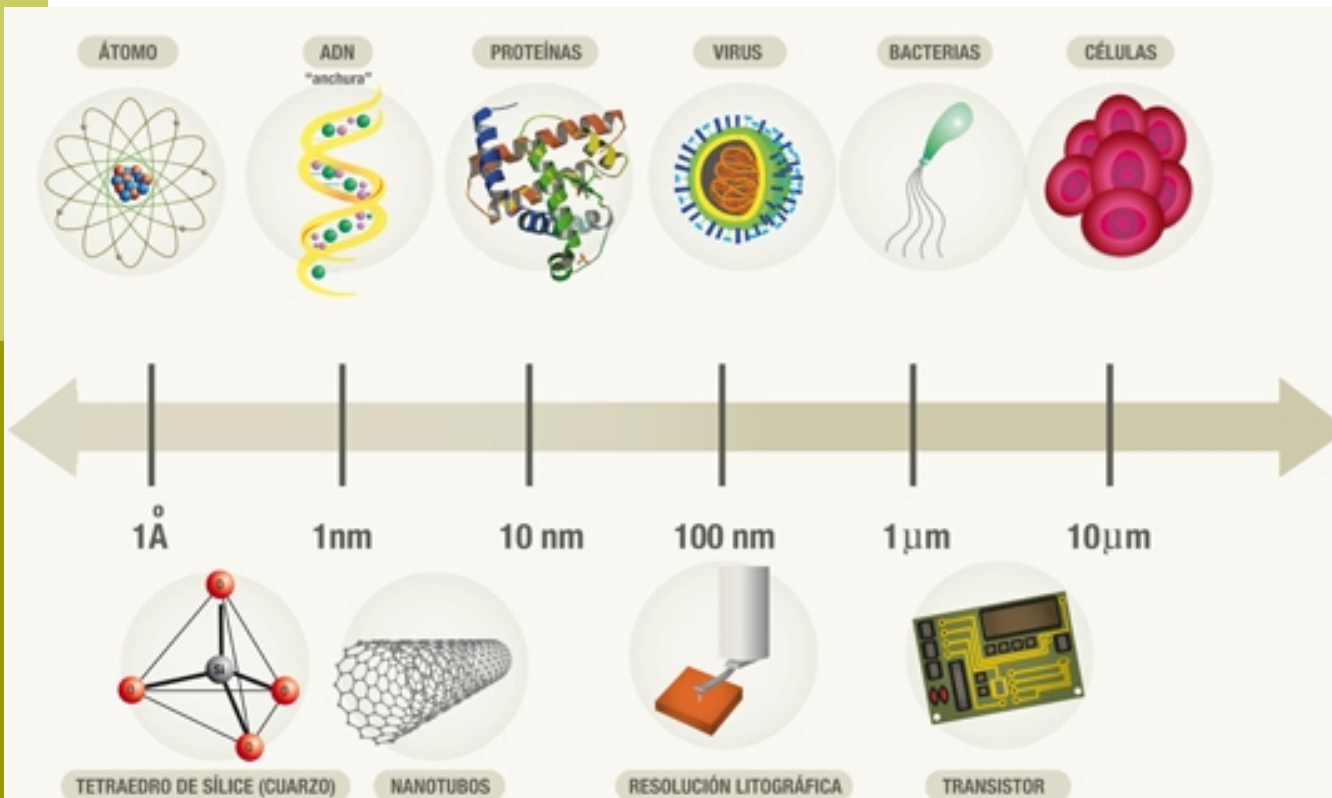
CdSe

Cristal
micrométrico

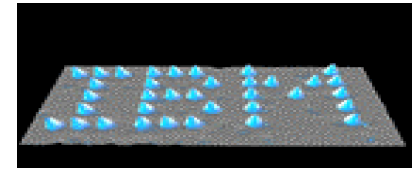


1.1 Conceptos: Escalas

- ❑ Célula: 7000 nm
- ❑ Molécula de H_2O : 0.3 nm



1.2 Un poco de Historia



1959

Feynman: primera charla hablando de máquinas moleculares de precisión atómica.

1974

Taniguchi utiliza el término "nano-technology" en un paper de ion-sputtering

1977

Drexler genera el concepto de "molecular nanotechnology" MIT (Engines of Creation)

1981

Primer paper con ingeniería molecular y precisión atómica
Se inventa el STM

1985

Descubrimiento de los Buckyball (Fullerenos)

1986

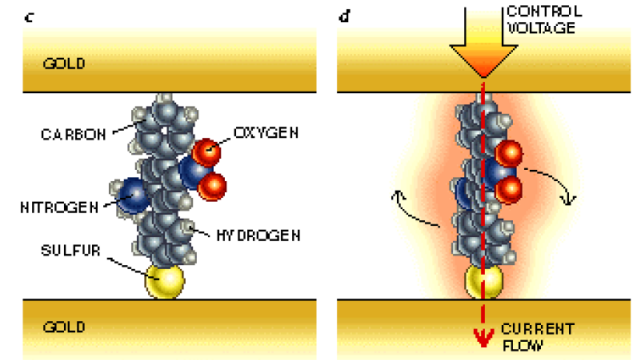
Se publica el primer libro
se inventa el Microscopio AFM

1987

Primer experimento sobre conductancia cuantizada

1988

Primer curso Universitario

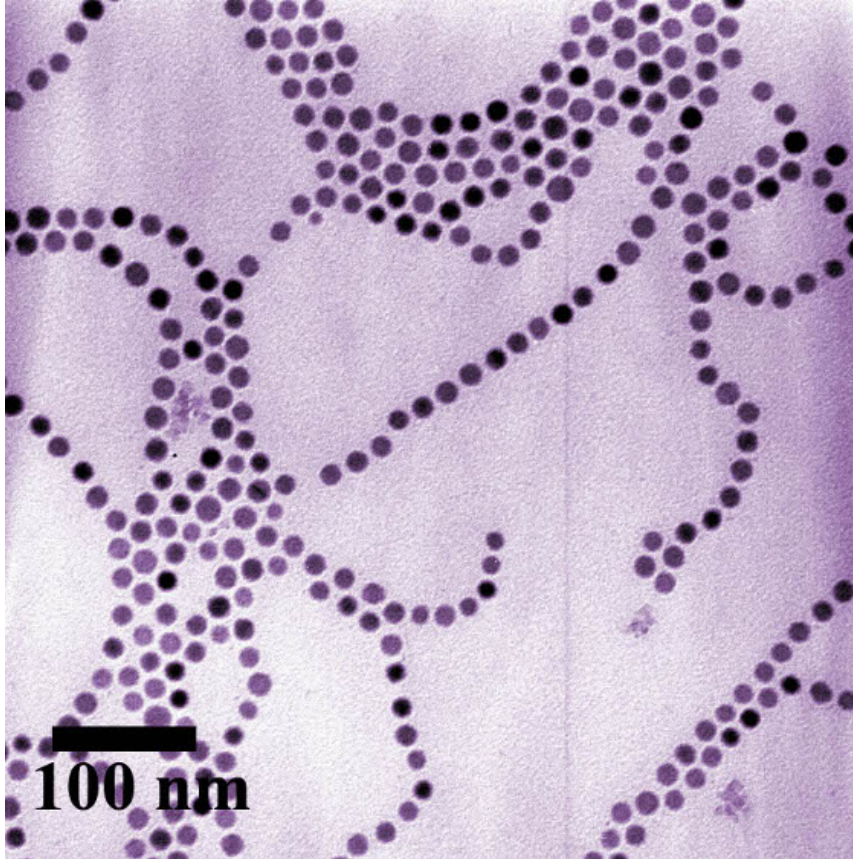
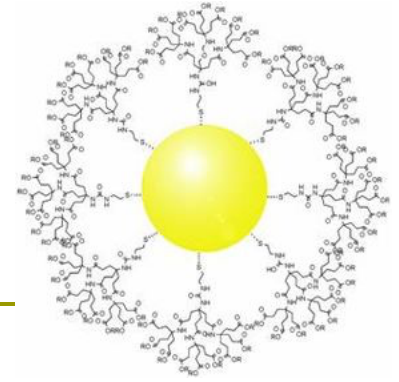


*"Capability to **manipulate**, **control**, **assemble**,
produce and **manufacture** things at atomic
precision"*

Richard Feynman
Nobel Prize in Physics 1965



1.2 Un poco de Historia



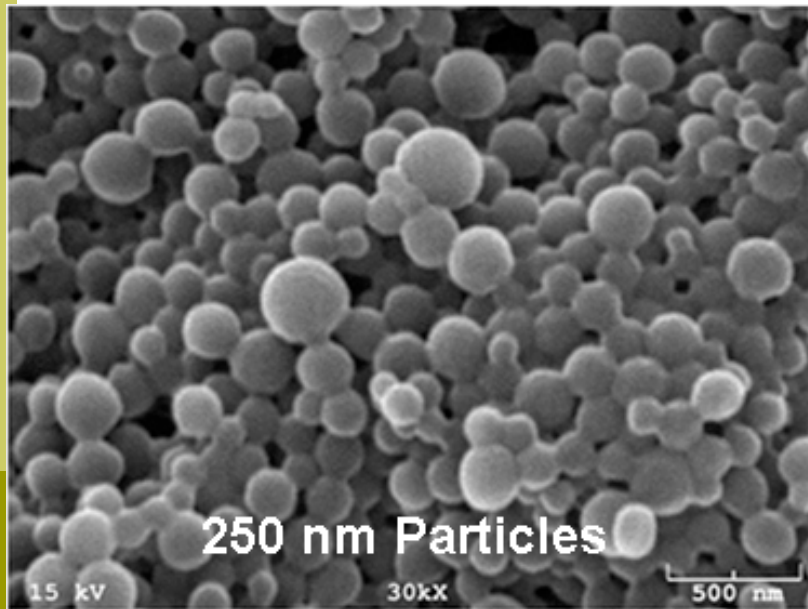
Nanopartículas de Oro



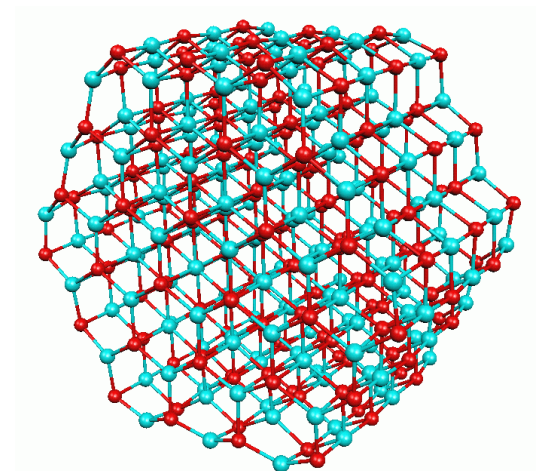
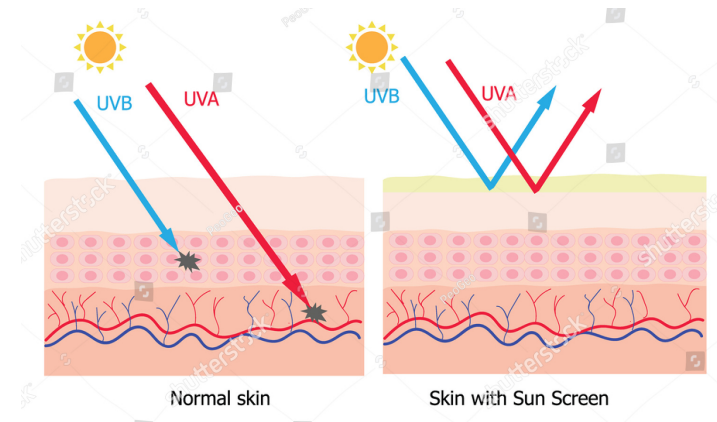
Copa de Licurgo:
Oro y plata

1.3 Productos Comerciales

Nanopartículas de óxido de Zinc y de Titanio: ZnO y TiO_2



Propiedades ópticas:
Absorben en el UV
Transparente en el Visible
Bloqueador Solar



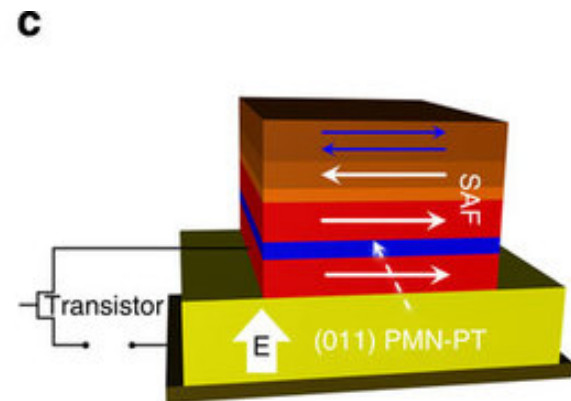
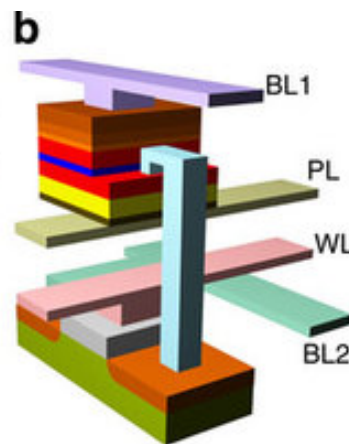
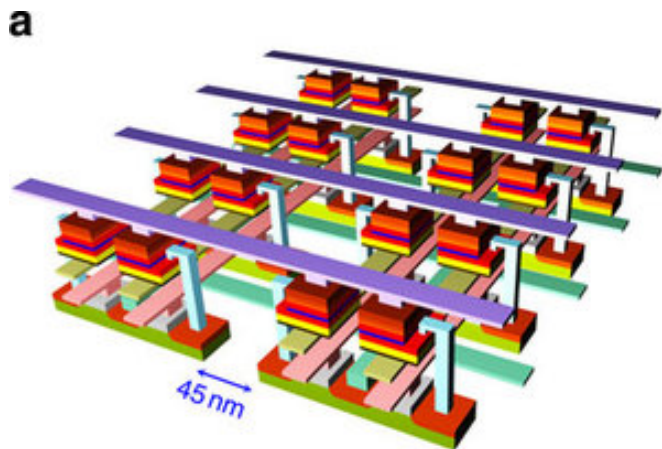
Nanopartícula de Óxido de Zinc

1.3 Almacenamiento de Datos

Incremento en la capacidad y velocidad del almacenamiento de datos



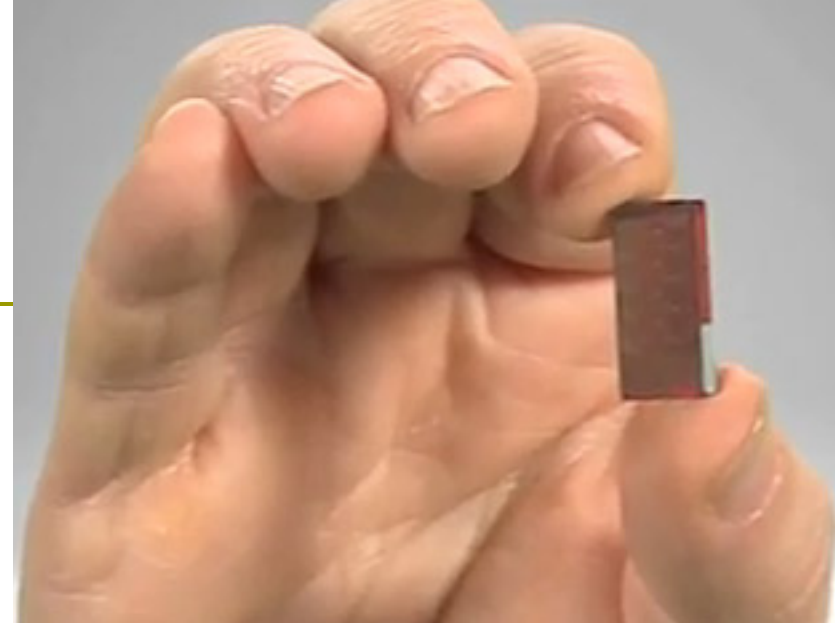
Pendrives



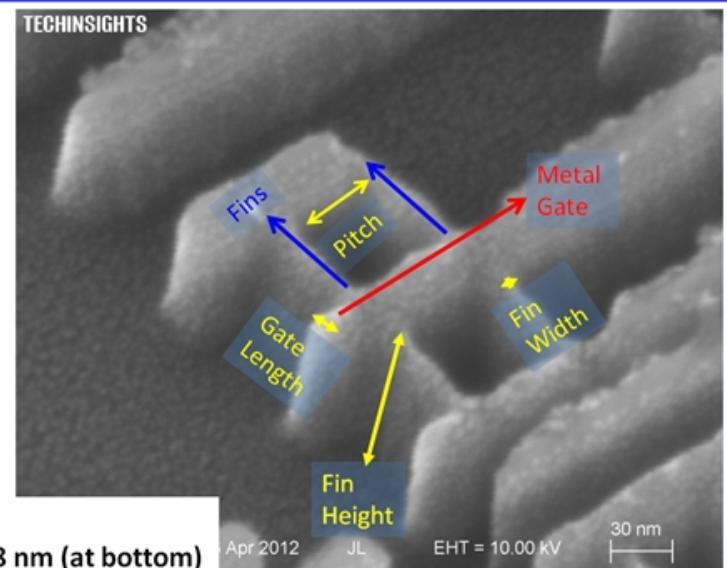
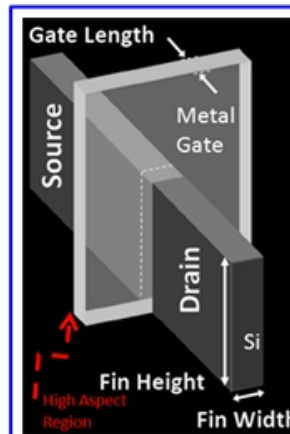
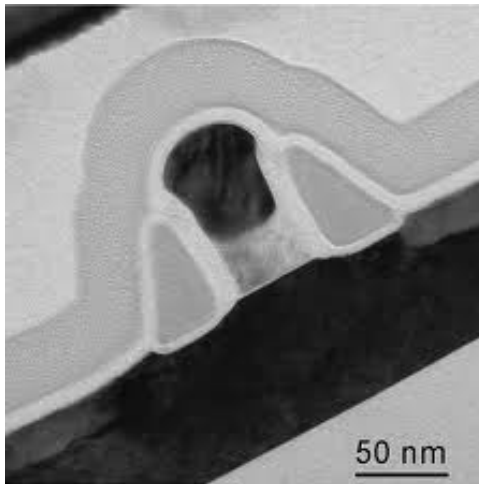
1.3 Procesadores

- Más rápidos
- Más eficientes
- Ecológicos
- Menor consumo energético

Intel 22 nm



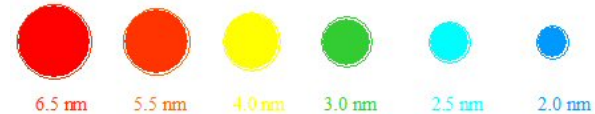
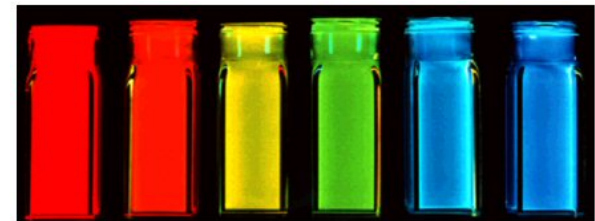
Procesadores Intel



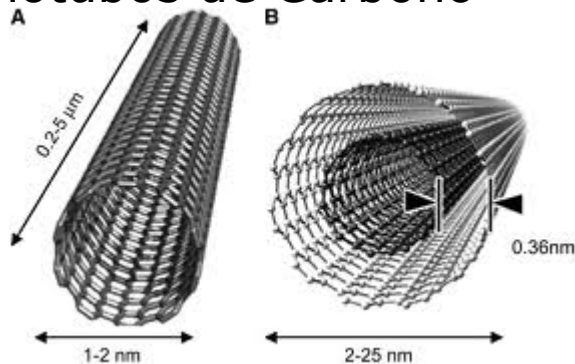
Average Gate height:
Average Fin width: 18 nm (at bottom)
Average Fin height: 35 nm
Average Fin pitch: 60 nm

Average Tri-Gate length: ~ 30 nm
Average Tri-Gate width: ~ 80 nm

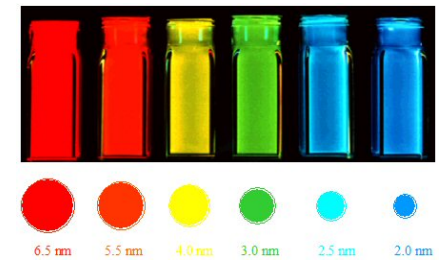
1.3 Nueva Serie de Pantallas LED



Nanotubos de Carbono



1.3 Tecnología de Pantallas

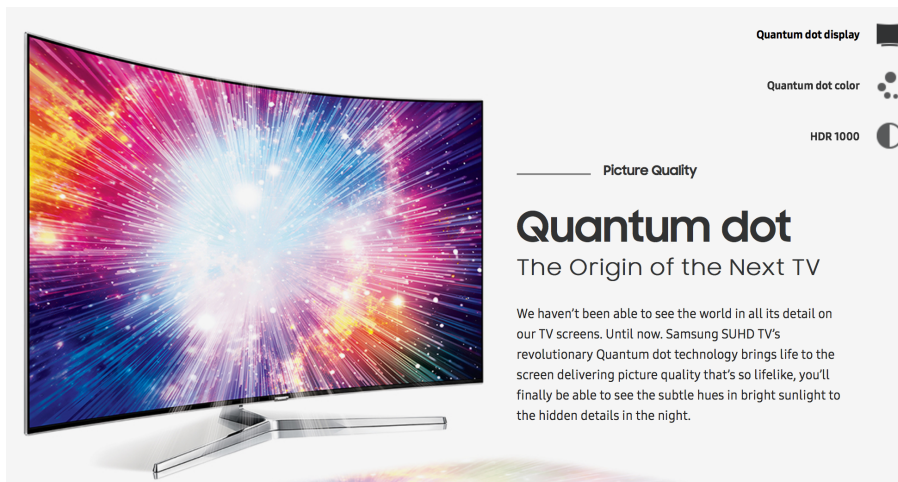
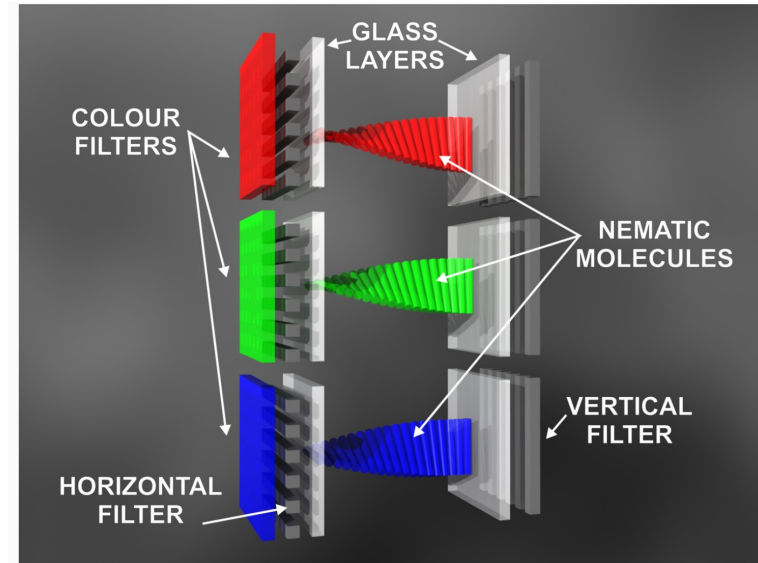


□ LCD:

- Luz Azul de fondo con filtro de fosforo para regular la intensidad de cada color:

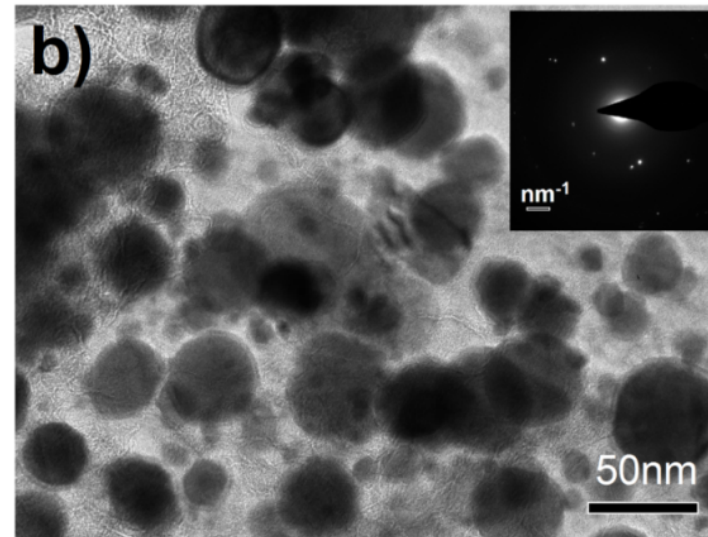
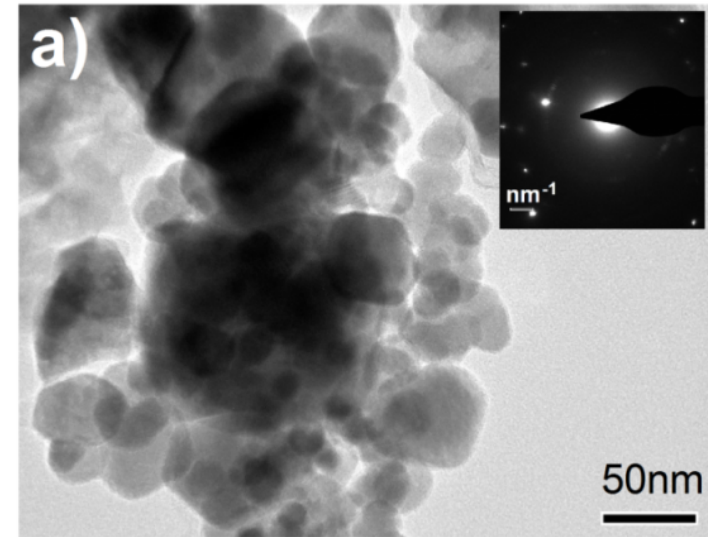
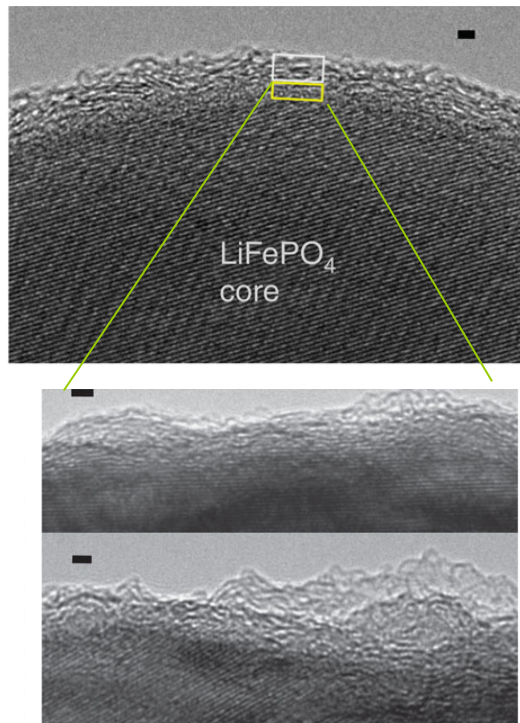
□ QDLED:

- Mantiene la alimentación trasera, pero no hay filtro de fosforo.
- Llega más luz y cada diodo emite más intensidad y a longitud de onda más definida.
- Samsung HD TV quantum dot



1.3 Baterías de ion-Litio

- Mayor durabilidad
- Mayor Carga
- Carga más rápida
- Seguridad

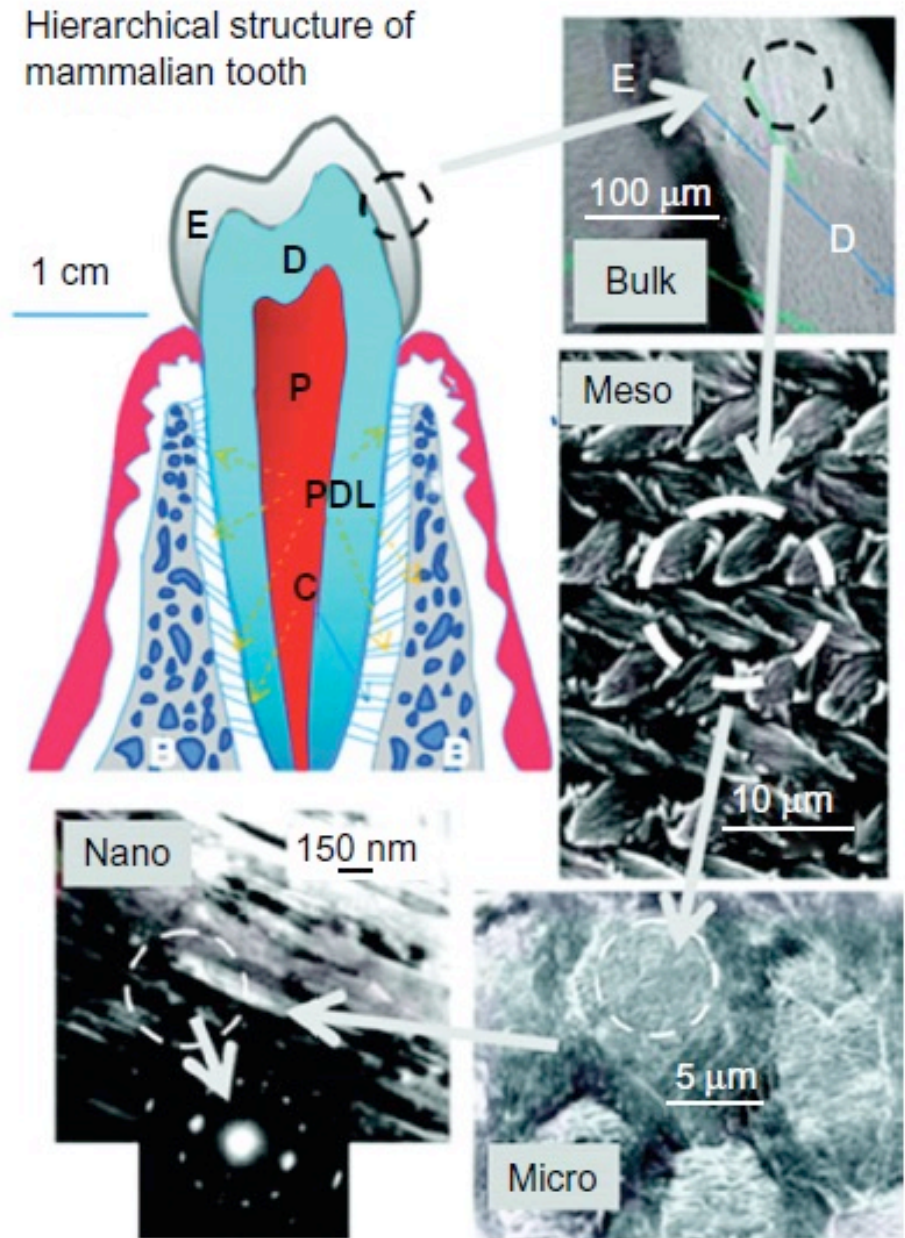
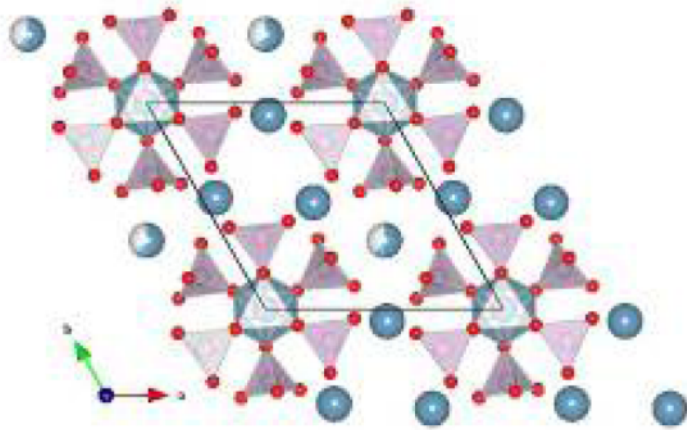
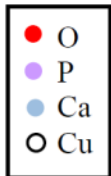


1.3 Aerogeles: Silicatos Porosos



1.3 Biomimética:

La naturaleza también usa la nanotecnología



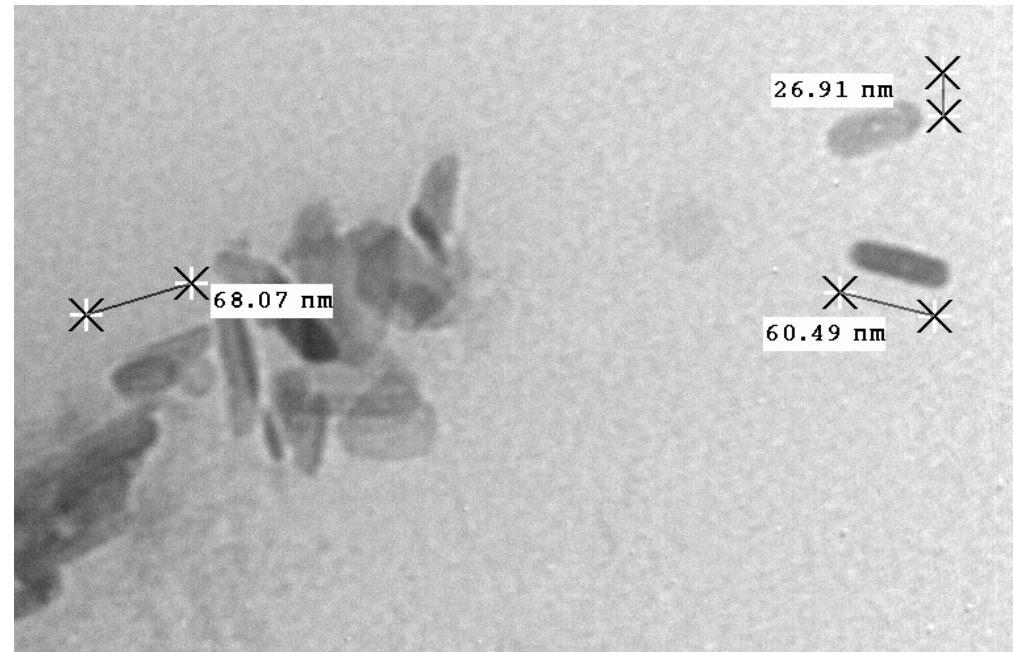
1.3 Síntesis Biomimética:

Nanocristales

La síntesis biomimética permite obtener nanocristales de HAP, de tamaño similar al que se presenta a nivel óseo.

- Largo: 30 - 50 nm
- Ancho: 20 - 25 nm
- Espesor: 1 - 4 nm

Condiciones biomiméticas:
37 °C y pH = 7



100 nm

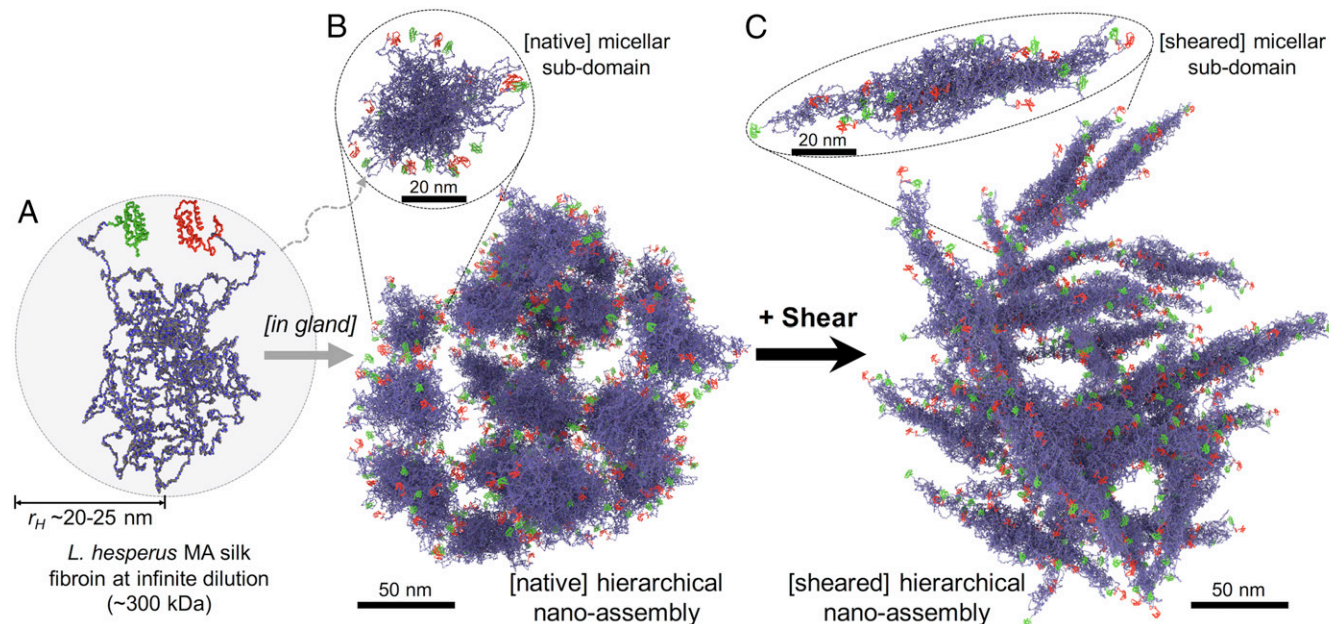
HV=80kV

TEM Mag = 150000x

1.3 Más ejemplos:

Hierarchical spidroin micellar nanoparticles as the fundamental precursors of spider silks

Lucas R. Parent^{a,b,c,1}, David Onofrei^{d,1}, Dian Xu^{e,f}, Dillan Stengel^d, John D. Roehling^g, J. Bennett Addison^d, Christopher Forman^{a,b,c}, Samrat A. Amin^{e,f}, Brian R. Cherry^{e,f}, Jeffery L. Yarger^{e,f}, Nathan C. Gianneschi^{a,b,c,2}, and Gregory P. Holland^{d,2}



1.3 Conceptos: Metodologías: Top-Down & Bottom-Up

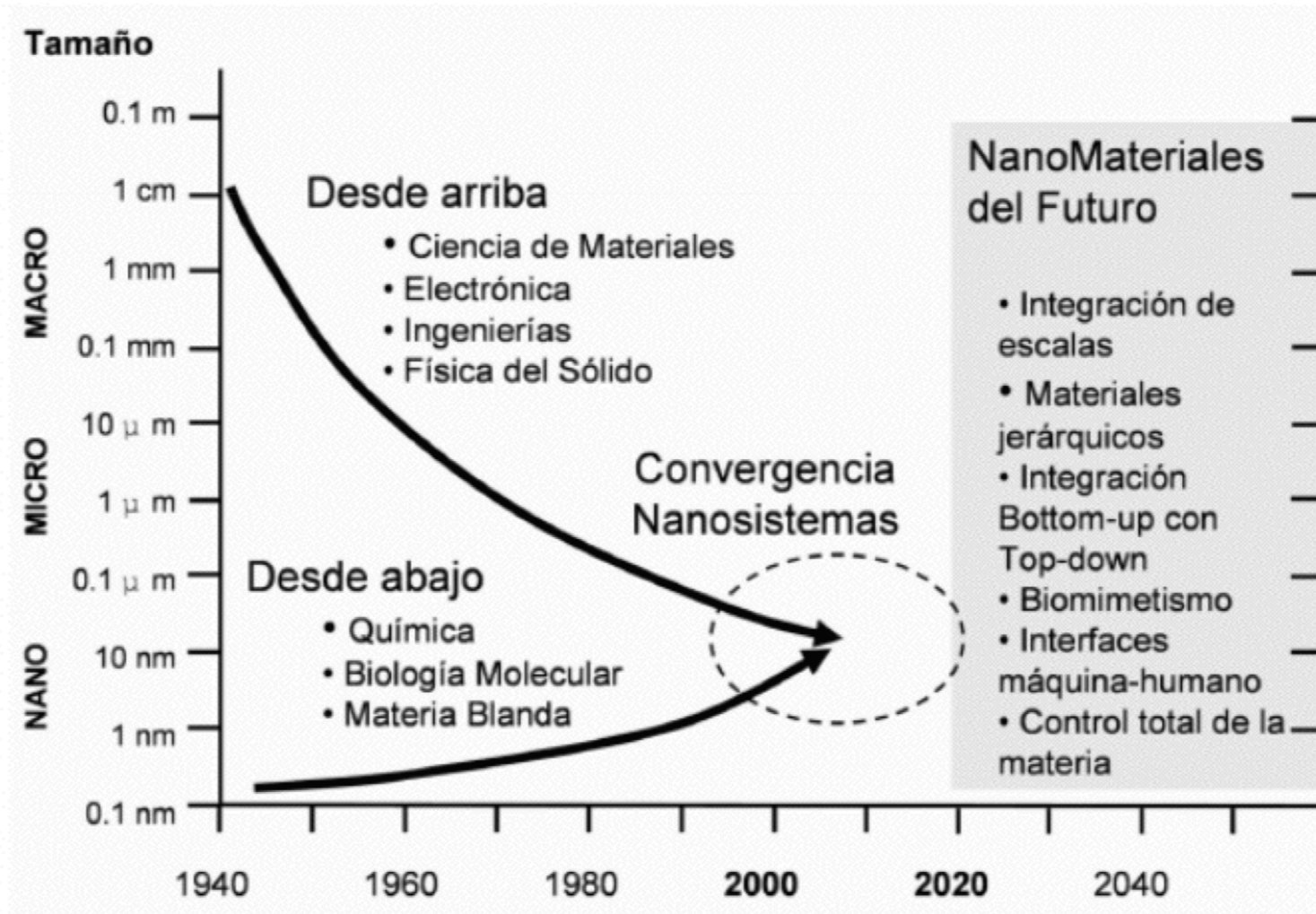
□ Top-down:

Reducción de tamaño. Los mecanismos y las estructuras se miniaturizan a escala nanométrica. Este tipo de Nanotecnología ha sido el más frecuente hasta la fecha.

□ Bottom-Up:

Auto ensamblado. Se comienza con una estructura nanométrica como una molécula y mediante un proceso de montaje o auto ensamblado, se produce el crecimiento. Este enfoque, que algunos consideran como el único y "verdadero" enfoque nanotecnológico, ha de permitir que la materia pueda controlarse de manera extremadamente precisa.

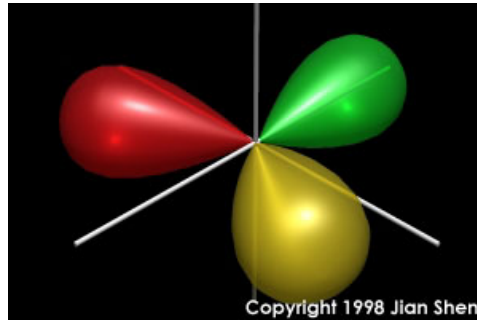
1.3 Top-Down & Bottom-Up



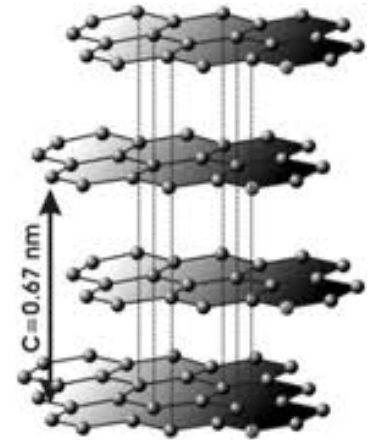
2. Materiales de Carbono



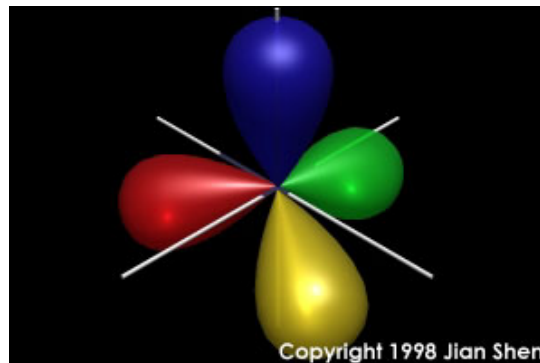
grafito



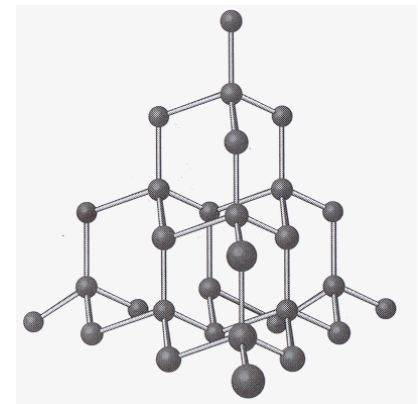
sp²



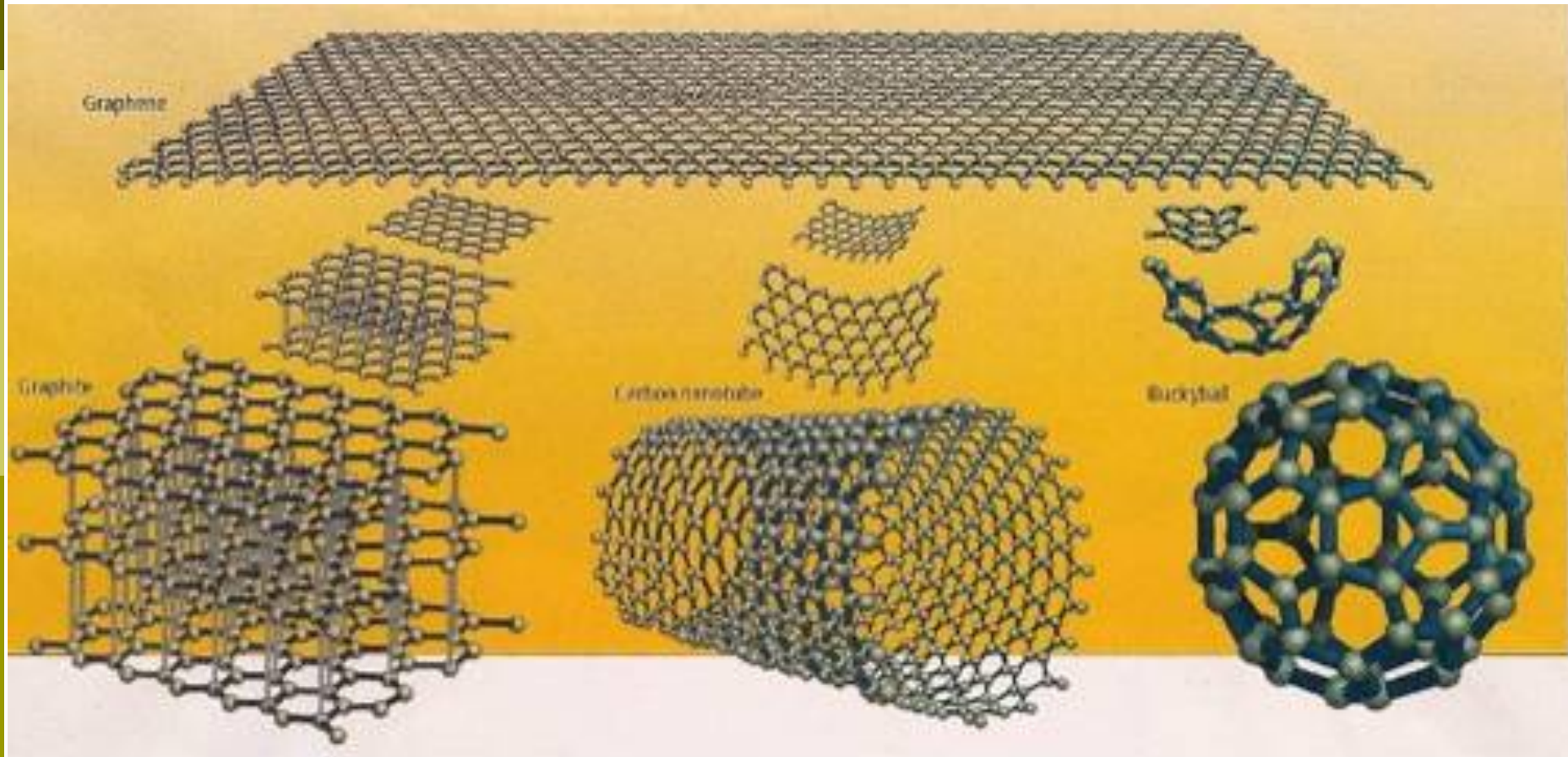
diamante



sp³

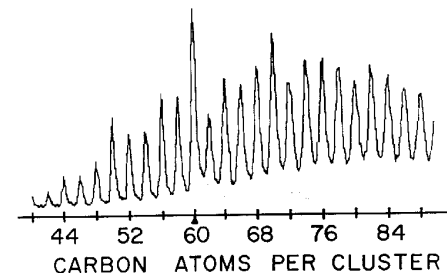
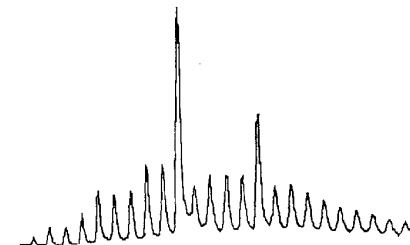
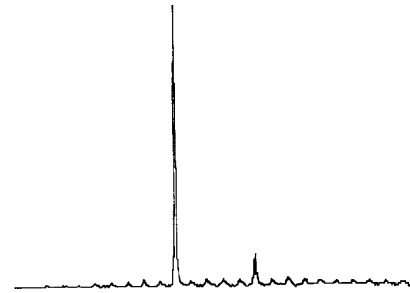
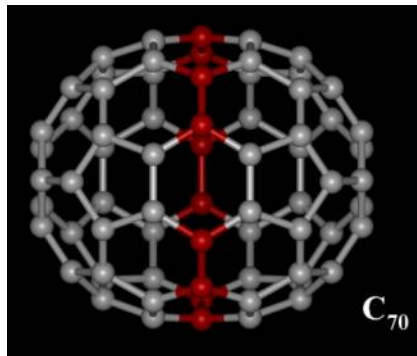
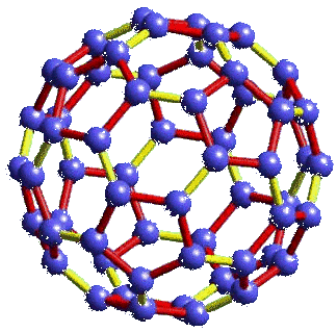


2. Otras formas alotrópicas

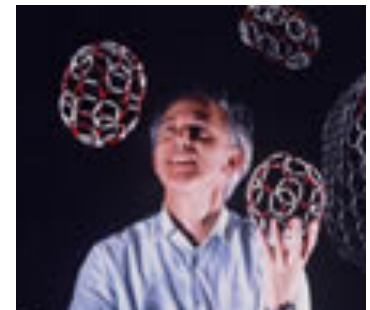


2. Fullerenos: C₆₀, C₇₀, etc.

Curl, Kroto y Smalley son desbubiertos en 1985
Reciben el Nobel de Química en 1996



**Domo geodésico diseñado por
R. Buckminster Fuller**



2. ¿Pero fueron los primeros?

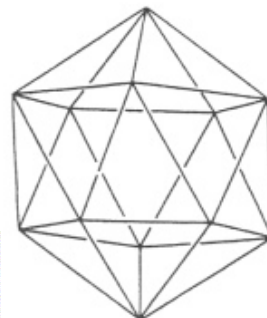
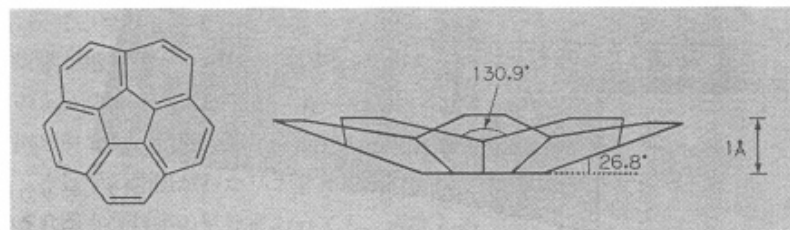
E. Osawa, predijo la posibilidad de una molécula estable de C_{60} en 1970 usando un simple modelo de Hückel.

Fue su único artículo publicado en Japonés!

Russian quantum chemists D. Bochvar and E. Galpern predicted the stability of C_{60} "footballene" in 1973 [Doklady Akademii Nauk 1972]

В 1973 году московские химики Дмитрий Бочвар и Елена Гальперн подсчитали, что квантовая химия теоретически допускает существование и некой новой разновидности углерода, молекула которого должна быть копией футбольного мяча: сфера, составленная из шестигранников или пятигранников.

サッカーボール分子 C_{60} の発想のきっかけとなったコランニュレン分子の構造



(12)



(13)



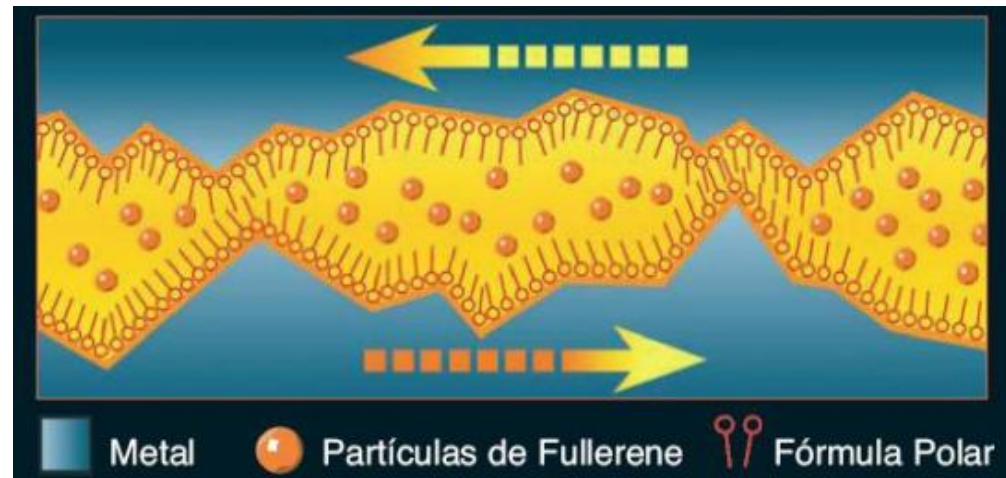


Fullerenes in Space.

Maier JP, Campbell EK. Angew Chem Int Ed Engl. 2017 Apr 24;56(18):4920-4929.

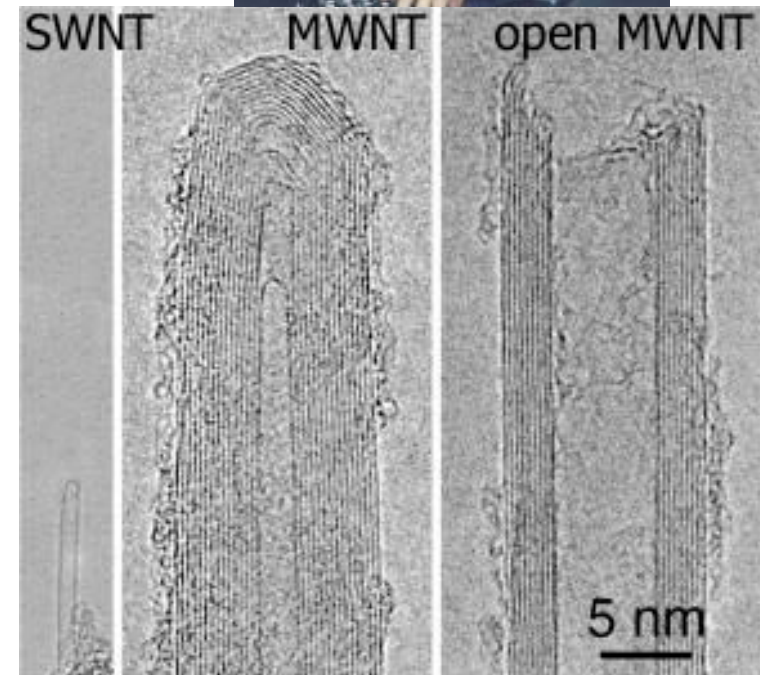
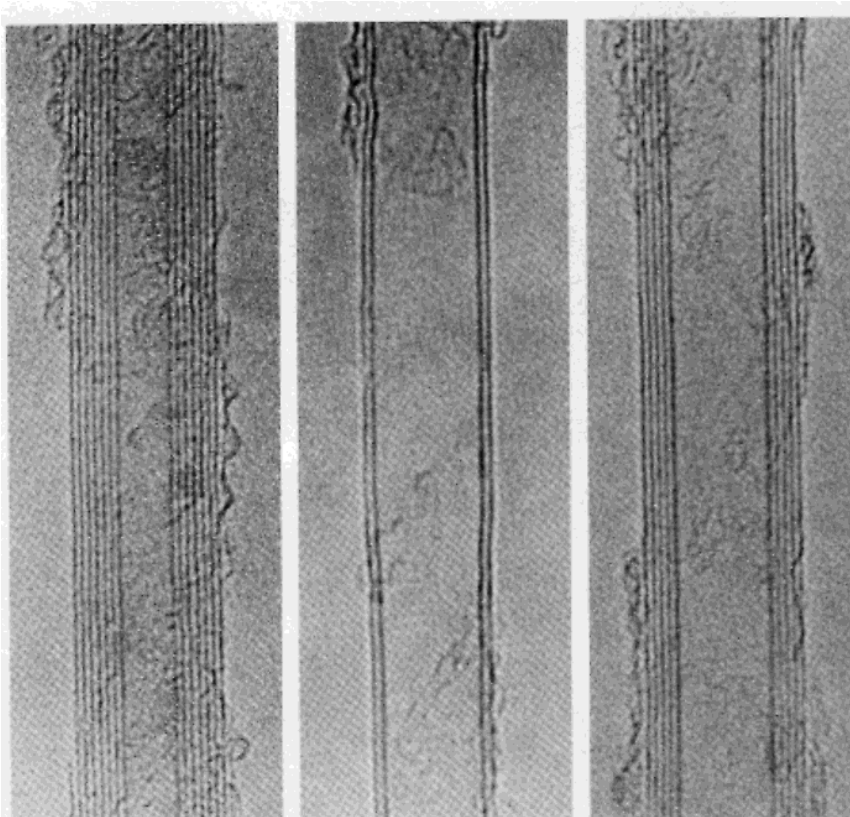
2. Fullerenos: Aplicaciones

- ❑ Lubricantes: aditivo para aceites (Bardhal)
- ❑ Almacenamiento de Hidrógeno
- ❑ Aceptor para celdas solares
- ❑ Nanovehículo para liberación de principios activos

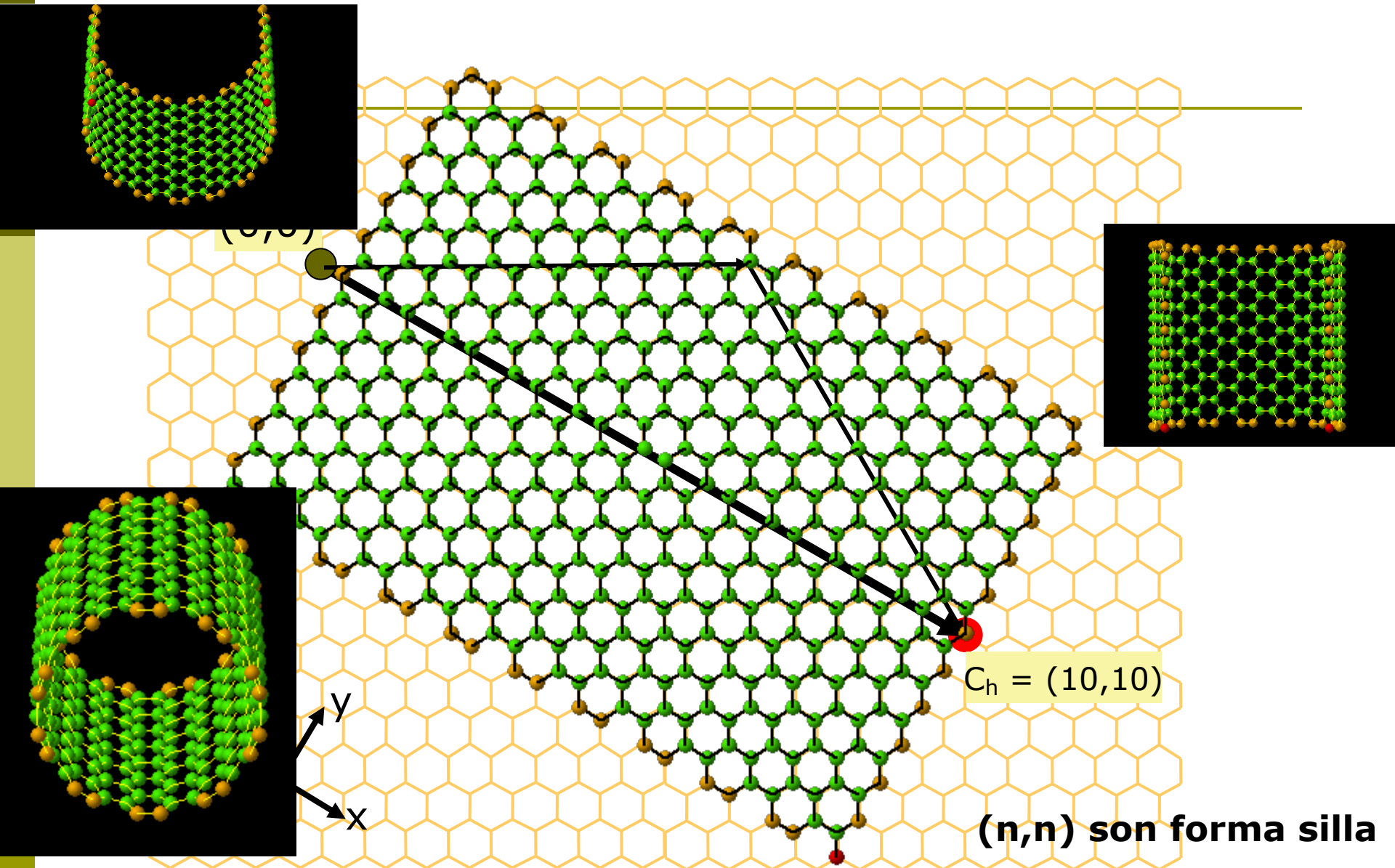


2. Nanotubos de Carbono:

"Helical microtubules of graphitic carbon",
S. Iijima, Nature 354, 56 (1991)

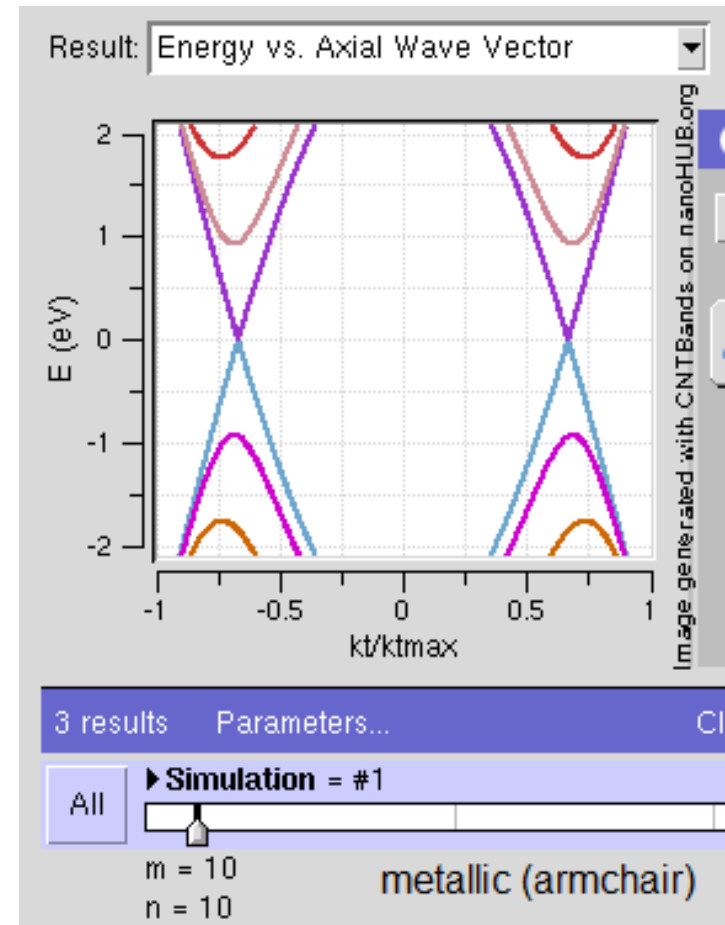
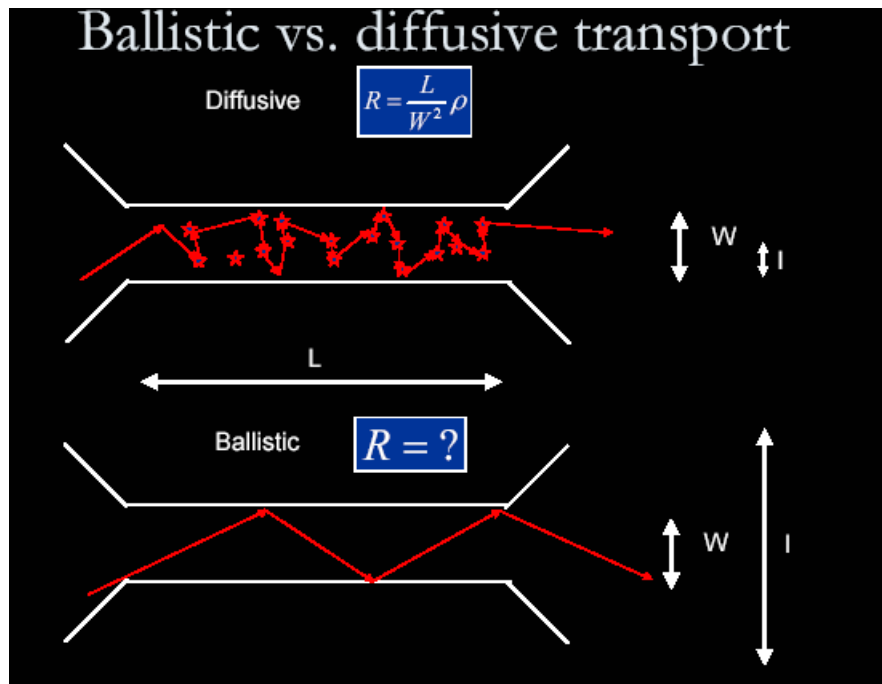


Plegamiento quilaridad (10,10) SWNT



Animation: Shigeo Maruyama, Tokyo University

2. CNT: Propiedades electrónicas



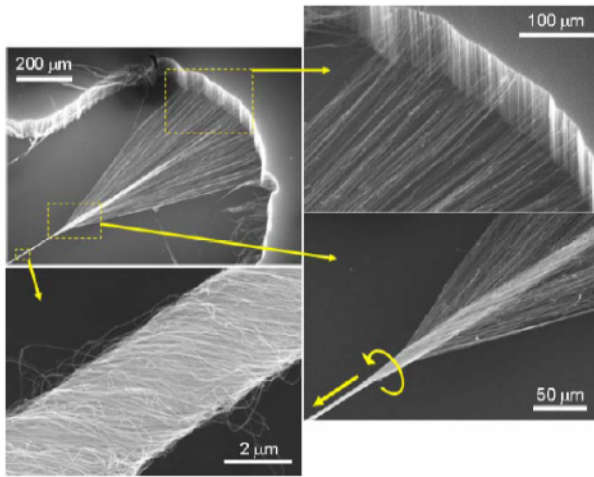
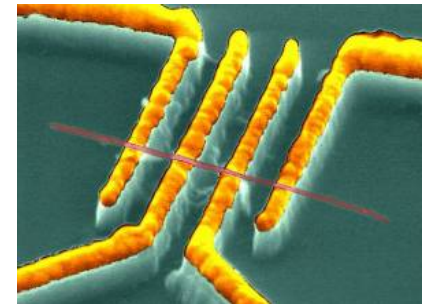
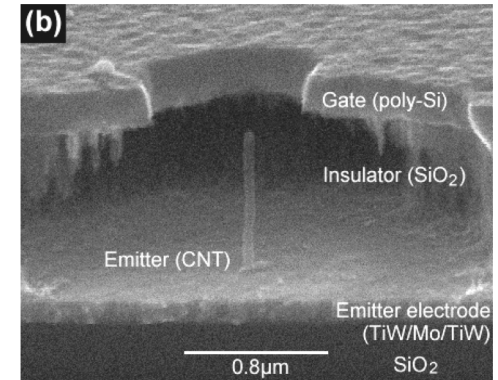
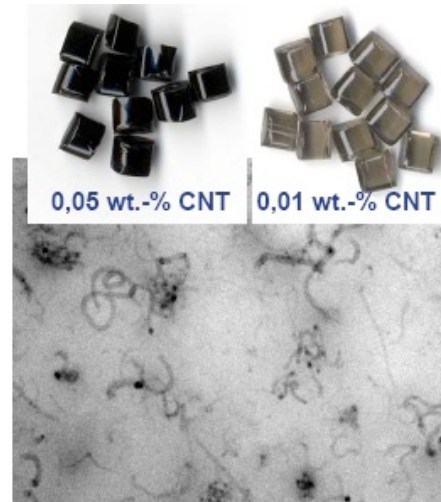
2. Tabla Periódica de los SWCNT

Periodic Table of Carbon Nanotubes



2. CNT: Aplicaciones

- Electrónica: pueden ser conductores y aislantes
- Refuerzo de polímeros: propiedades mecánicas.
- Sensores
- Transporte de Calor
- Fibras



2. Grafeno:

Premio Nobel de Física 2010

Novoselov, et al Science 306 (2004),666



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010

Nobel Prize Award Ceremony

Andre Geim

Konstantin Novoselov



Photo: U. Montan

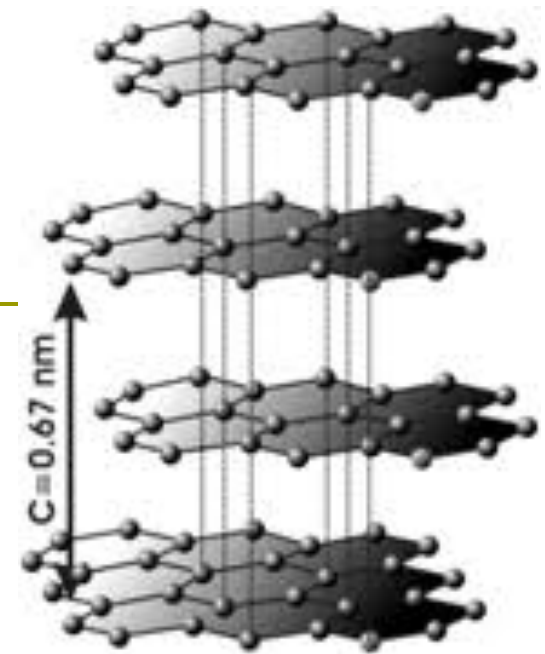
Andre Geim



Photo: U. Montan

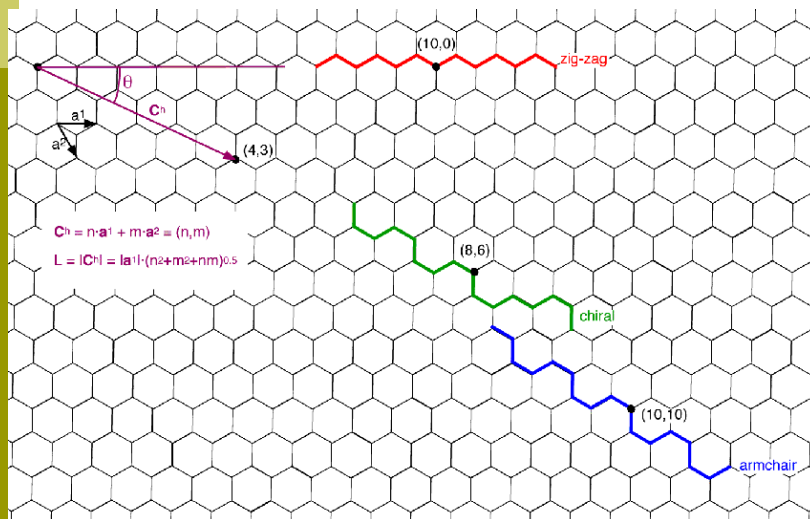
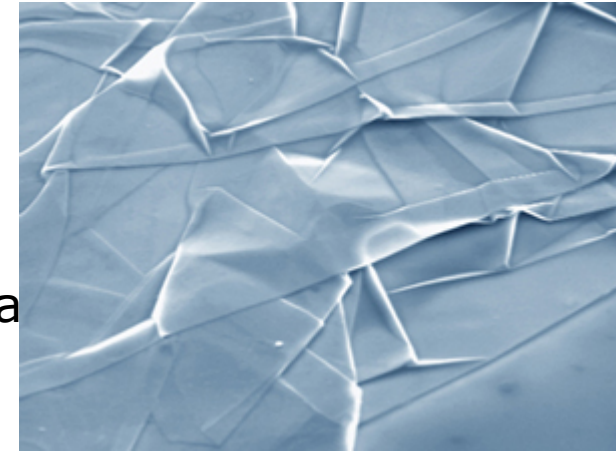
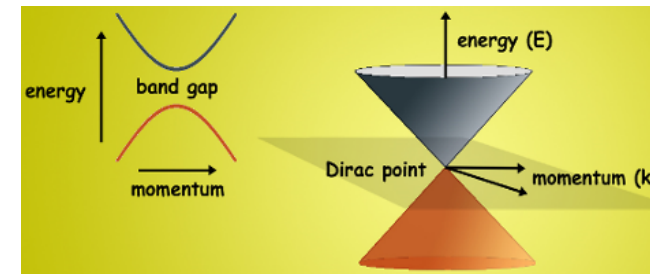
Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

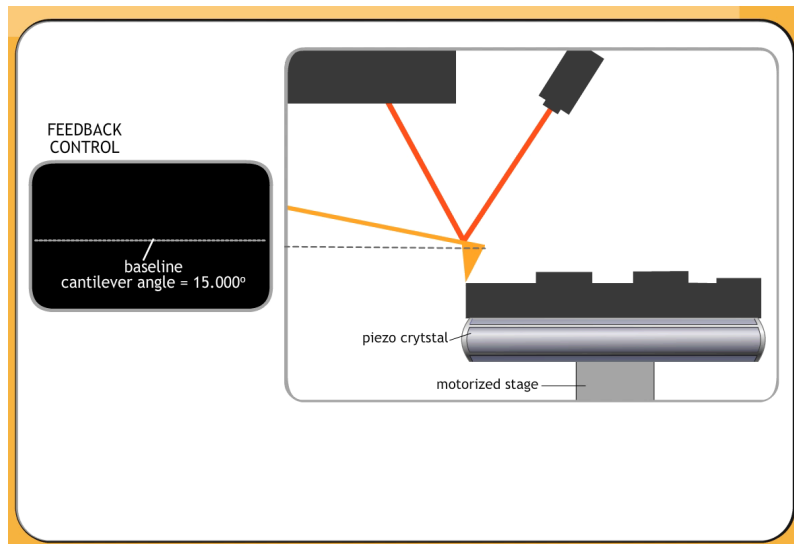


2. Grafeno: Propiedades

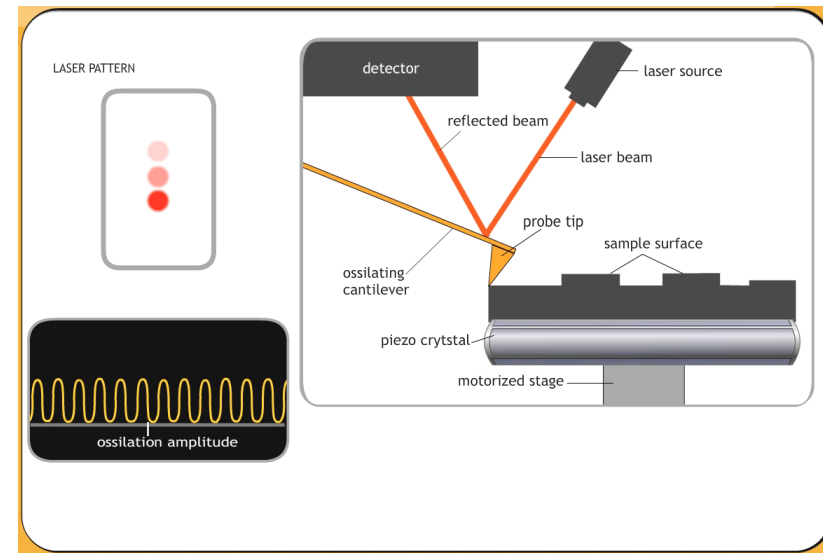
- Comportamiento fermiónico de masa cero
- Velocidad de portadores cercana a la de la luz
- Alta conductividad eléctrica
- Alta conductividad térmica
- Es el material con mayor dureza conocido hasta el momento



2. Microscopio de Fuerza Atómica

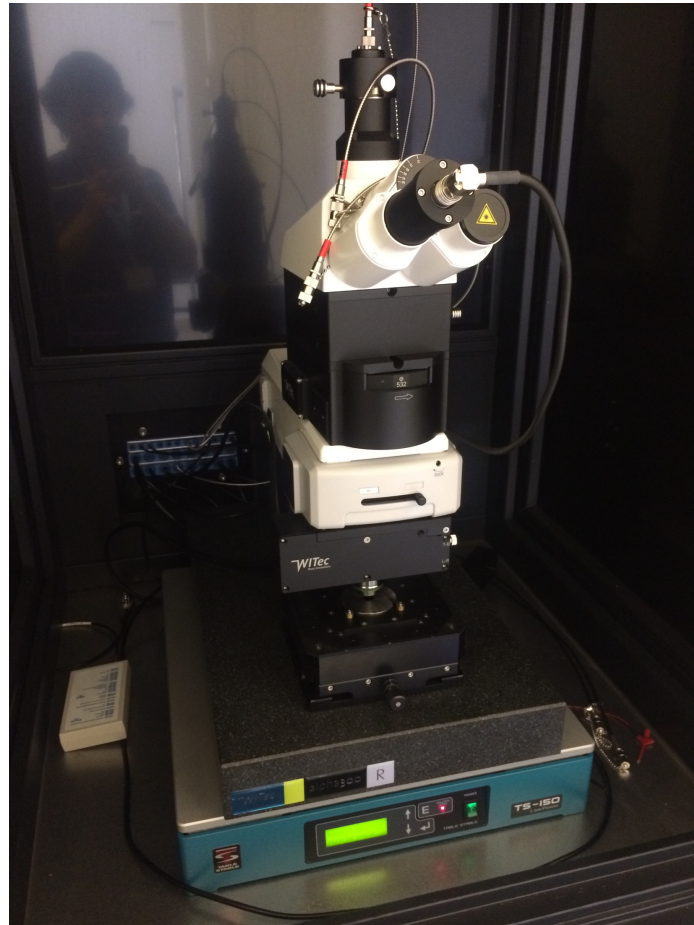
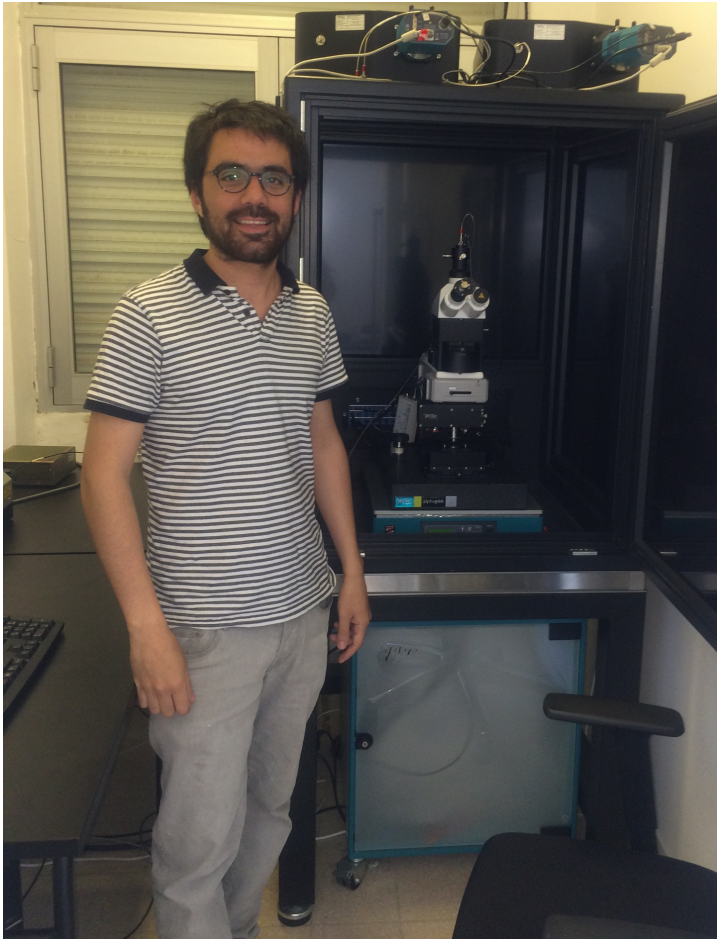


Contacto



AC Mode

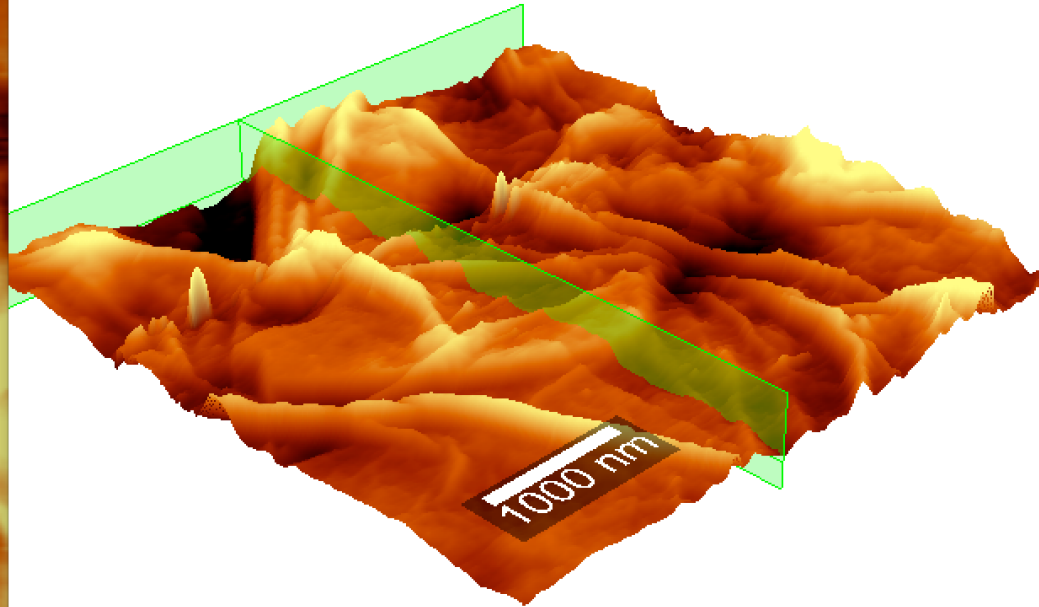
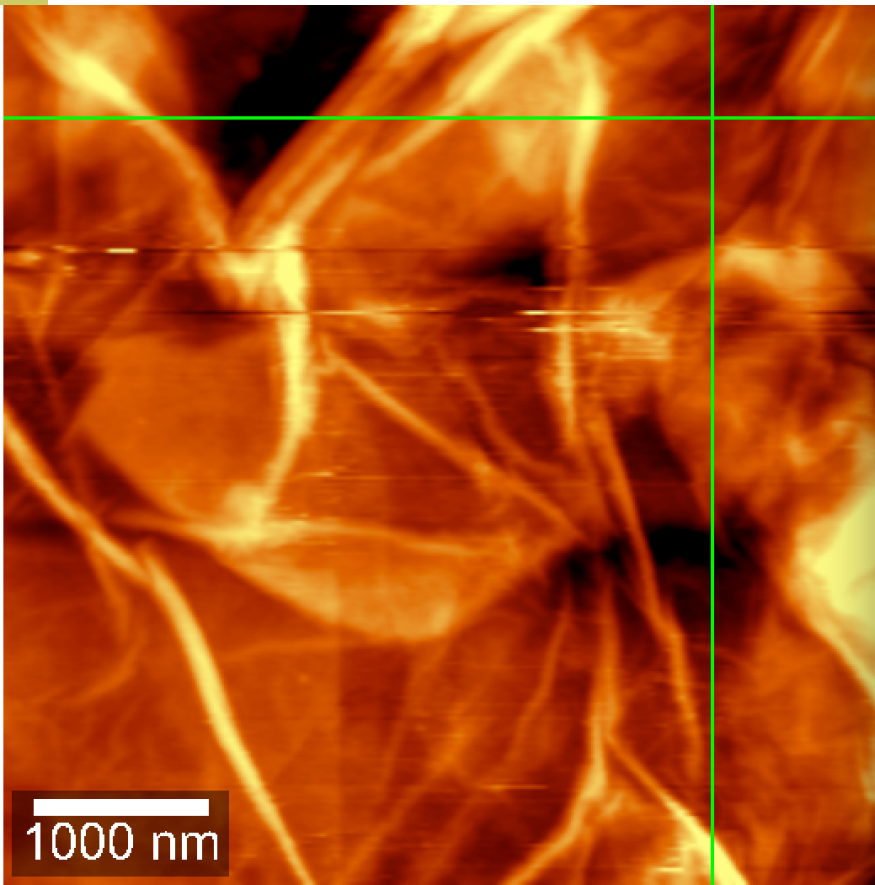
2. Microscopio Raman+AFM



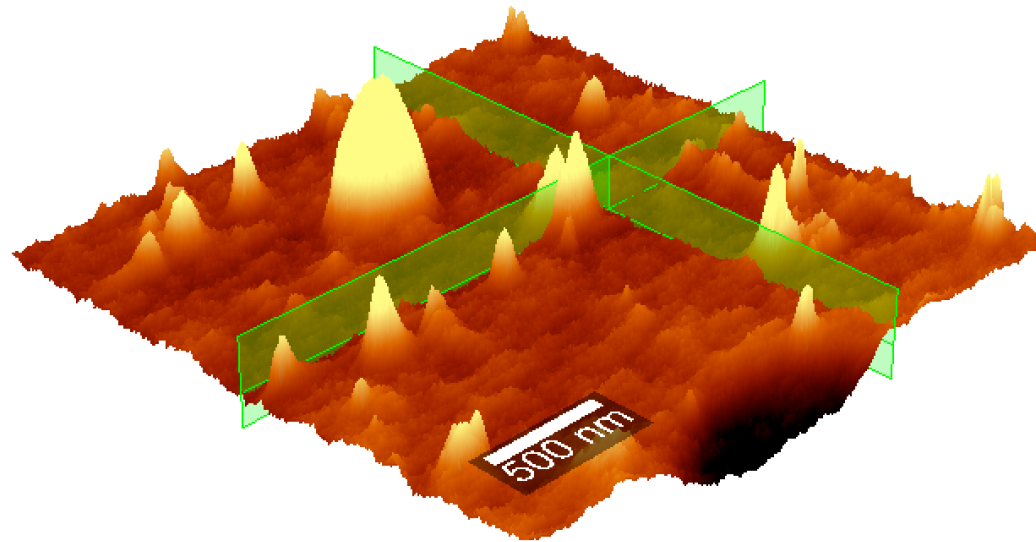
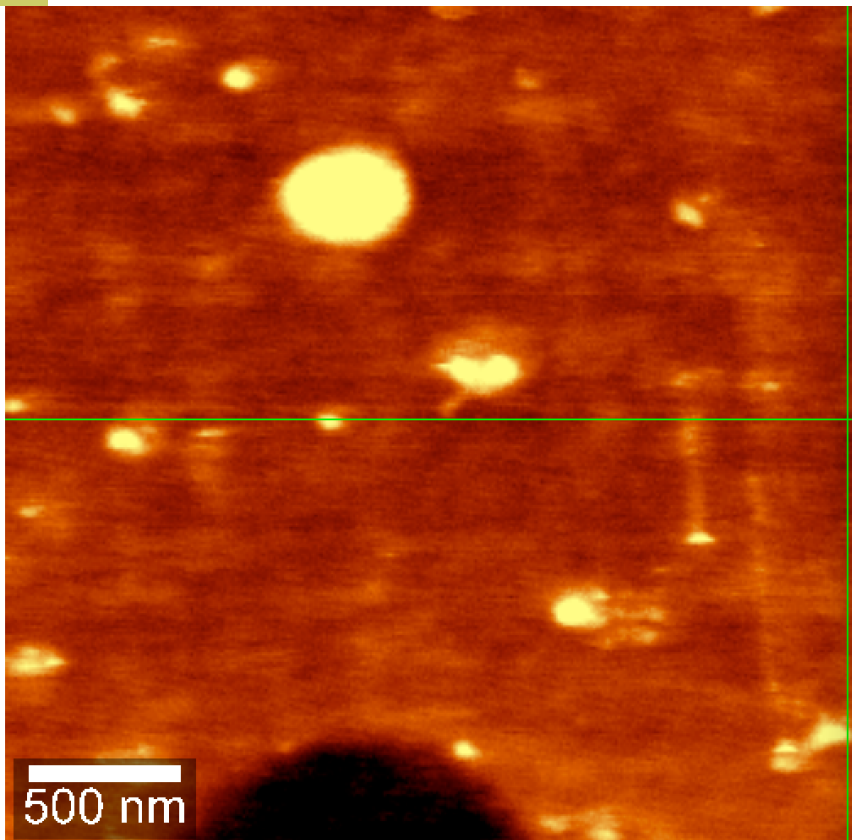
Centro NanoMat, Facultad de Química. UdelaR

2. Grafeno: Microscopia de Fuerza Atómica (AFM)

Hoja de Grafeno preparada por mixer de alta velocidad y tensoactivos.

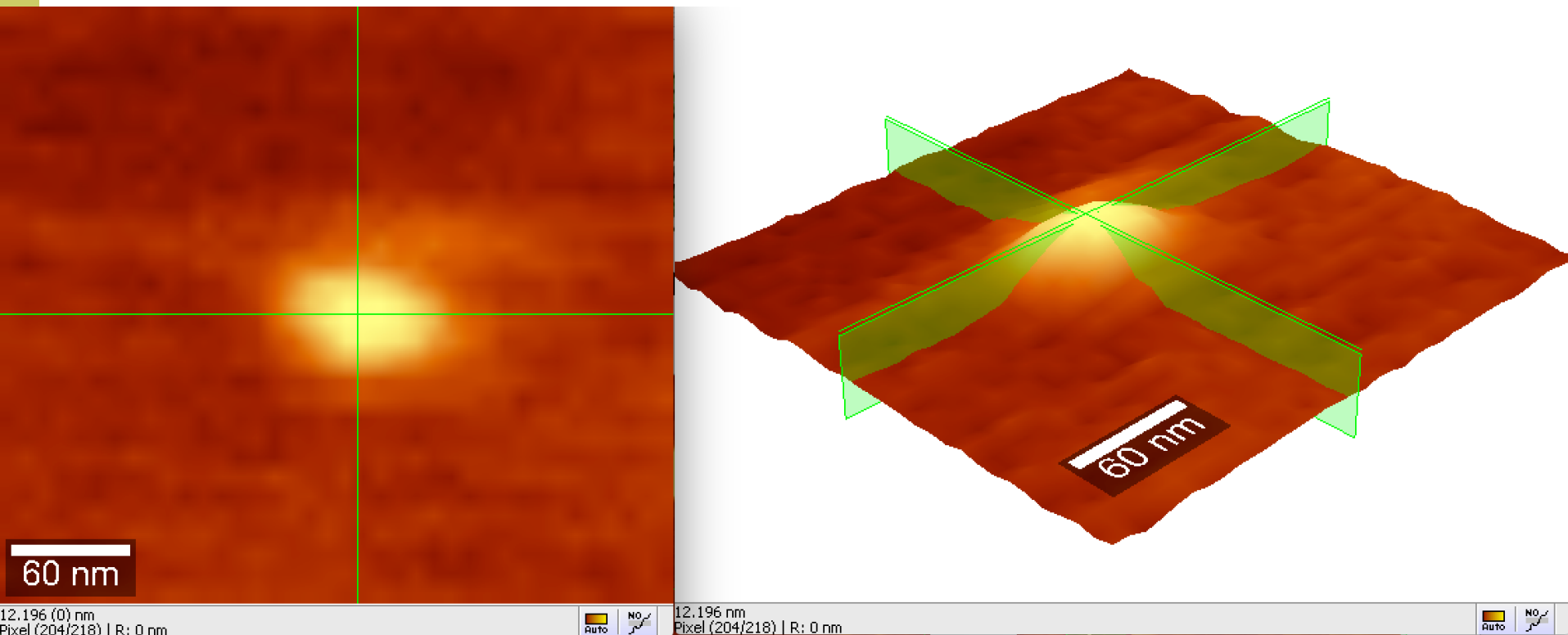


2. Grafeno: Puntos Cuánticos

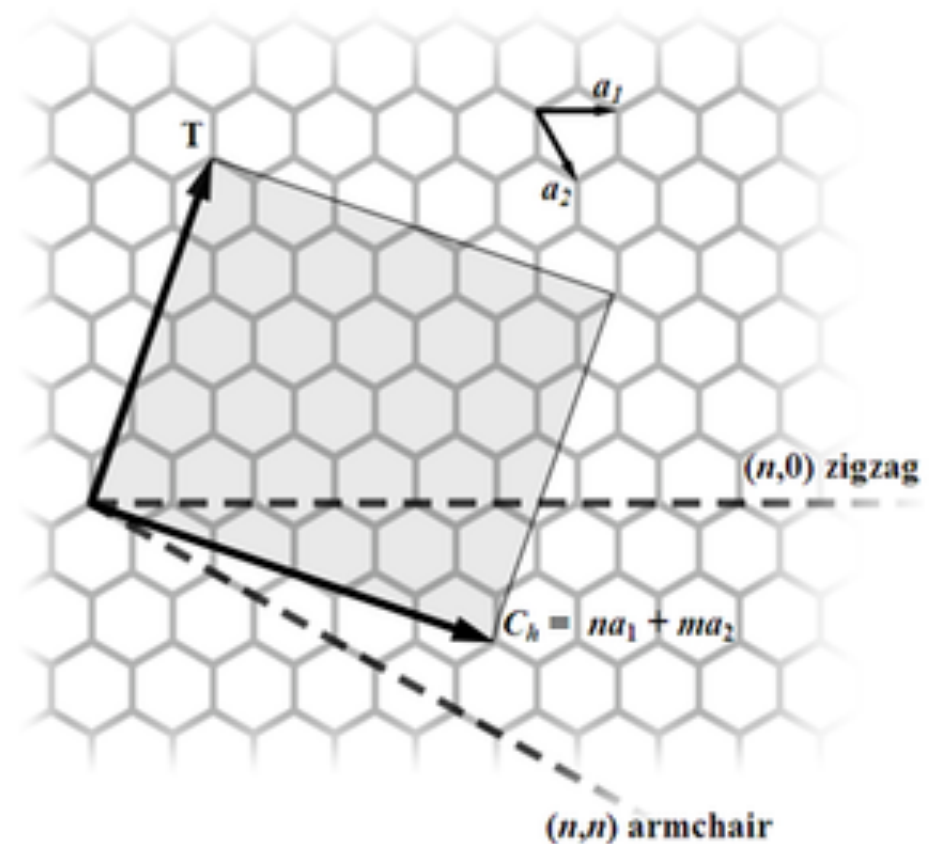
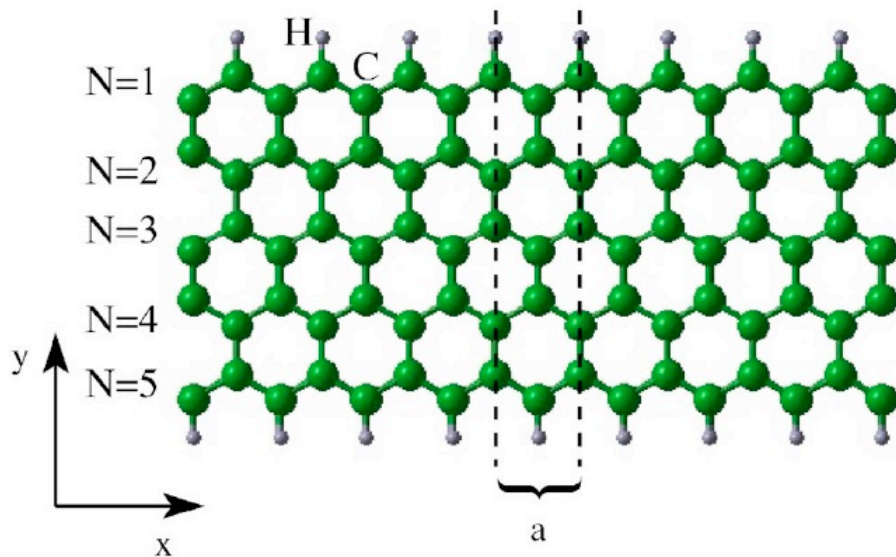


2. Puntos Cuánticos de Grafeno

- ▣ Puntos cuánticos de grafeno (GQD)
- ▣ 60 nm de diámetro y 12 nm de alto

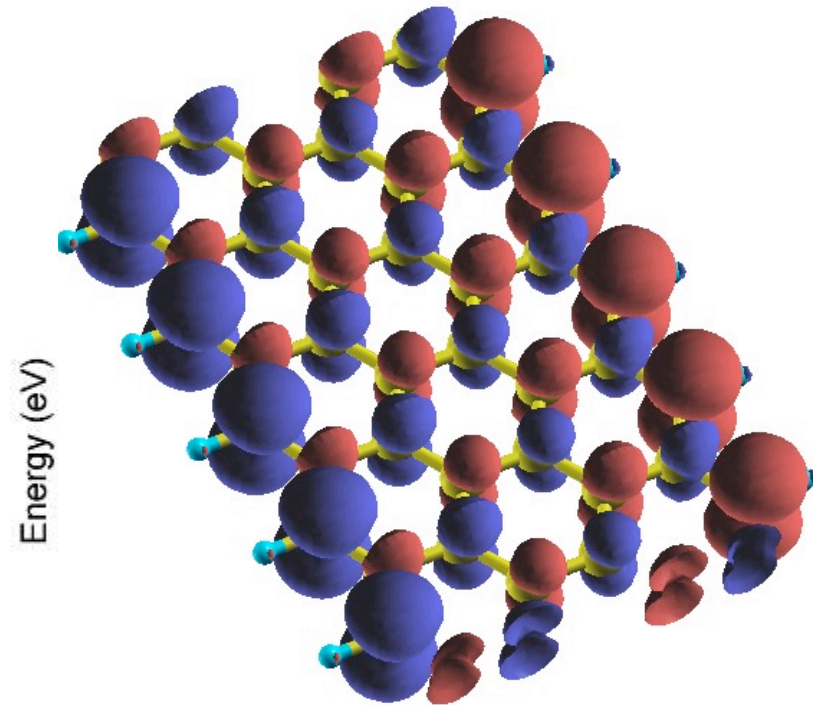
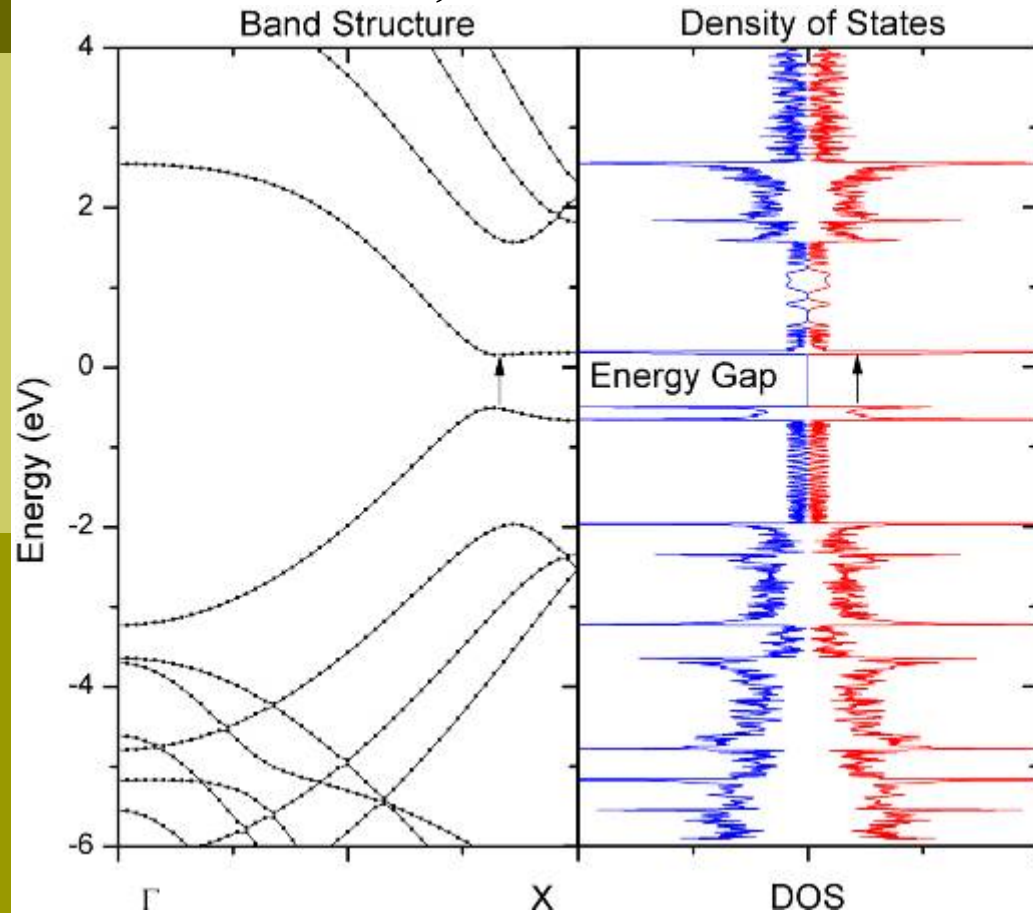


2. Zigzag graphene nanoribbons (ZGNR)

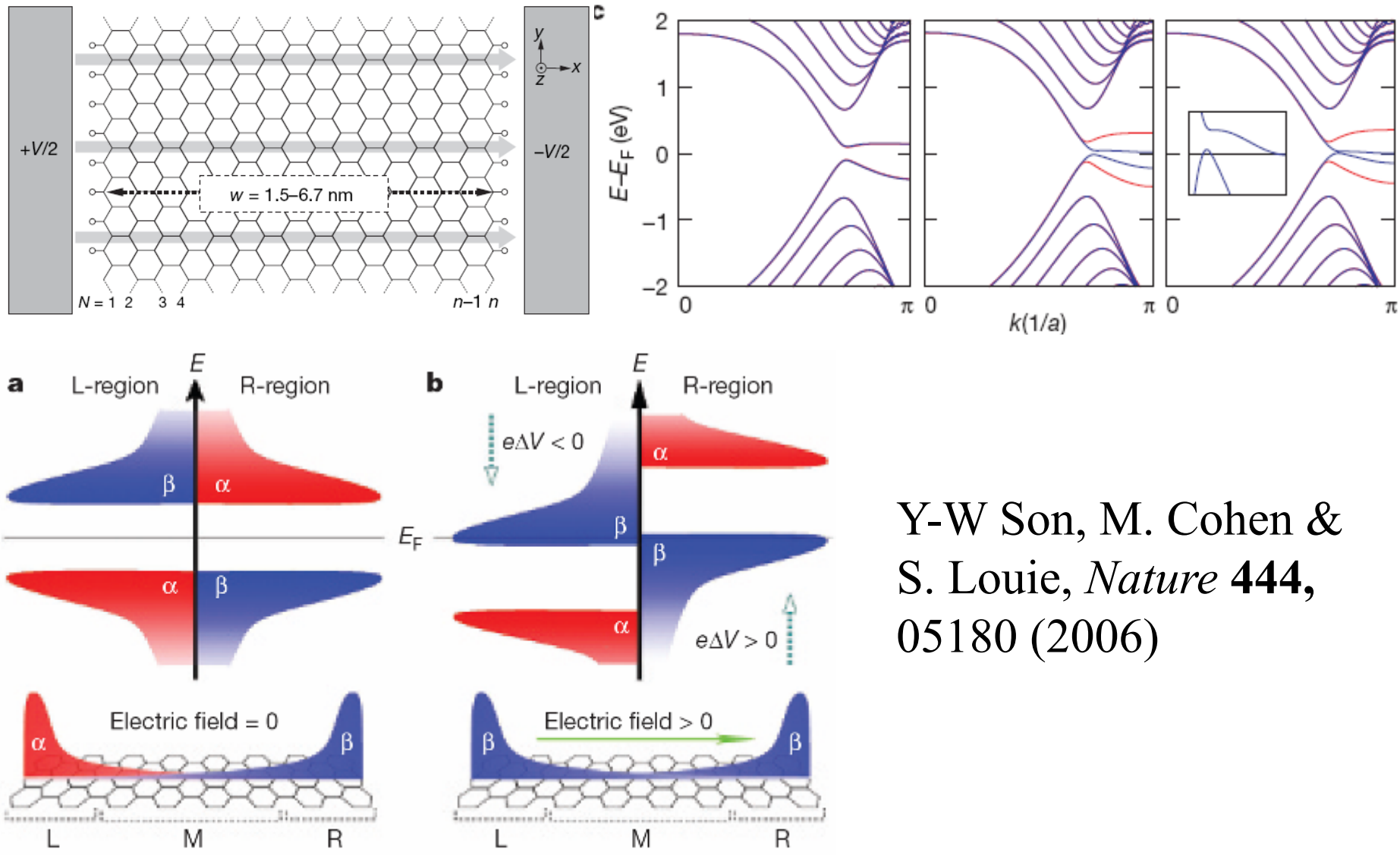


2. ZGNR: Prop. electrónicas

□ H-ZGNR, N=4: an AF-state



2. Half-Metal GNR



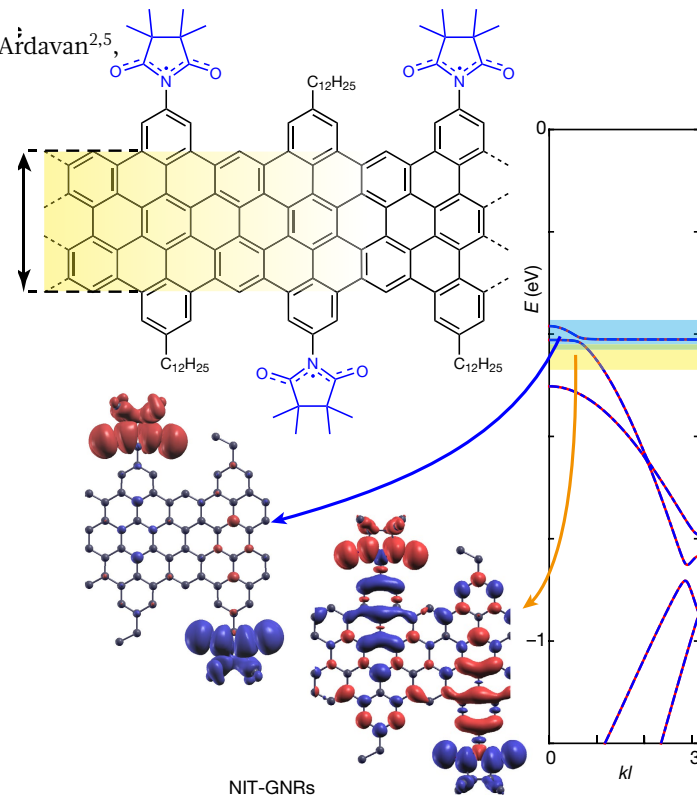
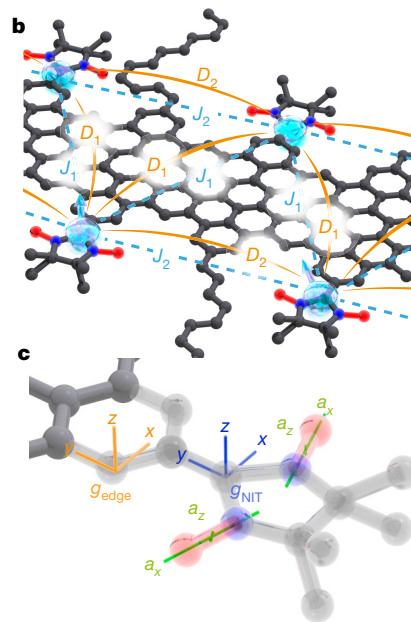
2. Evidencia Experimental

LETTER

<https://doi.org/10.1038/s41586-018-0154-7>

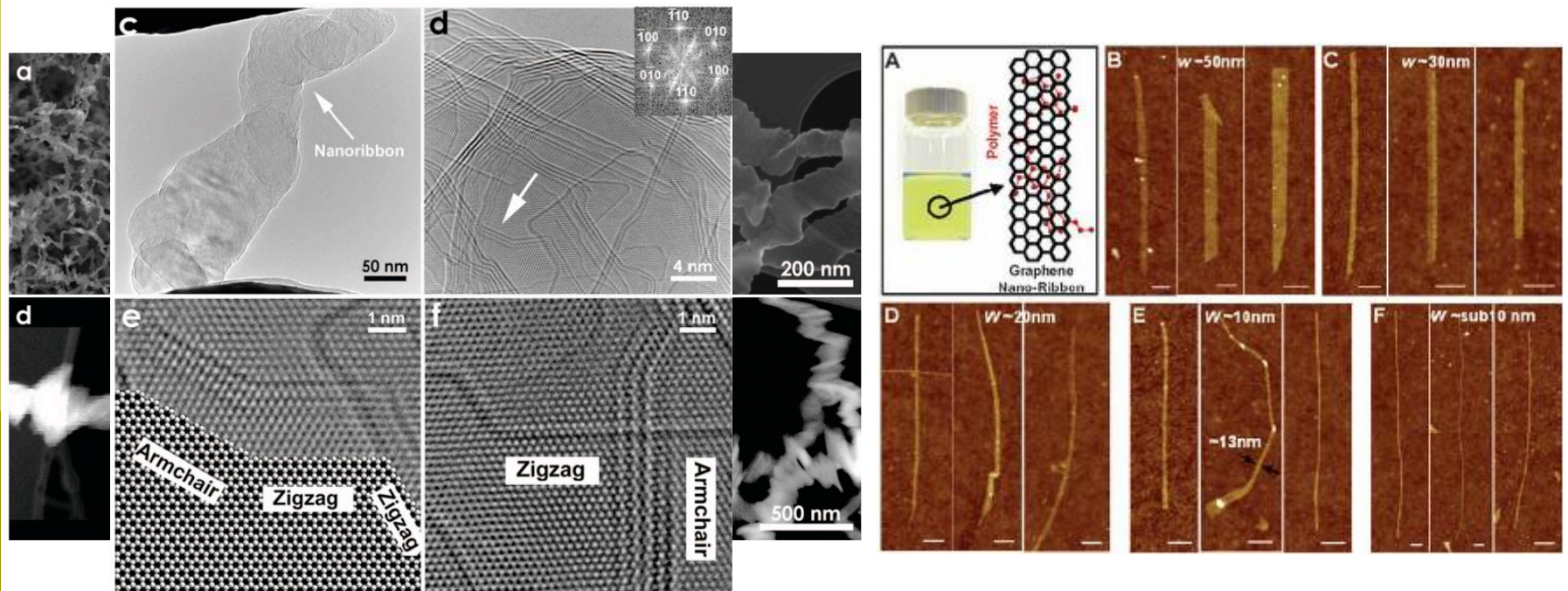
Magnetic edge states and coherent manipulation of graphene nanoribbons

Michael Slota^{1,2}, Ashok Keerthi³, William K. Myers², Evgeny Tretyakov⁴, Martin Baumgarten³, Arzhang Ardavan^{2,5}, Hatef Sadeghi⁶, Colin J. Lambert⁶, Akimitsu Narita³, Klaus Müllen³ & Lapo Bogani^{1,2*}



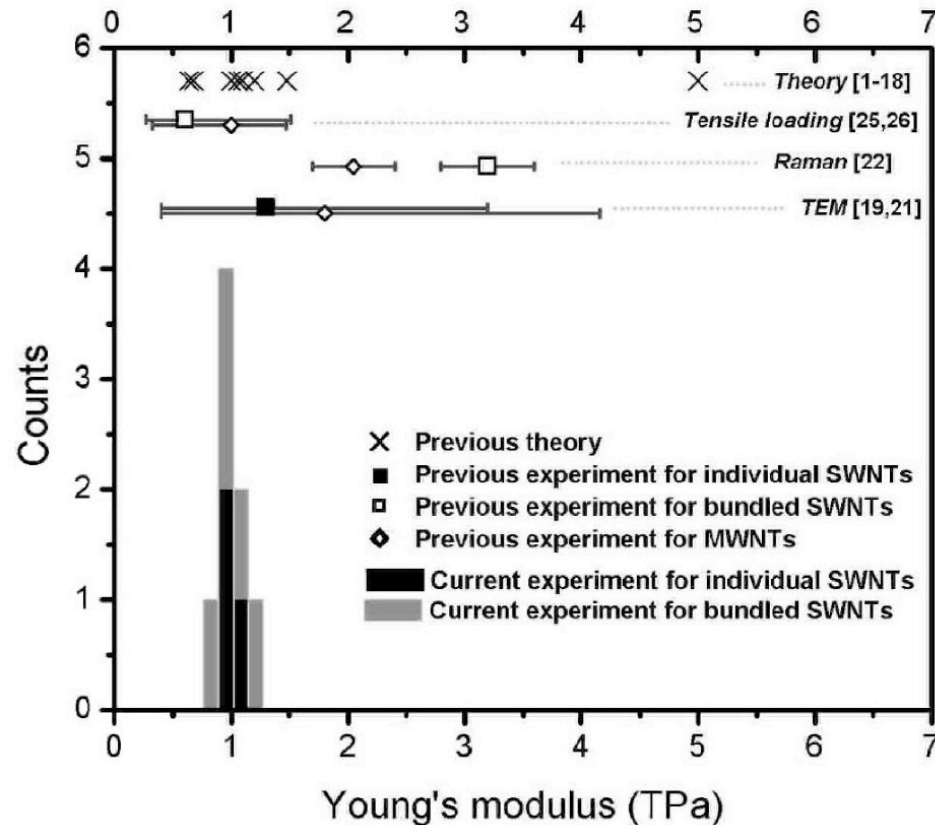
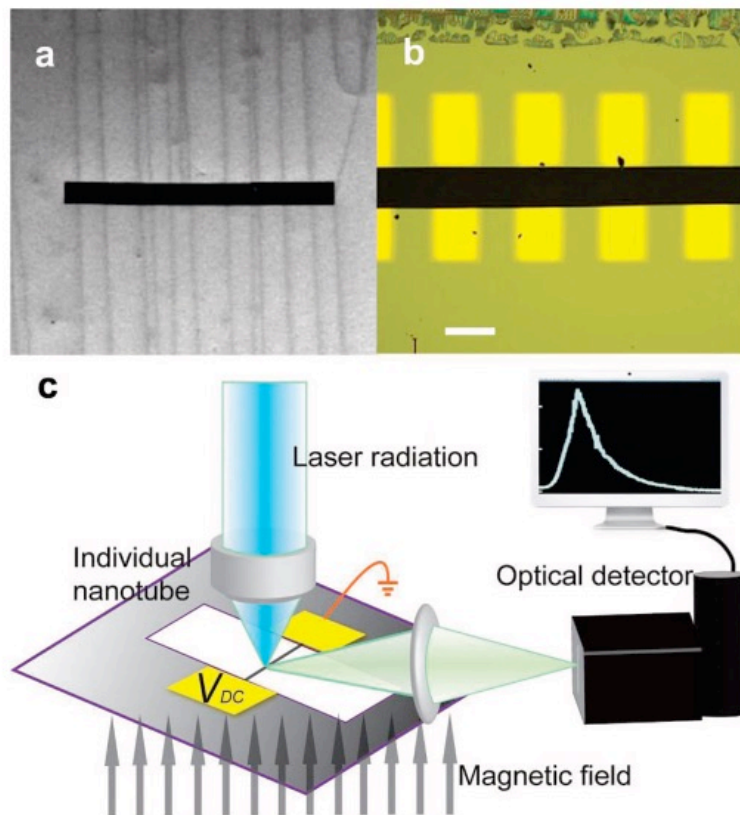
2. GNR: rutas de síntesis

Chemical derived, ultrasmooth GNR semiconductors
Xiaolin Li *et al*, *Science* **319** (2008) 1229



Bulk Production of a New Form of sp^2 Carbon: Crystalline Graphene Nanoribbons.
Campos-Delgado *et al*, *Nano Letters* **8** (2008) 2773

2. ¿Propiedades Mecánicas?



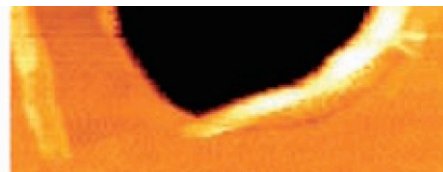
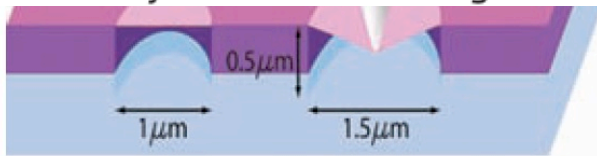
Determination of the Young's Modulus of Structurally Defined Carbon Nanotubes

Yang Wu *et al*, *Nano Lett.* **8** (12), 4158-4161 (2008)

3. ¿ Experimentos?



We measured the elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes by nanoindentation in an atomic force microscope. The force-displacement behavior is interpreted within a framework of nonlinear elastic stress-strain response, and yields second- and third-order elastic stiffnesses of 340 newtons per meter (N m^{-1}) and -690 N m^{-1} , respectively. The breaking strength is 42 N m^{-1} and represents the intrinsic strength of a defect-free sheet. These quantities correspond to a Young's modulus of $E = 1.0$ terapascals, third-order elastic stiffness of $D = -2.0$ terapascals, and intrinsic strength of $\sigma_{\text{int}} = 130$ gigapascals for bulk graphite. **These experiments establish graphene as the strongest material ever measured,** and show that atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime.



Effective Young's Modulus (TPa)

1.4

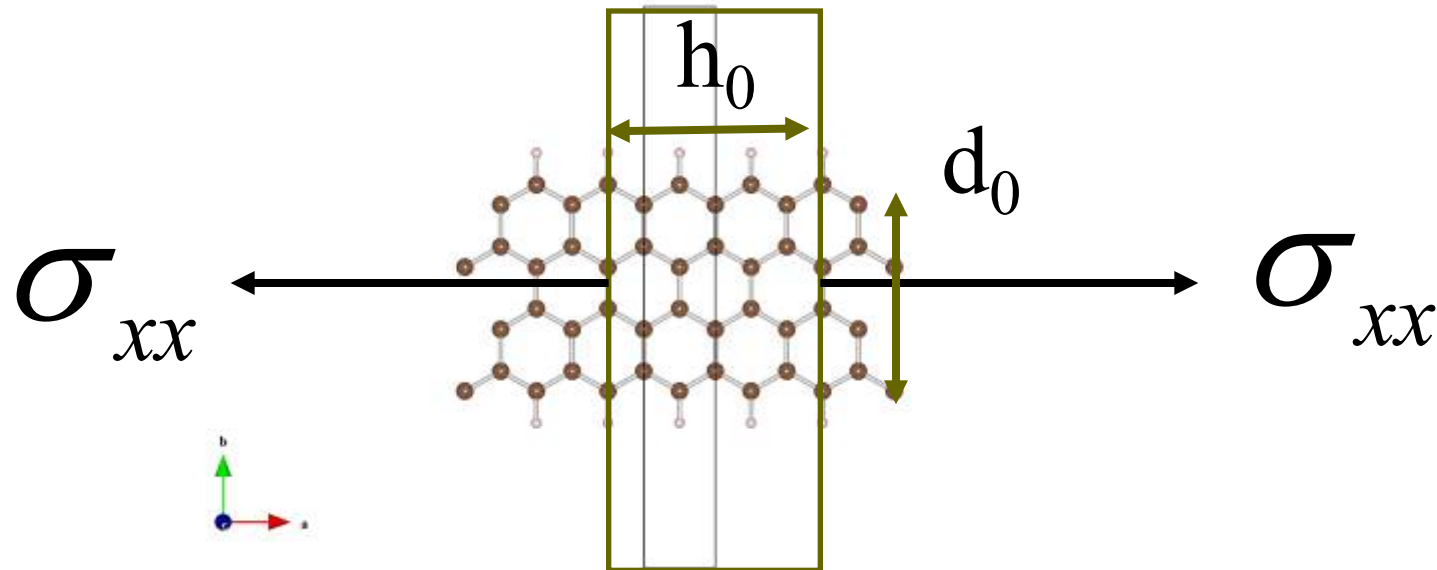
235 268 302 335 369 402 436 469
 E^{2D} (N/m)

“Strength of Monolayer Graphene Measurement of the Elastic Properties and Intrinsic”

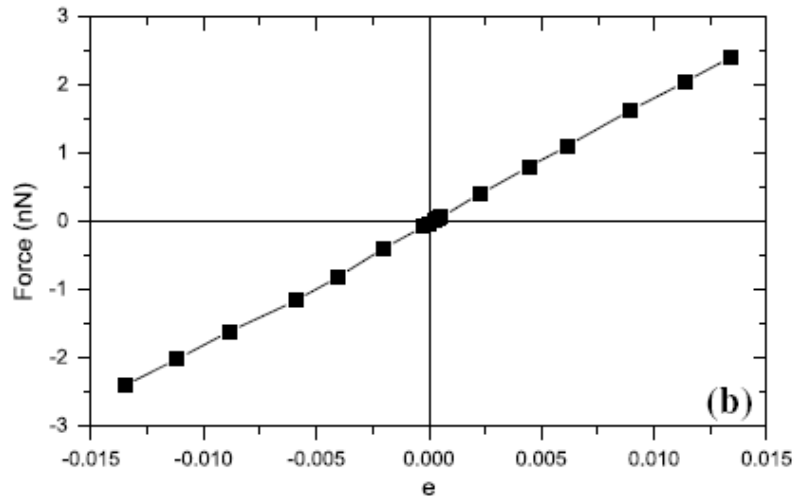
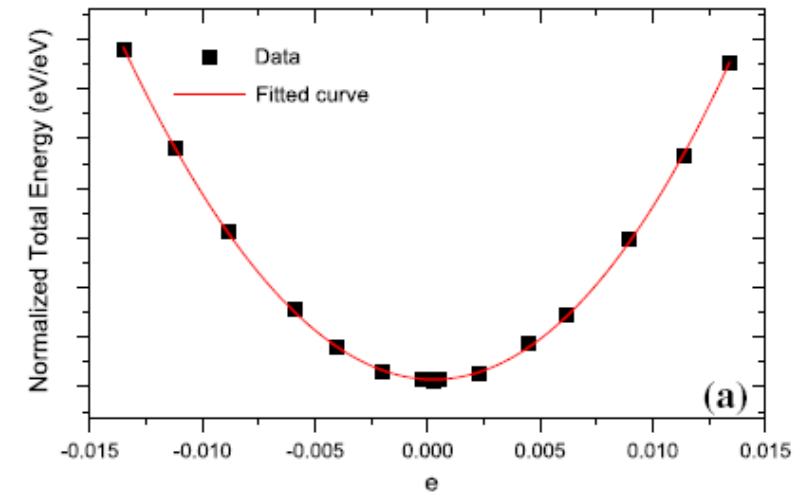
Lee *et al.* *Science* **321**, 385 (2008)

2. Propiedades mecánicas: H-ZGNR

- Esfuerzo vs. deformación
- E_{gap}
- Determinación del modulo Young's Modulus



2. H-ZGNR, N=4

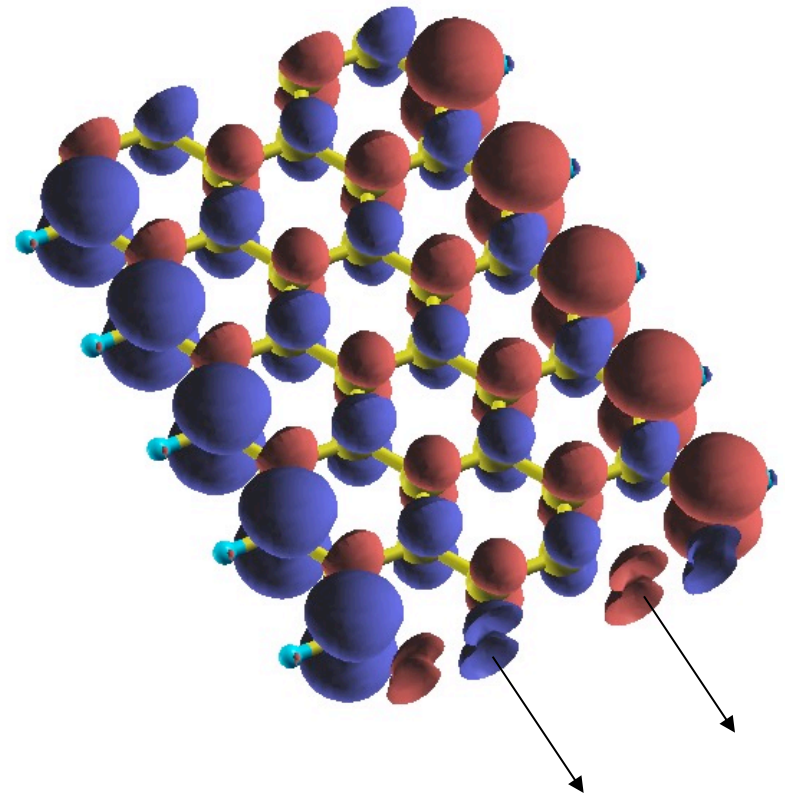


Force	E_{gap}	Mom. Mag.	E_{total}	a
nN	eV	μ_B	eV	Å
-5.67	0.60	0.251	-5123.29053	9.78
-3.68	0.60	0.257	-5123.48784	9.85
-1.92	0.61	0.261	-5123.59075	9.91
-0.97	0.62	0.263	-5123.61926	9.94
-0.10	0.63	0.265	-5123.6293	9.97
0.00	0.63	0.265	-5123.62951	9.97
0.01	0.63	0.265	-5123.62849	9.97
0.87	0.63	0.267	-5123.62166	10.00
1.75	0.63	0.269	-5123.59939	10.03
3.72	0.65	0.275	-5123.47918	10.10
5.80	0.66	0.28	-5123.26005	10.18
8.04	0.67	0.288	-5122.90206	10.26
9.90	0.68	0.295	-5122.51931	10.33
16.07	0.72	0.316	-5120.6051	10.58
20.48	0.76	0.337	-5118.60822	10.77
25.17	0.81	0.36	-5115.84421	10.98
34.71	0.94	0.428	-5107.1579	11.50
40.59	1.11	0.507	-5097.44148	11.98

2. Mechanical Properties

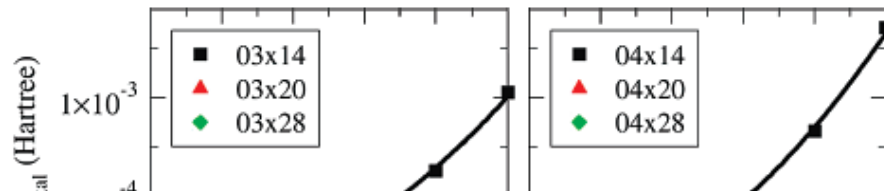
Reference	E^{3D} (TPa)	ν	Remarks
<i>Graphene</i>			
[10]	0.799	—	Graphene (force field)
[17]	1.02	0.149	Graphene (<i>ab initio</i>)
[18]	1.11	—	Graphene (<i>ab initio</i>)
[19]	1.012	0.245	Graphene (Brenner ^a)
[19]	0.669	0.416	Graphene (Brenner ^b)
[20]	0.694	0.412	Graphene (Brenner)
[24]	1.11	0.45	Graphene (truss model)
Present work	0.96	0.17	Graphene (<i>ab initio</i>)
<i>Carbon nanotubes</i>			
[21]	0.694	—	SWNT (Brenner)
[23]	0.97	0.28	SWNT (empirical model)
[25]	0.213–2.08	0.16	SWNT (MM)
[26]	0.32–1.47	—	SWNT (experiments)
[27]	0.7	—	SWNT (MD)
[28]	1.0	0.25	DWNT (vibrations)
[29]	0.81–1.13	—	SWNT (experiments)
[30] ^c	0.8–1.05	—	SWNTS (<i>ab initio</i>)
[30]	1.05	—	SWNT (5, 5)-(<i>ab initio</i>)
Present work	1.01	—	SWNT (5, 5)-(<i>ab initio</i>)

^a Non-minimized potential; ^b minimized potential; ^c this result was converted to E^{3D} for comparison purposes, using:
 $E^{3D} = E^{2D}c_0$.

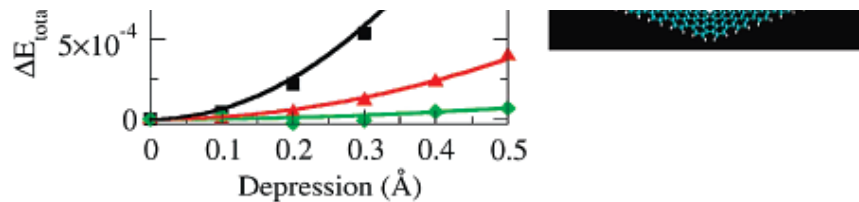


Faccio *et al*, J. Phys.: Condens. Matter 21 (2009) 285304

2. Otros resultados



Graphene nanoribbons present diverse electronic properties ranging from semiconducting^{1–3} to half-metallic,⁴ depending on their geometry, dimensions, and chemical composition.^{5,6,7} Here we present a route to control these properties via externally applied mechanical deformations. Using state-of-the-art density functional theory calculations combined with classical elasticity theory considerations, we find a remarkable Young's modulus value of ~ 7 TPa for ultranarrow graphene strips and a pronounced electromechanical response toward bending and torsional deformations. Given the current advances in the synthesis of nanoscale graphene derivatives, our predictions can be experimentally verified opening the way to the design and fabrication of miniature electromechanical sensors and devices based on ultranarrow graphene nanoribbons.



“Electromechanical Properties of Suspended Graphene Nanoribbons”

O. Hod, G. E. Scuseria, Nano Letters **9** (2009) 2619

2. Polímero+GQD: Propiedades Eléctricas

- Modificación de propiedades eléctricas de polímeros conductores (PANI), con agregado de GQD.

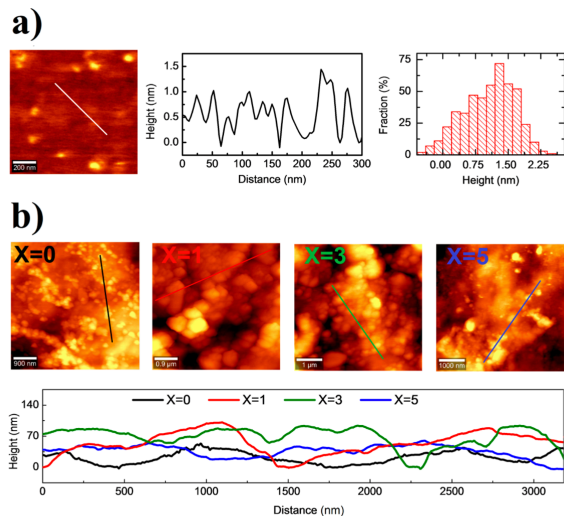


Figure 1. AFM images for (a) GOQD samples and (b) PANI-GOQD-X nanocomposites with X = 0, 1, 3, and 5. Topography analysis was obtained from the cross-section marked with lines in the images. GOQD histogram shown in (a) was obtained from a large representative cross-section.

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PHYSICAL CHEMISTRY C

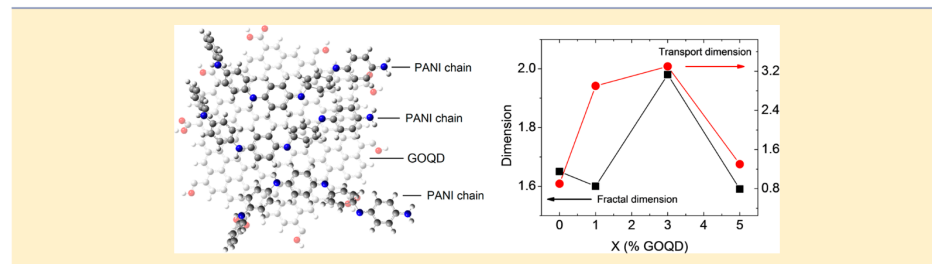
Article

pubs.acs.org/JPCCC

Tuning Electrical Transport Mechanism of Polyaniline–Graphene Oxide Quantum Dots Nanocomposites for Potential Electronic Device Applications

Dominique Mombrú, Mariano Romero,* Ricardo Faccio, and Álvaro W. Mombrú*

Centro NanoMat/CryssMat/Física, DETEMA, Facultad de Química, Universidad de la República, C.P. 11100 Montevideo, Uruguay



DOI: 10.1021/acs.jpcc.6b08954

J. Phys. Chem. C 2016, 120, 25117–25123

2. Dinámica Molecular: PANI-GQD

Table 3. Wavelength, Oscillation Strength, and Major Contribution for PANI-COOH, GQD-COOH, and PANI-GQD-COOH

	wavelength (nm)	oscillation strength	major contribution
PANI-COOH	372.2	0.7049	HOMO-1→LUMO+1 (73%)
	350.9	0.3953	HOMO-1→LUMO+6 (38%)
GQD-COOH	773.2	1.2795	HOMO-1→LUMO (37%) HOMO→LUMO+1 (35%)
	772.0	1.232	HOMO-1→LUMO+1 (45%) HOMO→LUMO (26%)
PANI-GQD-COOH	915.4	0.062	HOMO-5→LUMO (53%)

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Article

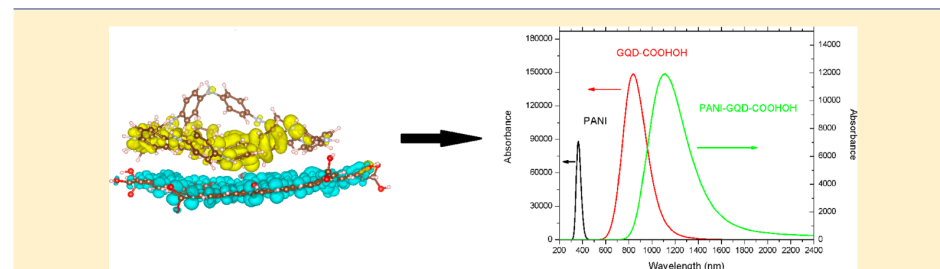
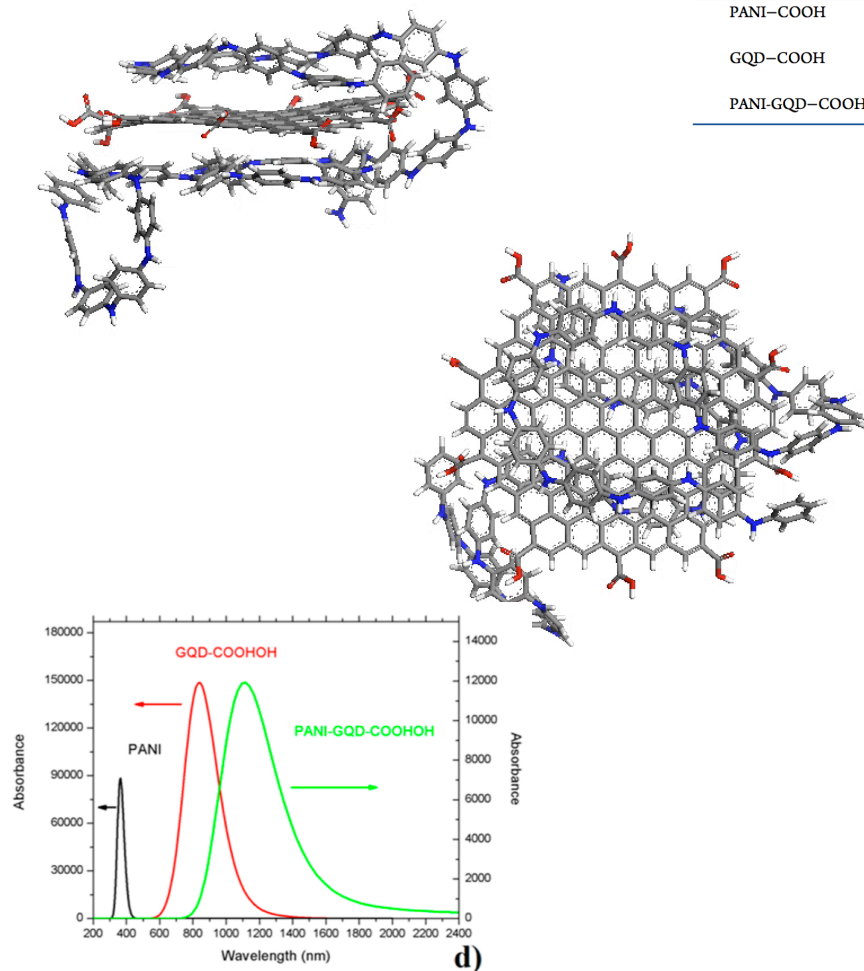
pubs.acs.org/JPC

Electronic Structure of Edge-Modified Graphene Quantum Dots Interacting with Polyaniline: Vibrational and Optical Properties

Dominique Mombrú,[†] Mariano Romero,^{*,†} Ricardo Faccio,^{*,†} and Álvaro W. Mombrú^{*,†}

[†]Centro NanoMat/CryssMat/Física, DETEMA, Facultad de Química, Universidad de la República, C.P. 11800, Montevideo, Uruguay

 Supporting Information



DOI: 10.1021/acs.jpcc.7b03604

J. Phys. Chem. C 2017, 121, 16576–16583

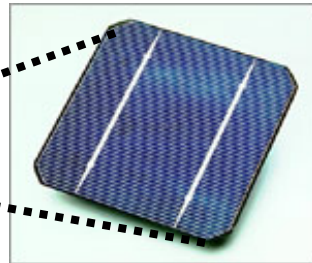
3. Celdas Solares



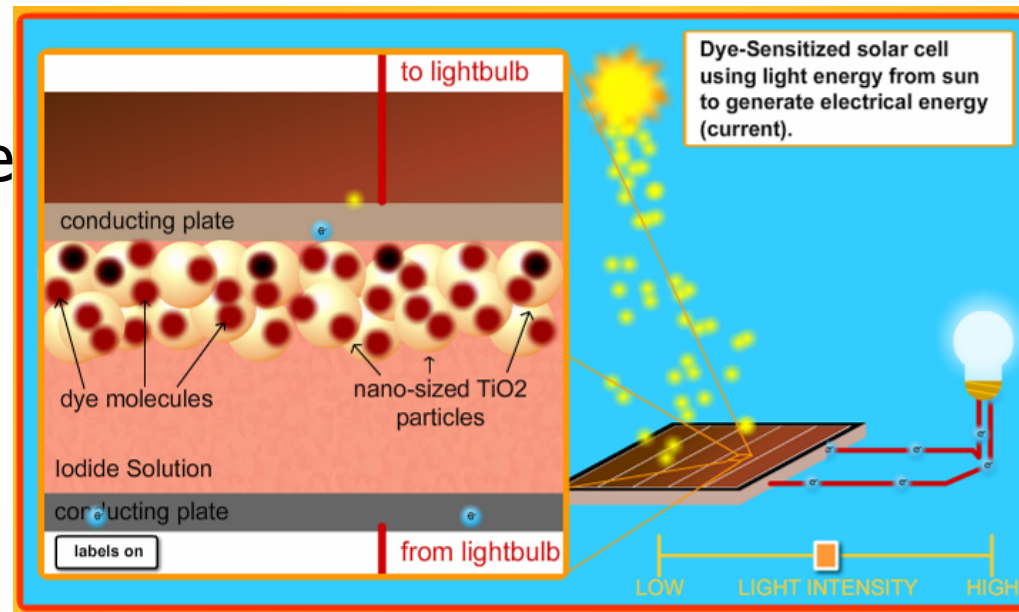
Uso de Nanotubos de TiO_2
Teoría y Experimento

3.1 Energía Solar

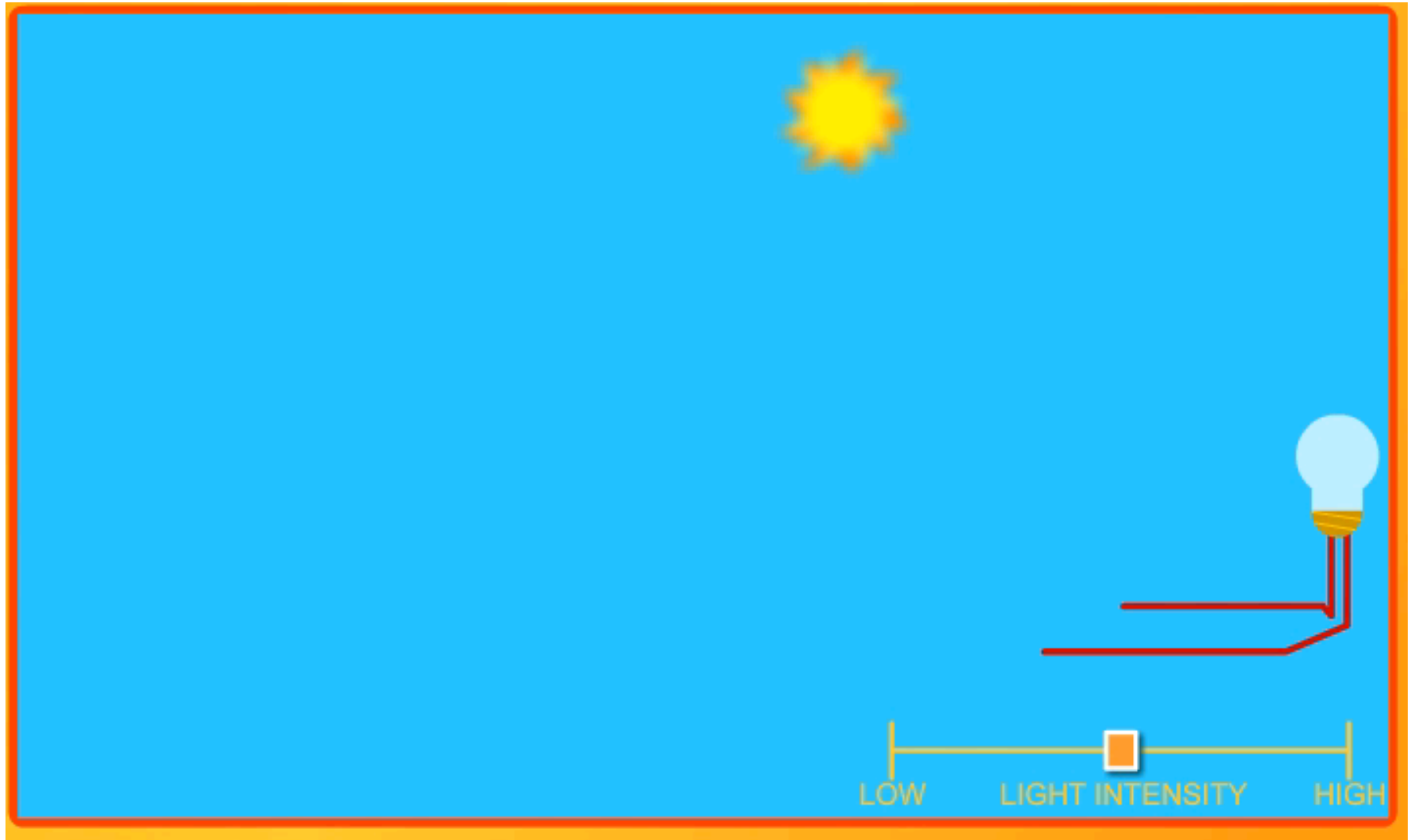
- Energía producida por el sol
- Limpia y renovable
- Convertible y usable (electricidad)



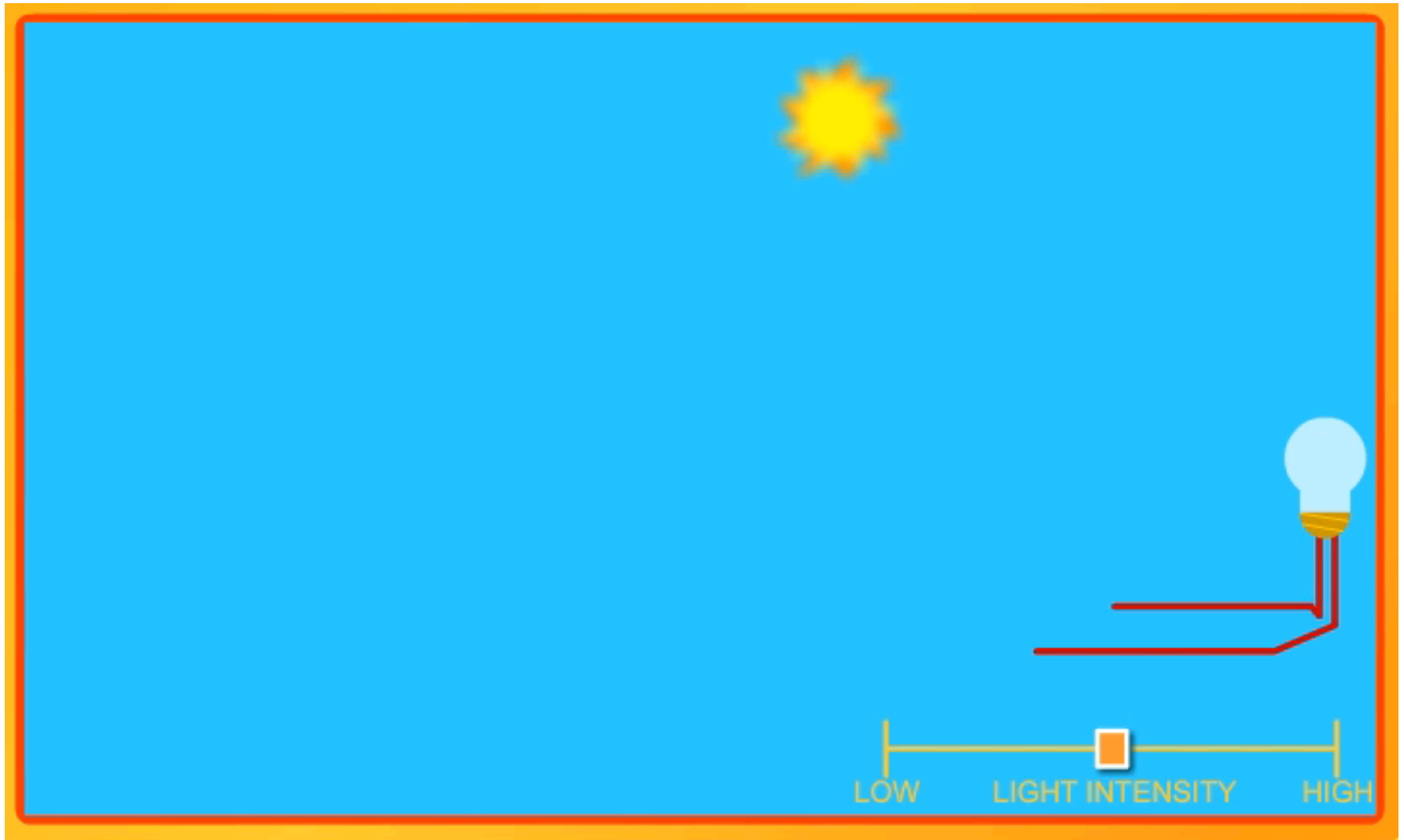
Panel solar -
fotovoltaico



3.1 Celda Solar Convencional

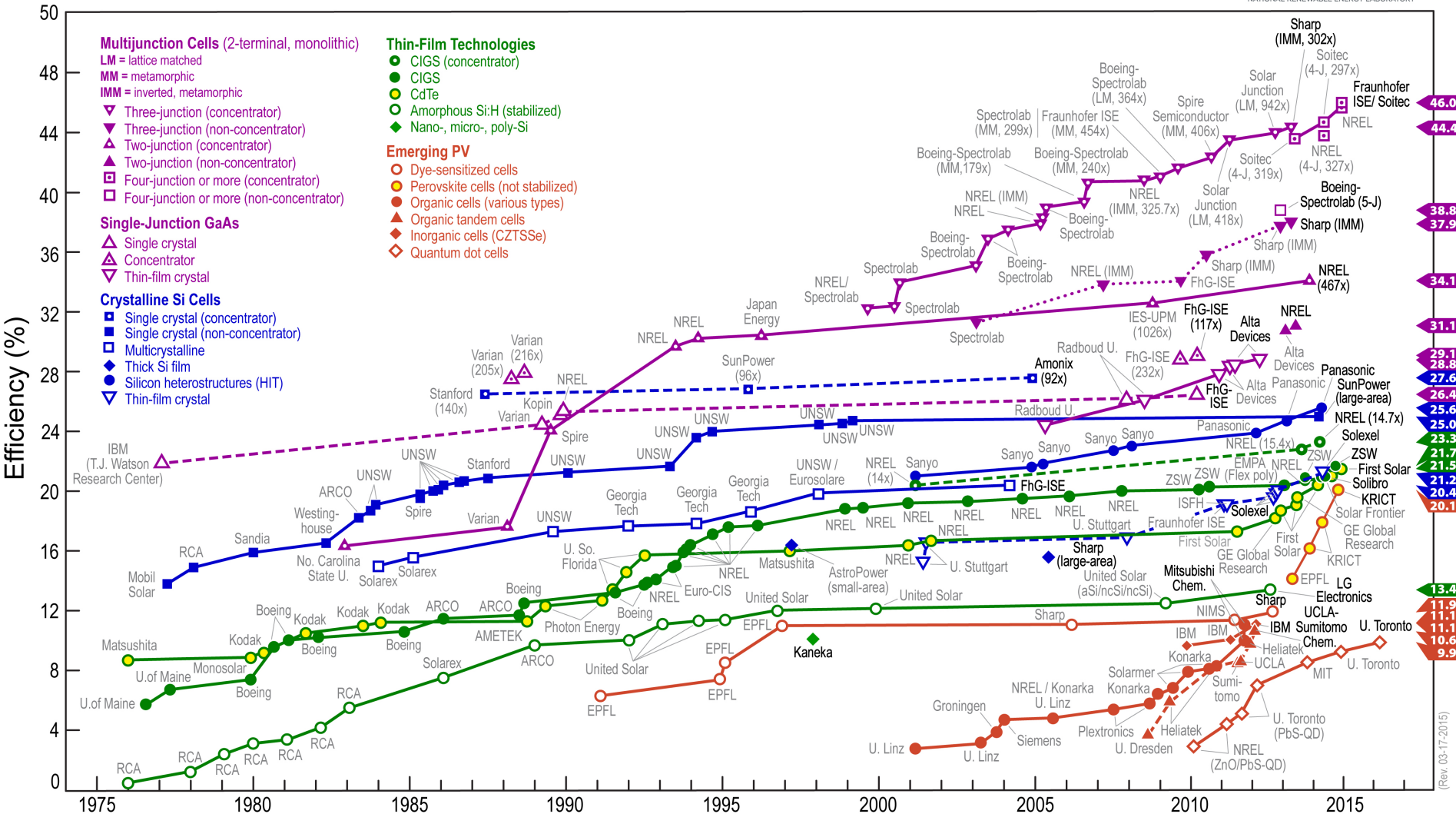


3.1 Celda Solar Nano



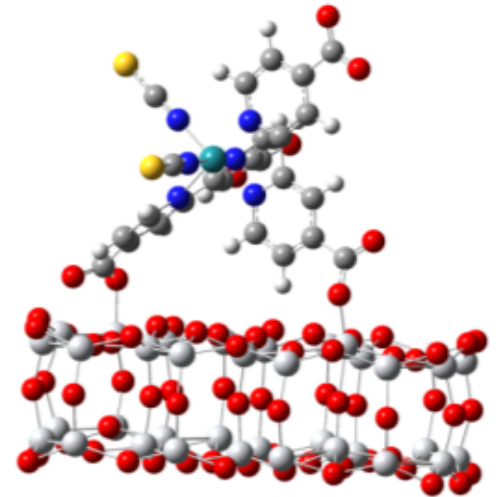
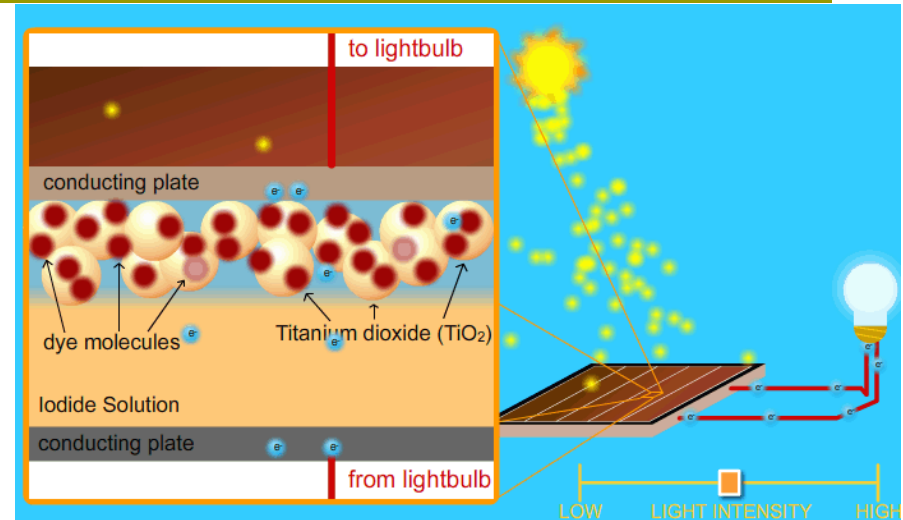
3.1 Evoluació de las eficiencias solares en función de la Tecnología

Best Research-Cell Efficiencies

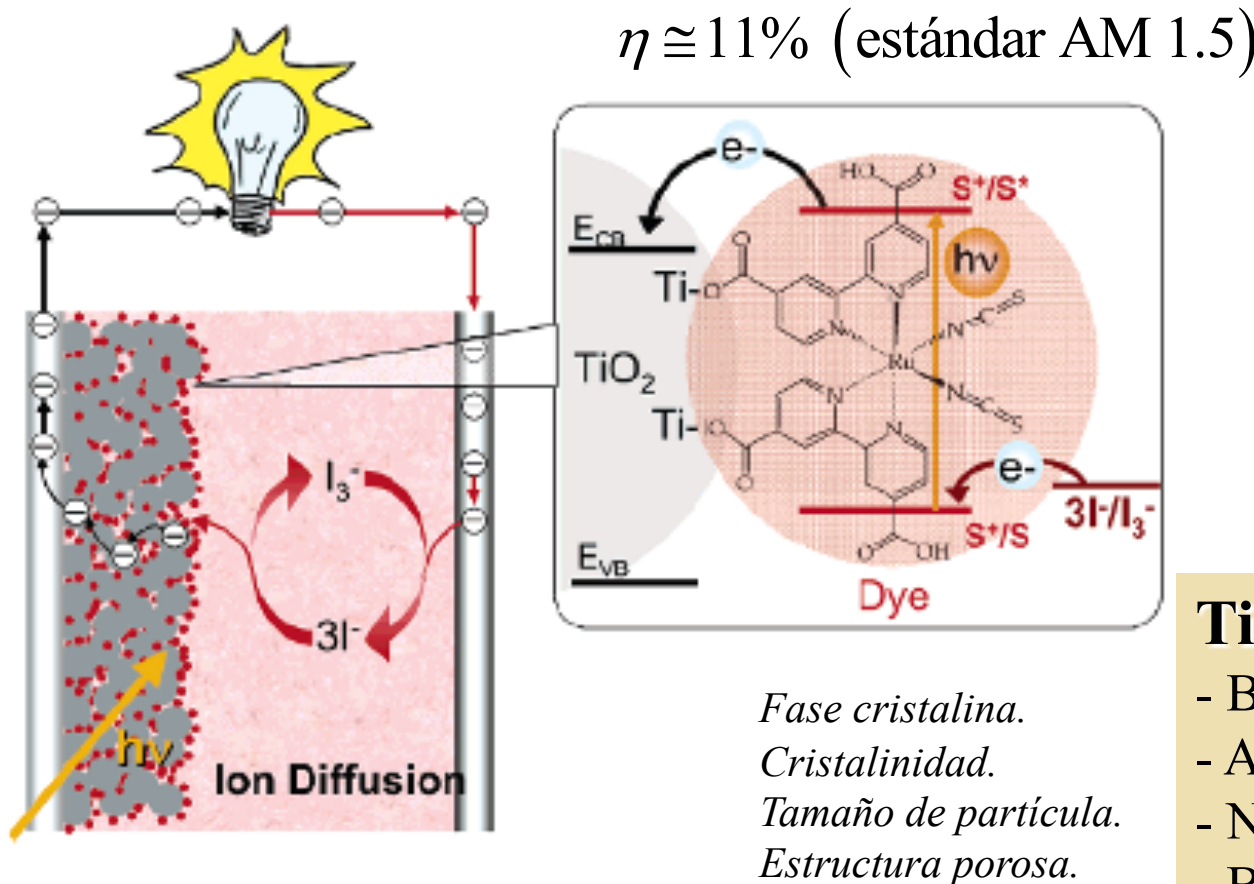


3.1 Celdas solares de sensibilización espectral (DSSC)

- Funcionamiento equivalente a las de Si
- Los electrones se arrancan del colorante y se inyectan en TiO_2 , para transportarlo fuera de la celda
- Los “huecos” permanecen en la tinta
- La separación hueco-electrón genera un voltaje y corriente.



3.1 Celdas solares de sensibilización espectral (DSSC)



☀ Foto-electrodo

- Conductor
- Semiconductor
- Colorante

☀ Contraelectrodo

- Conductor
- Catalizador

☀ Electrolito

TiO₂

- Bajo costo
- Ampliamente disponible
- No tóxico
- Biocompatible

• Grätzel M., *Inorg. Chem.* **2005**, 44, 6841

• Faccio, R; Fernández-Werner, L.; Pardo, H.; W. Mombrú, A. *Recent Patents on Nanotechnology* **2011**, 5(1), 46-61.

3.1 Primera Celda funcionando en el Centro NanoMat



3.1 Armado de Celdas: TNT

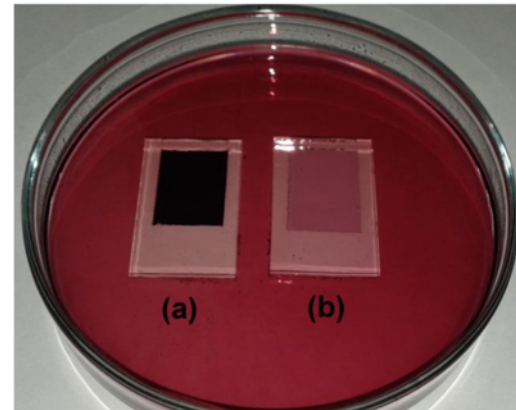
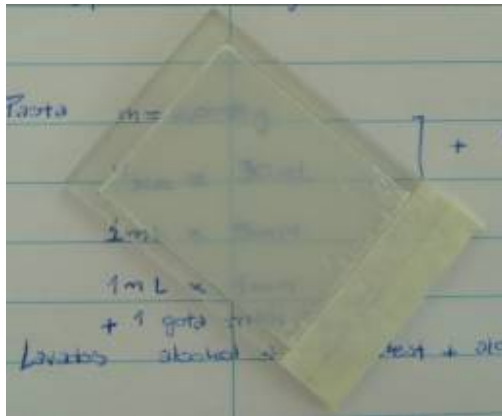


Figura 2.6-1: Fotoelectrodos basados en NTs (a) y en anatasa nanométrica (b) embebidos en solución colorante.

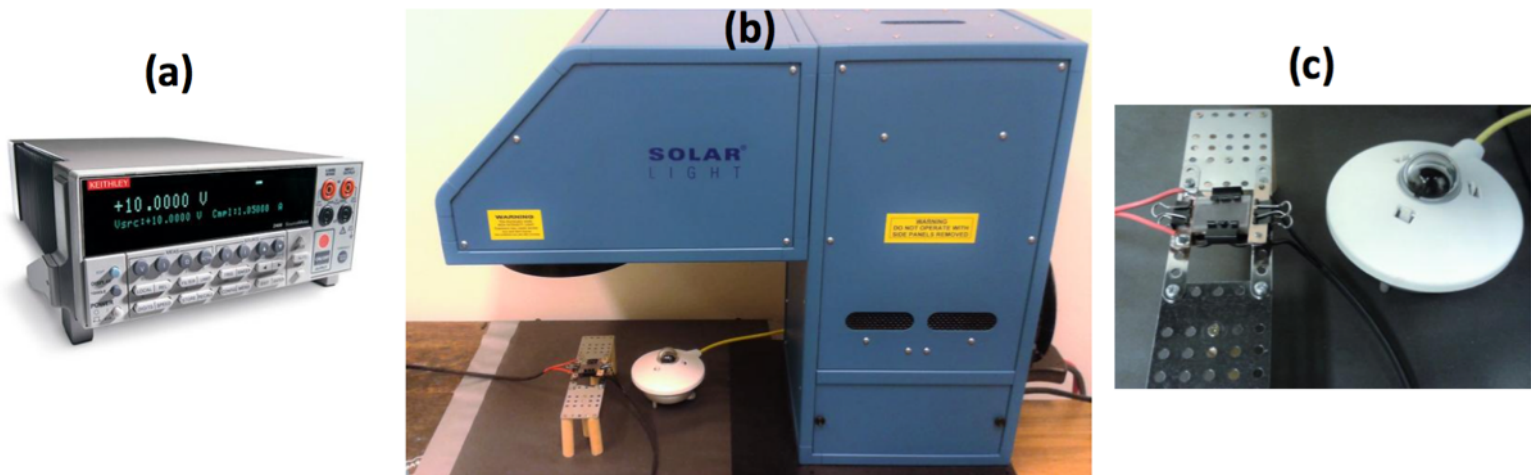
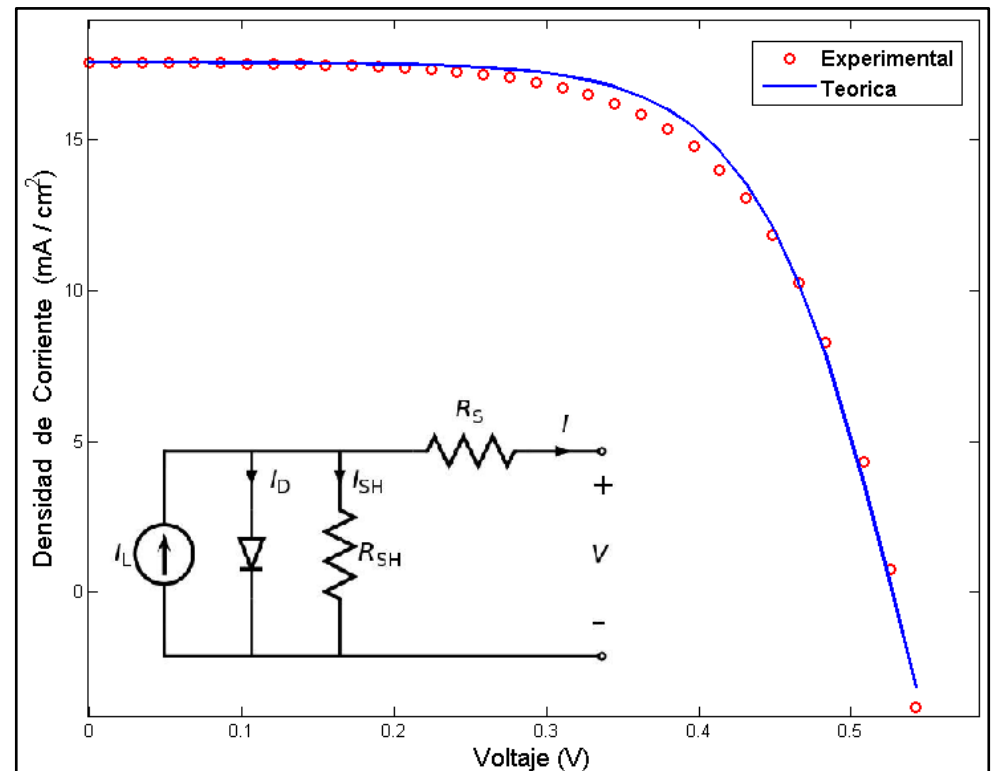
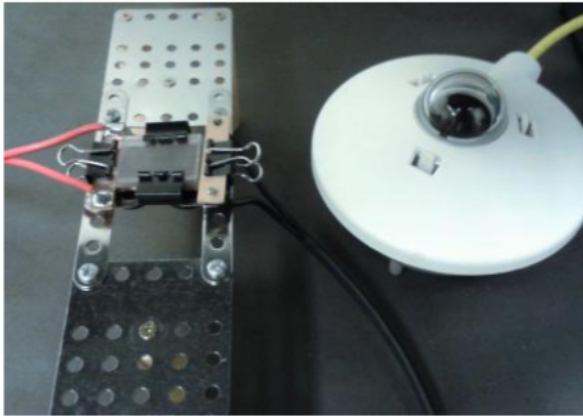


Figura 2.6-3: KEITHLEY 2400 (a), simulador solar utilizado como fuente de luz (b), prototipo DSSC con fotoelectrodo basado en NTs con electrodos conectados y piranómetro (c).

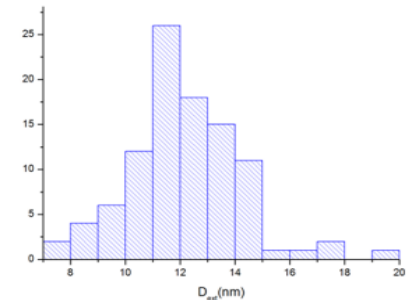
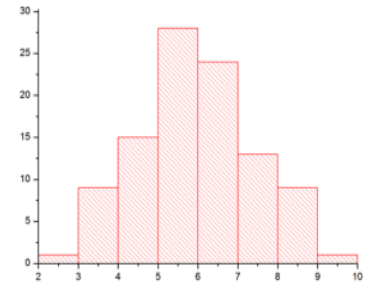
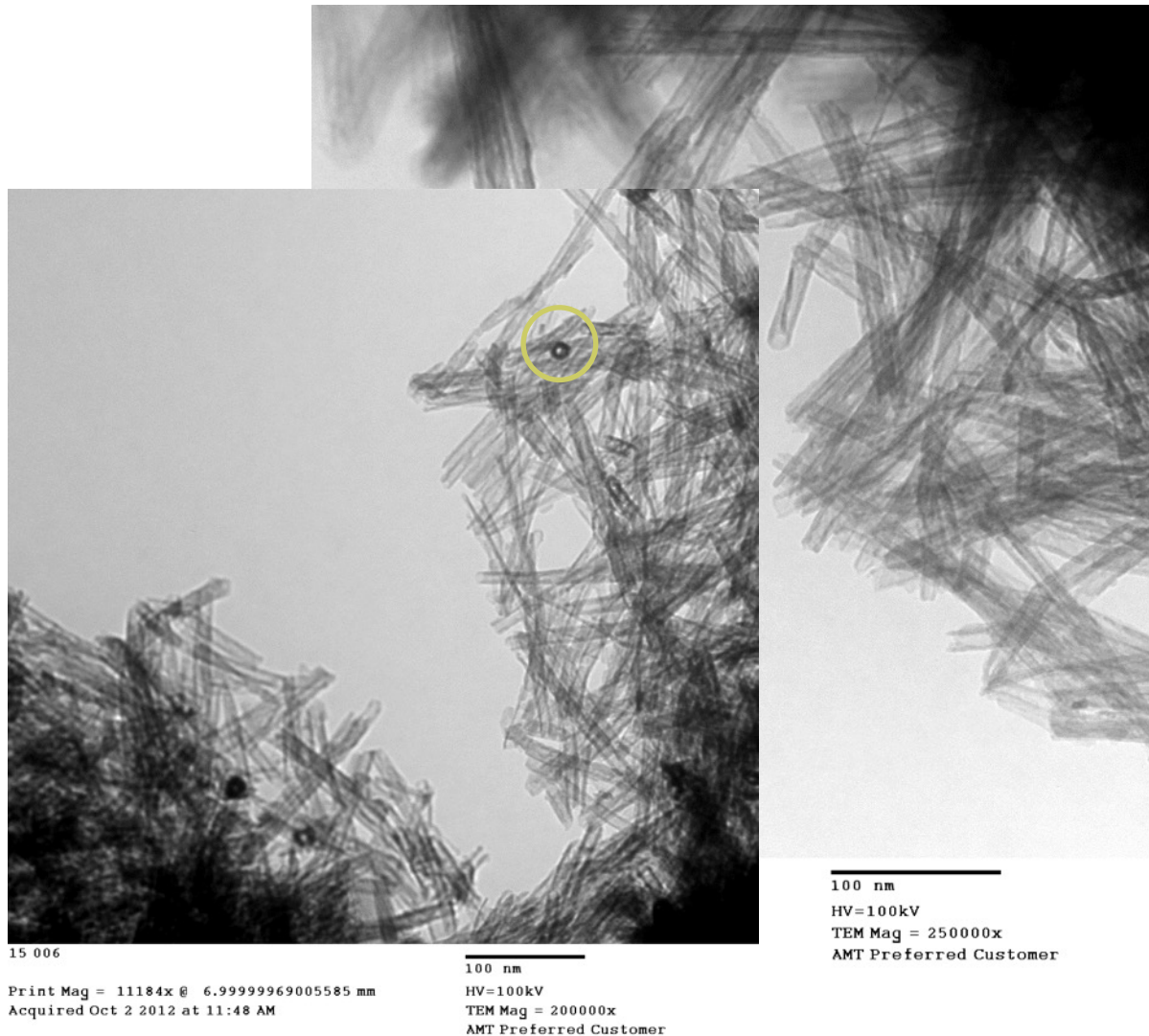
3. Eficiencias de las Celdas con NT

Curva J-V para el prototipo basado en NPs de Anatasa

Eficiencia de conversión: 5.96(5)%



3. Caracterización de NT: TEM



TEM

NT abiertos en
ambos extremos

$$D_{\text{int}} = 6(1) \text{ nm}$$
$$D_{\text{ext}} = 12(1) \text{ nm}$$



$$D_m \approx 9(1) \text{ nm y } e \approx 3(1) \text{ nm}$$

3. Caracterización Estructural

□ Microscopia Electrónica:

- Morfología
- Estructura cristalina local
- TEM
- HRTEM

□ SAXS:

- Dispersión a bajo ángulo
- Contraste de densidad electrónica.
- Morfología

□ Difracción de Rayos X:

- Orden de Largo Alcance
- Polimorfos de TiO_2
- Tamaño de dominio cristalino
- Dispersión Debye

□ Microscopia Raman:

- Estructura local y extendida
- Muestras cristalinas y amorfas

3. Eficiencias de las Celdas: Anatasa versus NT de TiO_2

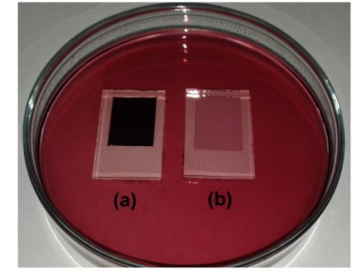
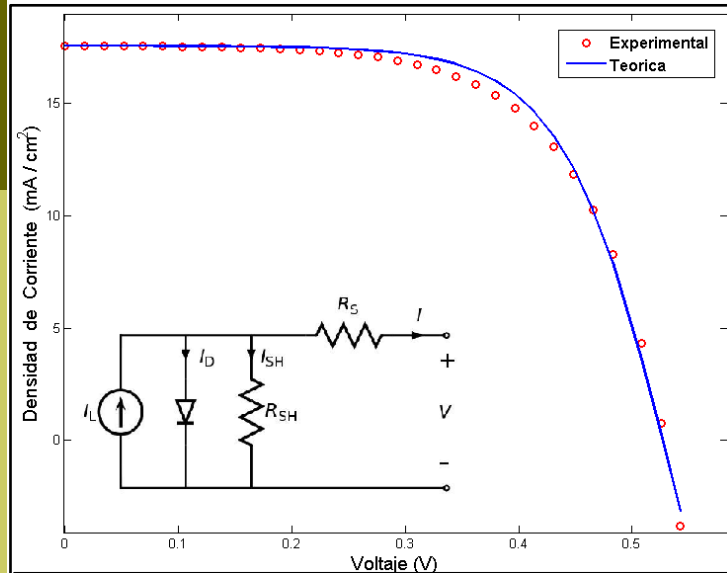
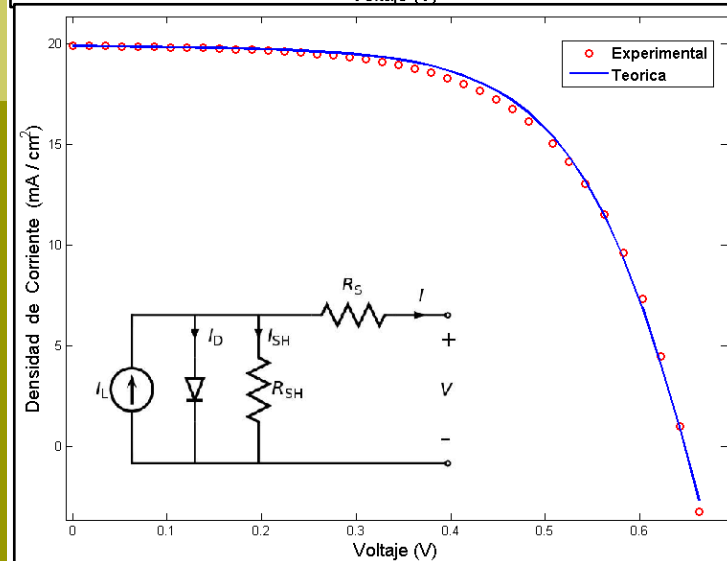


Figura 2.6-1: Fotoelectrodos basados en NTs (a) y en anatasa nanométrica (b) embebidos en solución colorante.



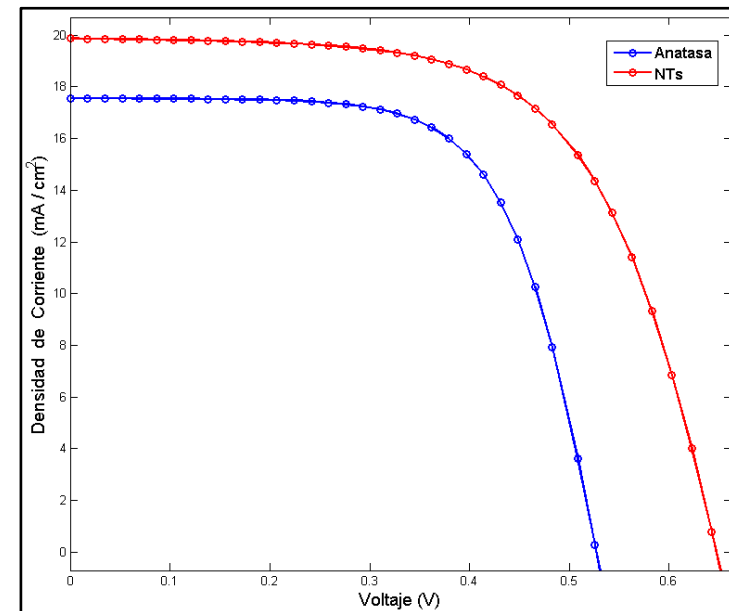
Curva J-V para el prototipo basado en NPs de anatasa

Eficiencia de conv: 5,96% (Anatasa)



Curva J-V para el prototipo basado en NTs de titanatos

Eficiencia de conv: 7,71% (TNT)



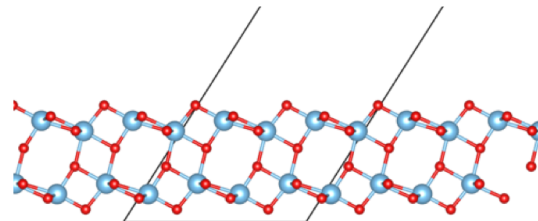
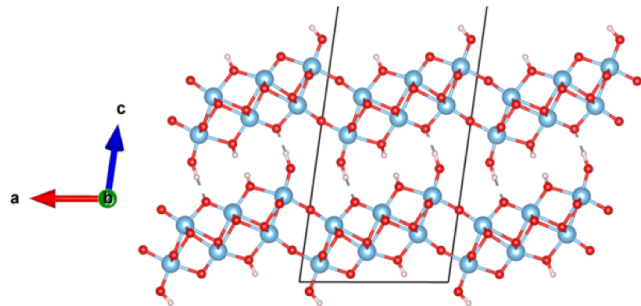
3. Eficiencias de las Celdas: Modelado y Estructura Electrónica

Superficies:

$\text{H}_2\text{Ti}_3\text{O}_7$

TiO_2 (anatasa)

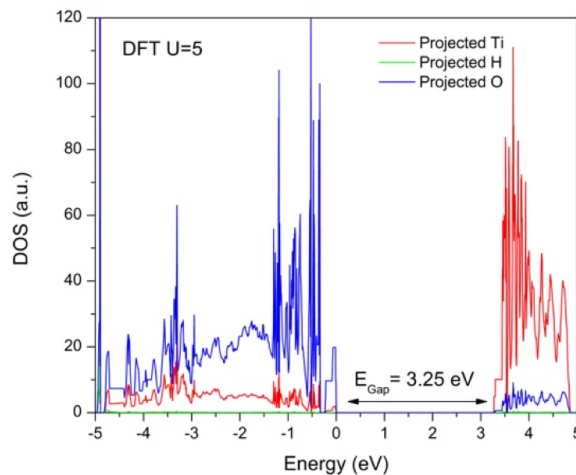
Alineamiento de Bandas



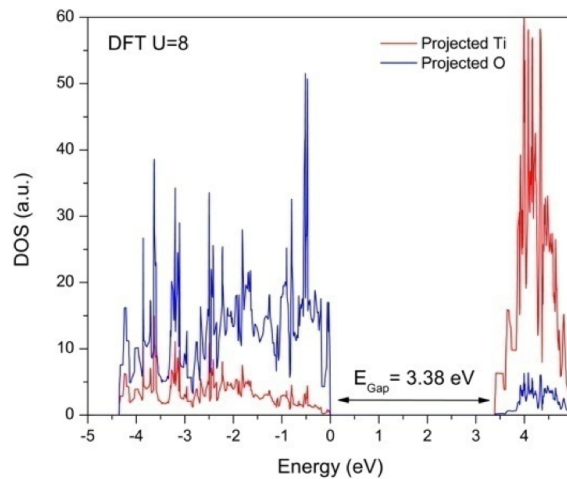
(a)

$E_{\text{gap}}(\text{exp}): 3.3 \text{ eV}$

$E_{\text{gap}}(\text{exp}): 3.2 \text{ eV}$

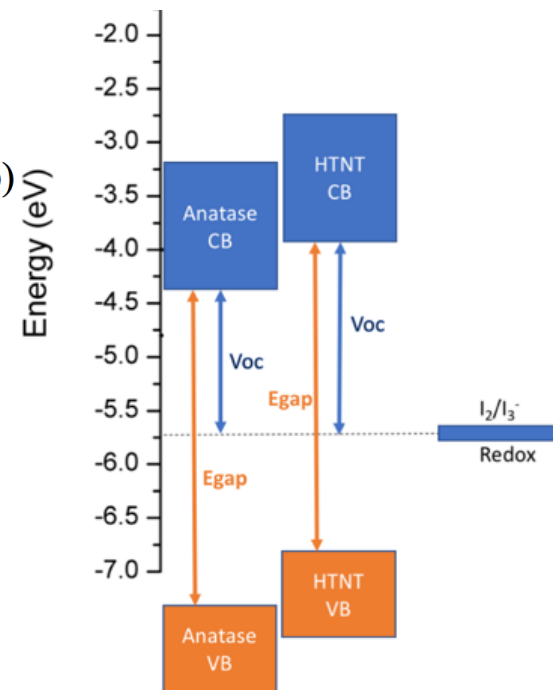


(c)



(d)

(b)



El menor valor de Φ para $\text{H}_2\text{Ti}_3\text{O}_7$ explica el aumento del V_{oc} .

3. Conclusiones Parciales

- ❑ Importancia de la complementariedad de Técnicas de Caracterización Estructural.
- ❑ Interacción Teórico-Experimental para generar modelos estructurales completos, compatibles con XRD y Raman
- ❑ Entender y predecir resultados experimentales de forma integral.
- ❑ **HTNT's:**
 - Caracterización de NT de $\text{H}_2\text{Ti}_3\text{O}_7$
 - Muy buena eficiencia de conversión $\sim 8\%$
 - Resultados coherentes con Simulación Computacional
- ❑ Es posible extender la metodología a nuevas superficies, actualmente se trabaja con Li-TNT.

L. Fernández-Werner, R. Faccio et al. App. Surf. Sci. 290 (2014) 180–187
L. Fernández-Werner, R. Faccio et al. J. Energy Storage 12 (2017), 66-77
E. Germán, R. Faccio & A. W. Mombrú. App. Surf. Sci. 426 (2017), 1182-1189.
E. Germán, R. Faccio & A. W. Mombrú. J. Phys. Comm. (2018), 55006 (1), 1-10.
E. Germán, R. Faccio & A. W. Mombrú. App. Surf. Sci. 428 (2018), 118-123.
F. Pignanelli, et al., Mater. Res. Bull., 106 (2018) 40-48.
M. Esteves, et al., Cer. Int. 2018 (en prensa)

4. Conclusiones Finales

- ❑ Nanotecnología ya está entre nosotros.
- ❑ La región cuenta con herramientas para investigar en Nanociencia y desarrollarse Nanotecnología.
- ❑ Aspectos de Control y Regulación.
- ❑ Nanociencia: interacción teórica-experimental es clave
 - Predecir el comportamiento de los materiales
 - Entender el comportamiento de los materiales
- ❑ Nanotecnología: Existen recursos estratégicos en la región como para desarrollarse en la nanotecnología.

Agradecimientos

□ Organización

□ Centro-NanoMat:

- Dr. Álvaro W. Mombrú
- Dra. Helena Pardo
- Dra. Luciana Fernández-Werner
- Dr. Mariano Romero
- Lic. Benjamín Montenegro
- Lic. Dominique Mombrú
- Lic. Fernando Pignanelli
- Lic. Martín Esteves

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E INNOVACIÓN



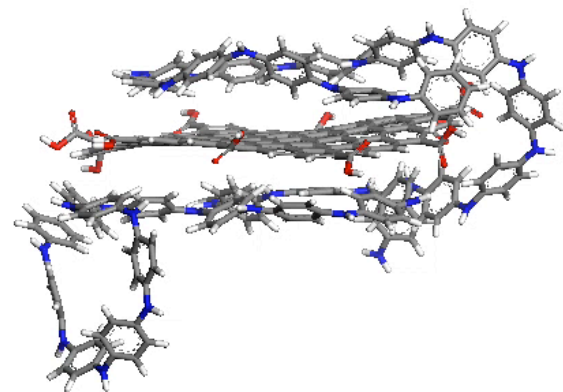
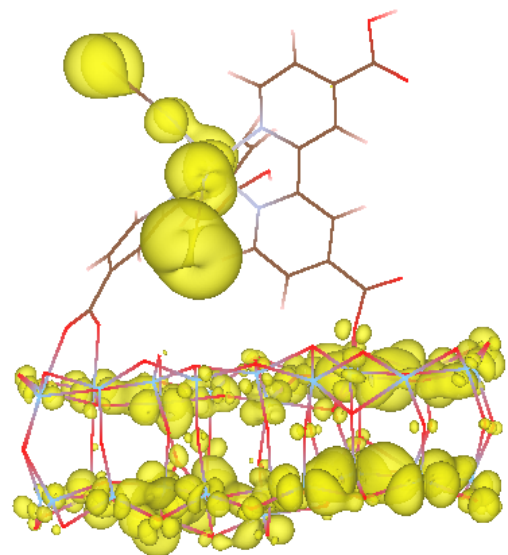
Charlas Académicas

¡Muchas Gracias!

¿Preguntas?



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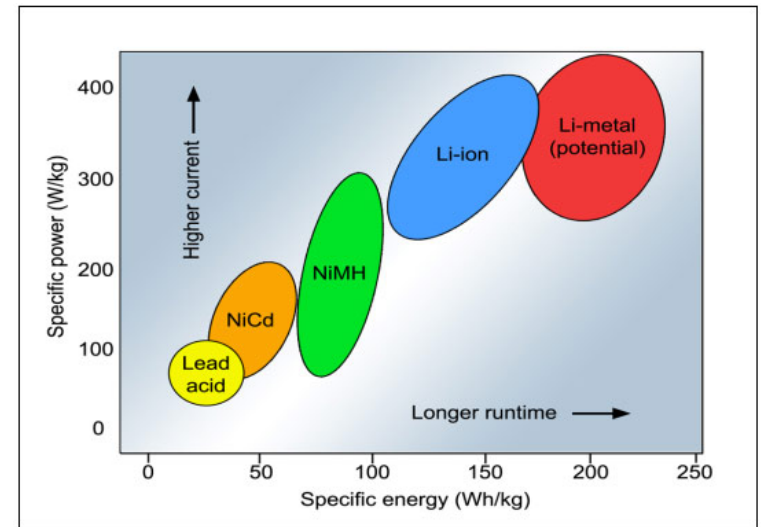
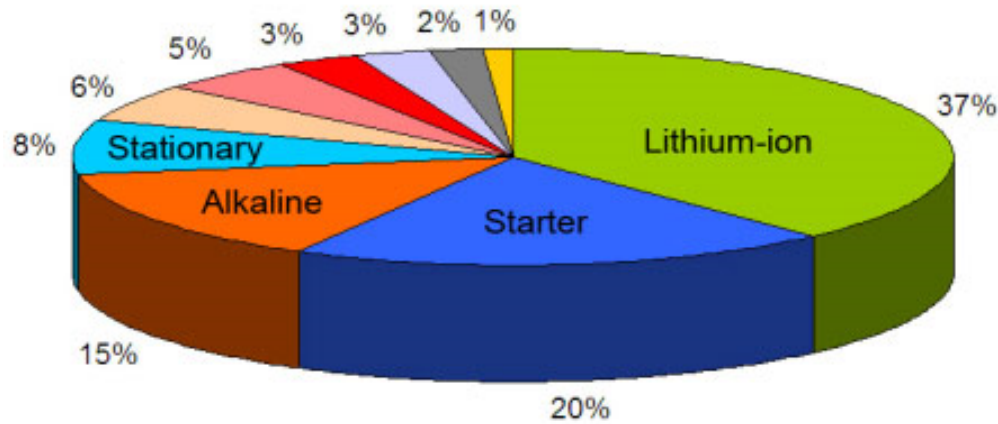




1. Materiales para Almacenamiento de Energía: Baterías de Litio

- ❑ El litio es un material importante por su bajo peso y buen desempeño.
- ❑ Recurso estratégico para la región: Argentina, Bolivia, Brasil y Chile suman más del 50% de la producción de Litio a nivel mundial.
- ❑ En el año 2010 el mercado de las baterías recargables de ion-litio alcanzó los U\$S 11000 millones.
- ❑ Demanda de baterías de litio dominada por los dispositivos electrónicos portátiles; pero el emergente mercado de aplicaciones para vehículos eléctricos (VE) y vehículos híbridos (PHEV)

1. Materiales para Almacenamiento de Energía: Baterías de Litio



Cátodo

Lithium cobalt oxide (LiCoO_2)

Lithium nickel manganese cobalt oxide (LiMnCoO_2)

Lithium iron phosphate (LiFePO_4)

Lithium nickel cobalt aluminum oxide (LiNiCoAlO_2)

Aplicaciones

cell phones, tablets, laptops, cameras

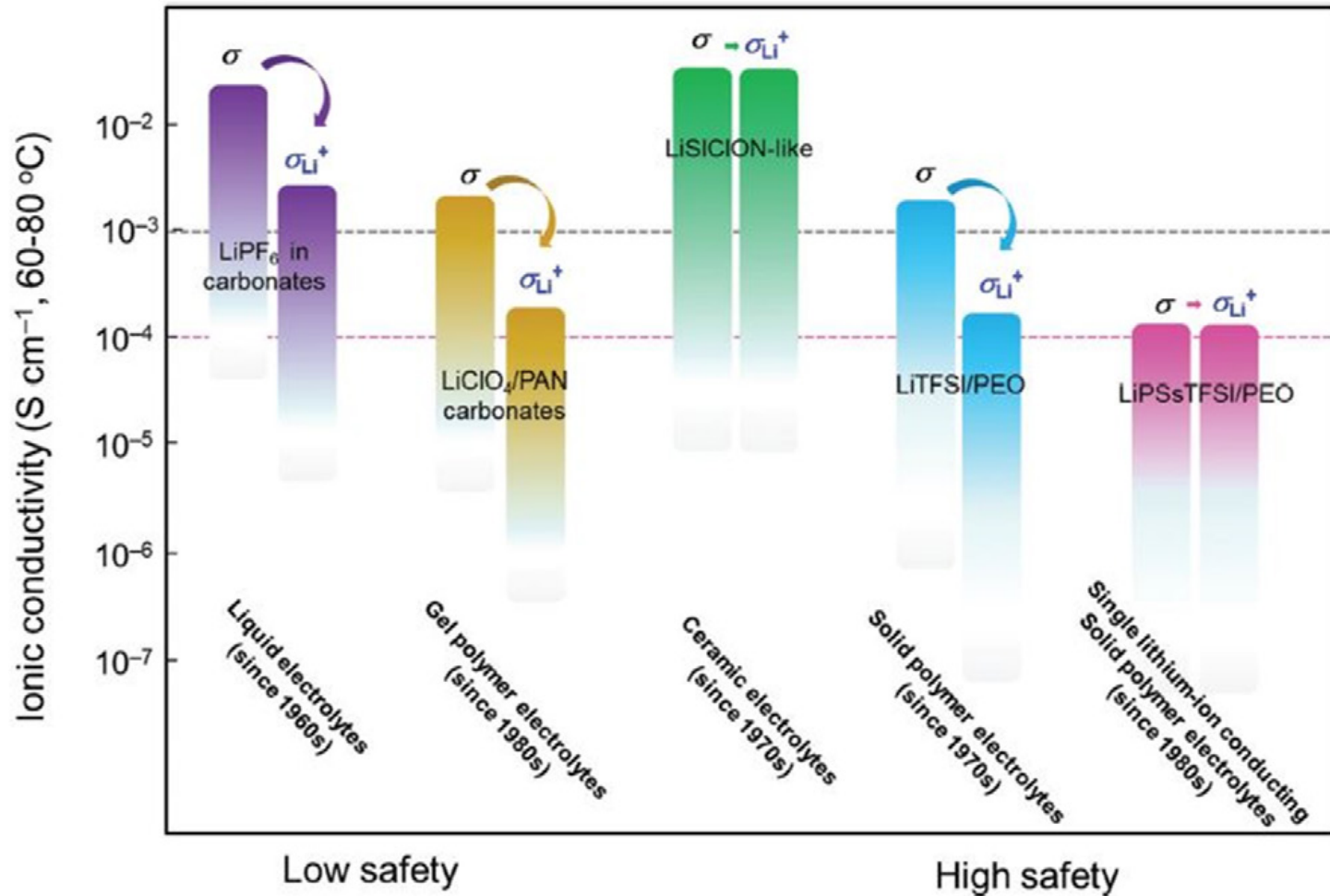
Chevy Volt

Electric vehicle

Tesla

https://batteryuniversity.com/index.php/learn/article/global_battery_markets

1. Materiales para Almacenamiento de Energía: Baterías de Litio



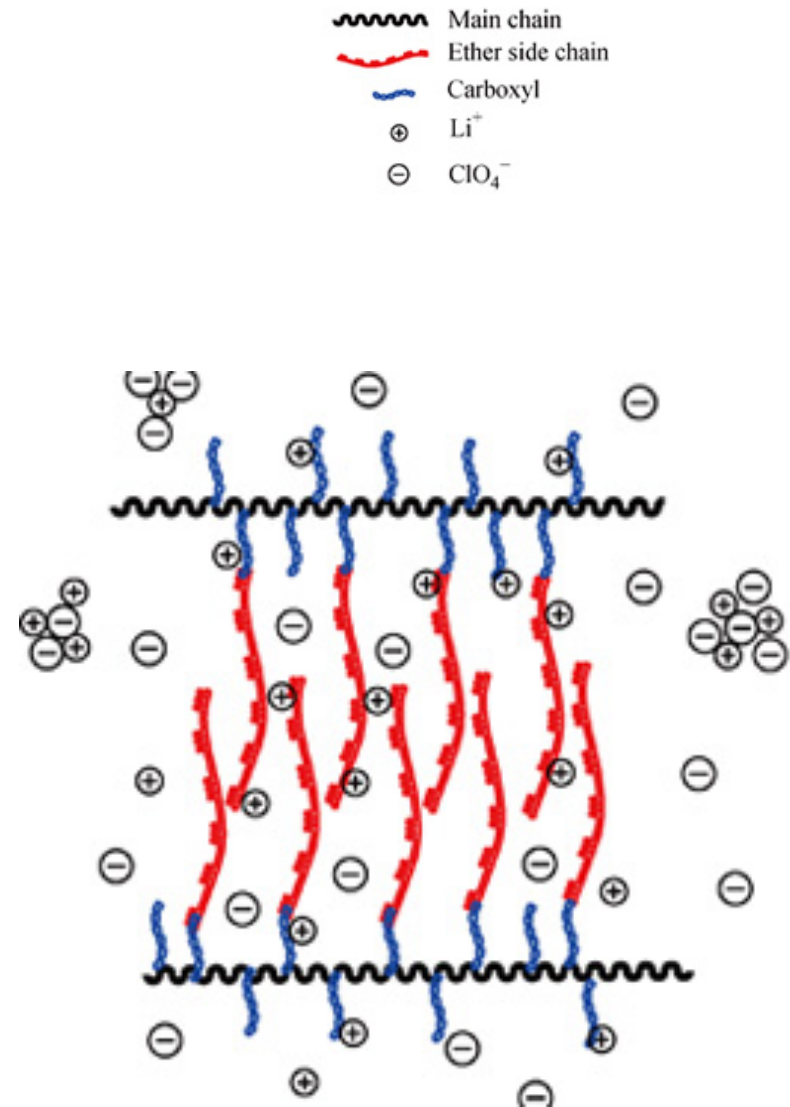
1. Electrolitos Sólidos vs Líquidos

□ Ventajas

- Mayor Durabilidad
- Mayor Estabilidad Térmica
- Posibilidad de Miniaturización
- Mejor Seguridad
- Mayor Eficiencia
- Mejor trato del Medio Ambiente

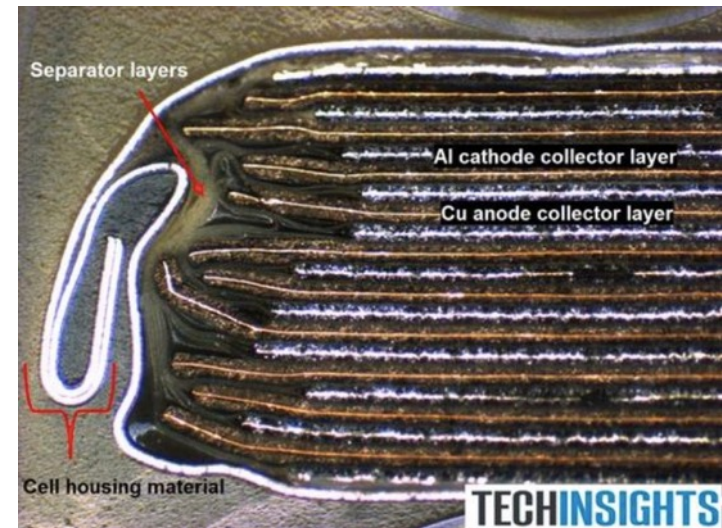
□ Desventajas

- Altas Energías de Activación
- Bajas Conductividades



1. Electrolitos Sólidos:

Samsung Recall Note 7: Uso de electrolitos líquidos



In the original run of devices, the battery, produced by a Samsung subsidiary, contained a design flaw that made electrodes on the top-right of the battery susceptible to bending. This weakened separation between positive and negative tabs of the battery, thus resulting in [thermal runaway](#) and [short circuits](#).

Some batteries were also missing insulation tape entirely. Samsung reported that these oversights resulted from the vendor's push to ramp up production of batteries for the replacement phones in order to meet demand.

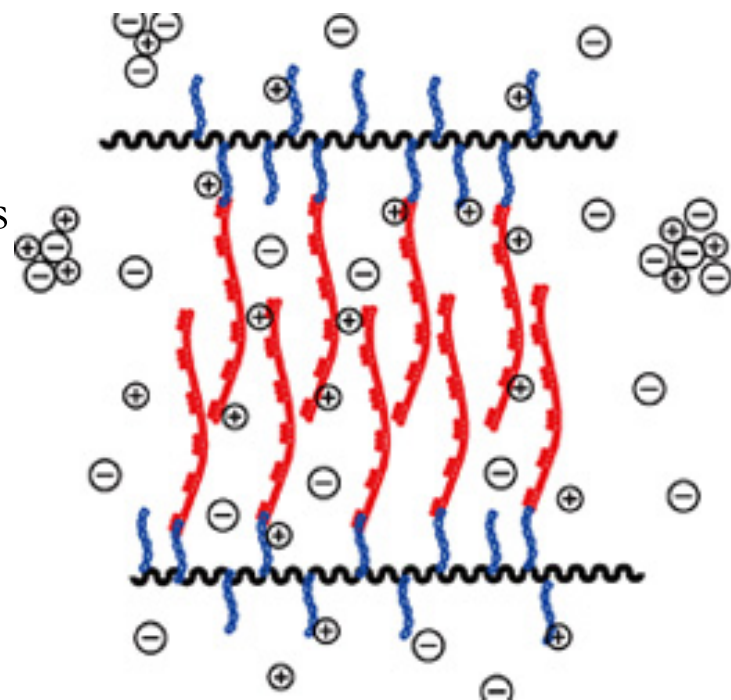
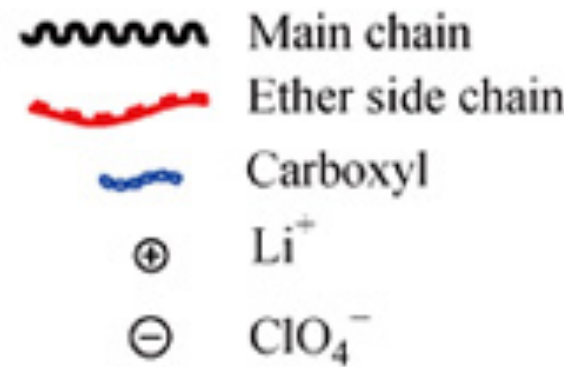
2. Estrategia y Metodología

Estrategia

- Disminuir la viscosidad intrínseca del polímero (T_g y T_m)
- Mejorar la afinidad entre el Li^+ y el polímero
- Mejorar conducción catiónica Li^+
- Bajar conducción aniónica (ej. ClO_4^-)

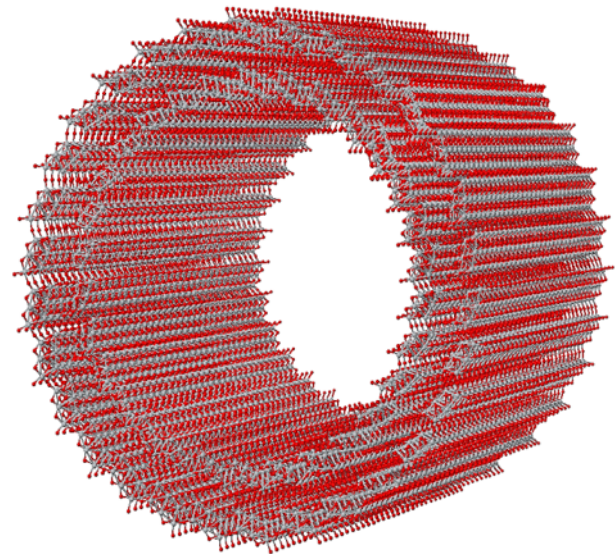
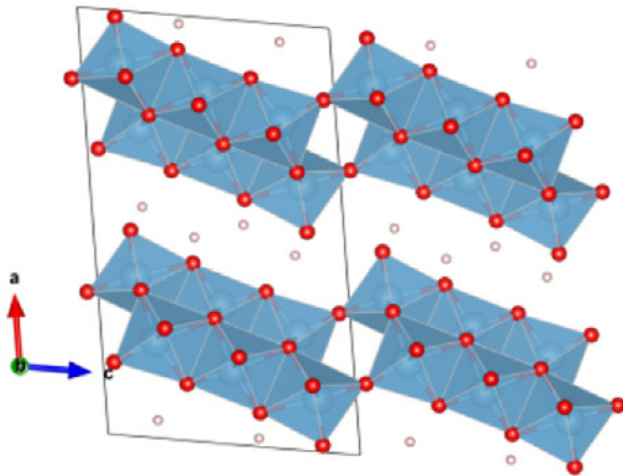
Metodología

- Síntesis de nuevos Materiales y Nanomateriales
- Agregado de cargas (fillers):
 - Modificación del T_g/T_m del Polímero
 - Afinidad anión con la carga
- Caracterización Químico Estructural
- Caracterización y evaluación de desempeño Eléctrico



2. Nanotubos de HTNT como fillers

- ❑ ¿Por qué?
- ❑ Los nanotubos de HTNT poseen un área específica importante.
- ❑ Se conoce la morfología y estructura de los nanotubos (bloque de construcción)
- ❑ Tiene estructura bicapa, que permite alojar otros iones

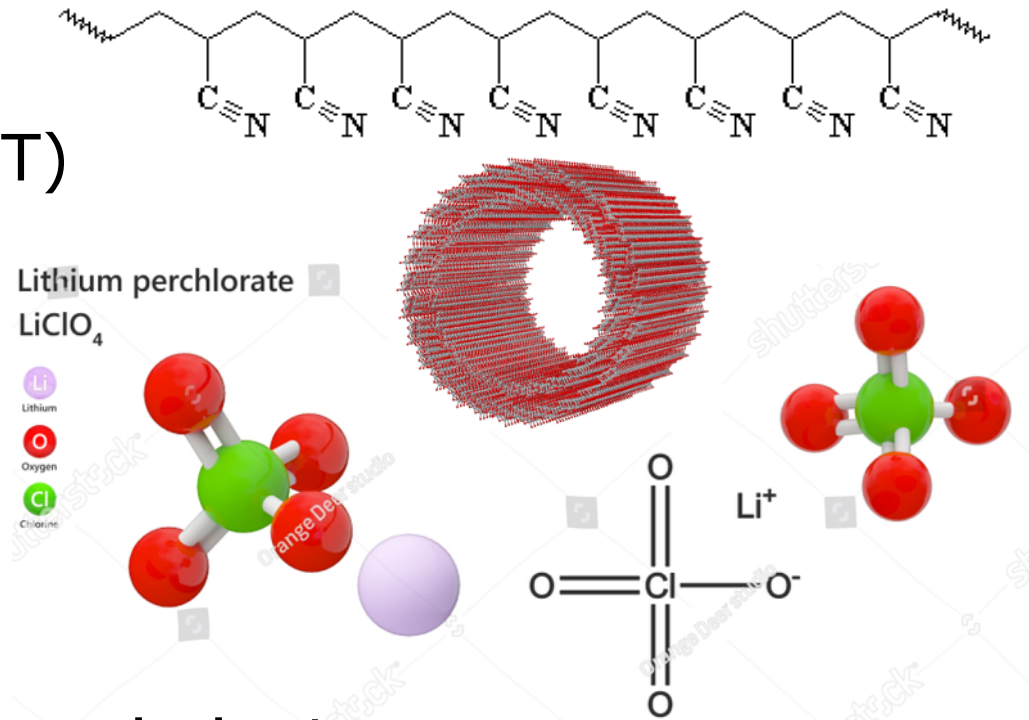


2. Selección del Sistema

- Polímero: PAN
- Carga: $\text{H}_3\text{Ti}_2\text{O}_7$ (HTNT)
- Sal: LiClO_4

Se espera:

- Disociar la sal
- Li^+ se asocie al PAN
- ClO_4^- limitado en su movimiento
- ¿asociado al HTNT?



3. Caracterización Estructural

- Small Angle X-ray Scattering (SAXS)
- XRD convencional
- DSC: calorímetra diferencial

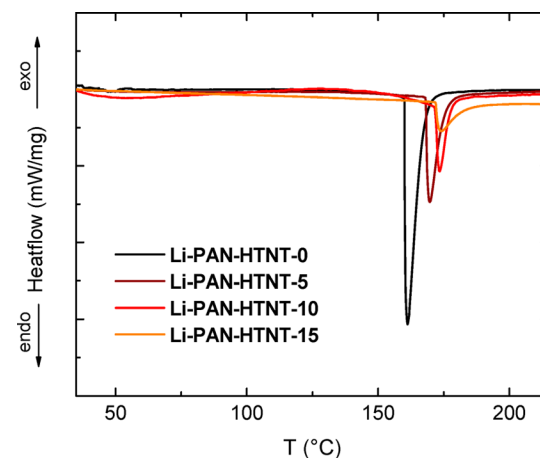
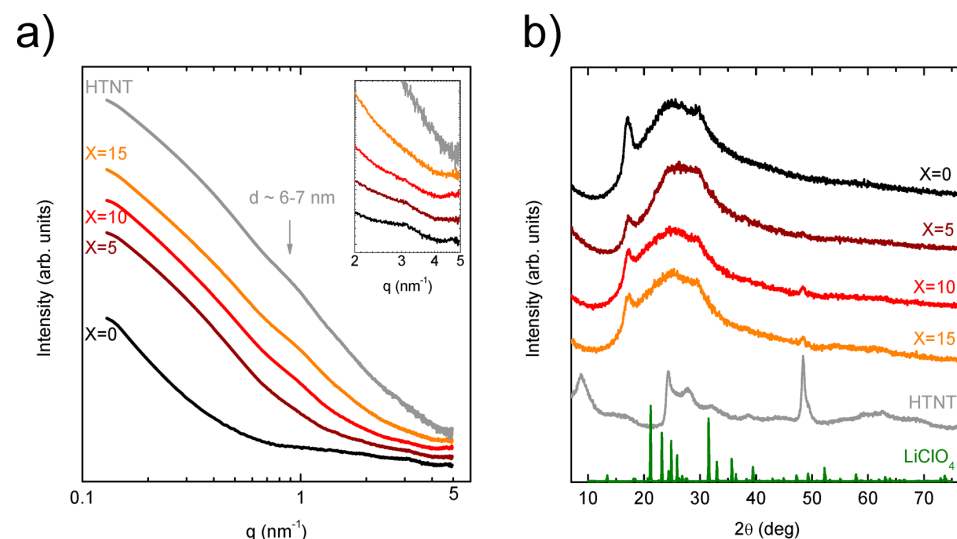


Figure 7. Differential scanning calorimetry profiles for Li-PAN-HTNT- X with $X = 0, 5, 10$, and 15 .

Table 2. DSC Analysis for Li-PAN-HTNT- X with $X = 0, 5, 10$, and 15 ^a

	$X = 0$	$X = 5$	$X = 10$	$X = 15$
T_m (°C)	161.2	169.7	173.4	173.9
ΔH_m (J/g)	159.03	74.74	35.26	34.69

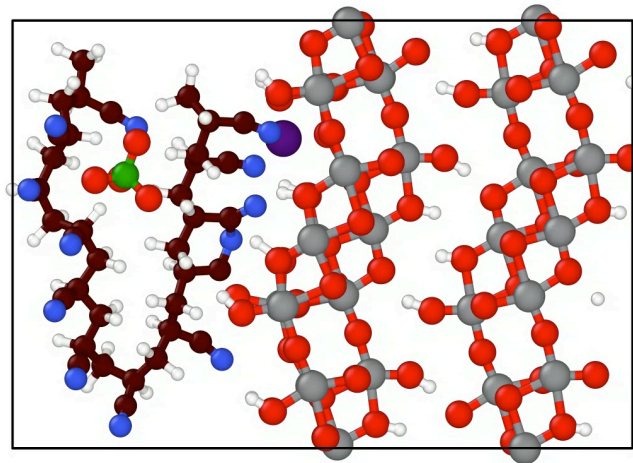
^aMelting temperature (T_m) and heat (ΔH_m) were obtained from DSC analysis.

Figure 3. (a) Small angle X-ray scattering and (b) X-ray powder diffraction patterns for Li-PAN-HTNT- X with $X = 0, 5, 10, 15$, HTNT samples, and crystalline LiClO₄ reference.

3. Dinámica Molecular

- NVT a 300 K (3 ps polímero + 500 fs DFT sistema total)
- $E_{\text{conf1}} - E_{\text{conf2}} = 5.0 \text{ eV}$

Conf. 1



Conf. 2

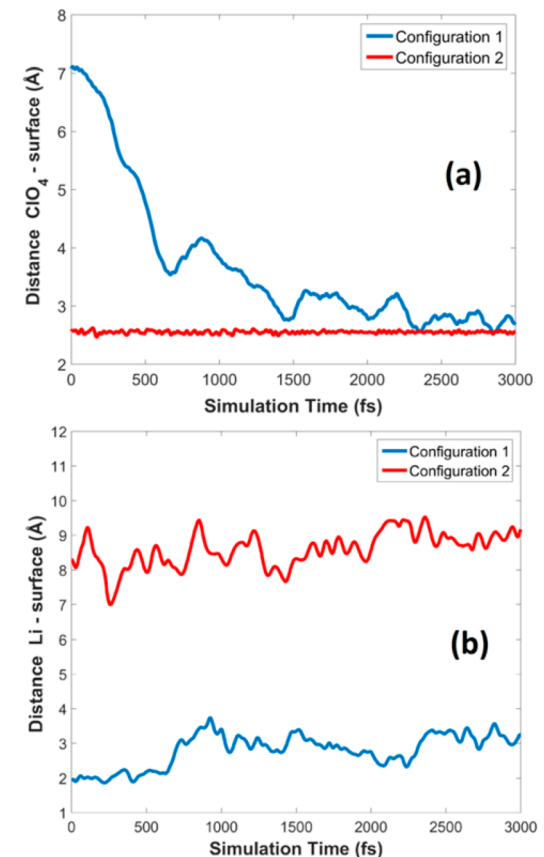
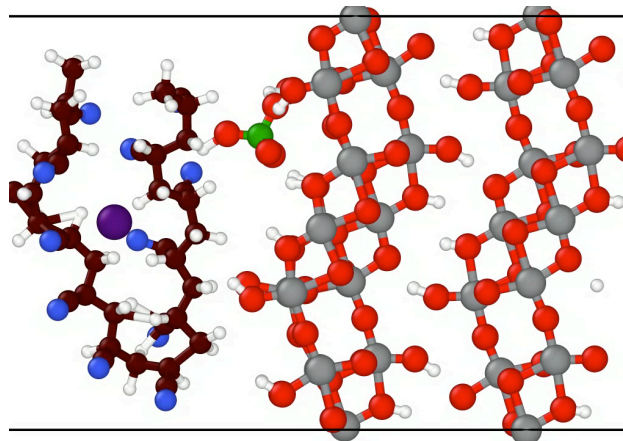


Figure 2. (a) Perchlorate and (b) lithium ions distance from HTNT surface in configurations 1 and 2 as a function of simulation time.

4. Caracterización Electroquímica

Propiedades Eléctricas

$$\sigma_{total} \sim 3.95 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$$

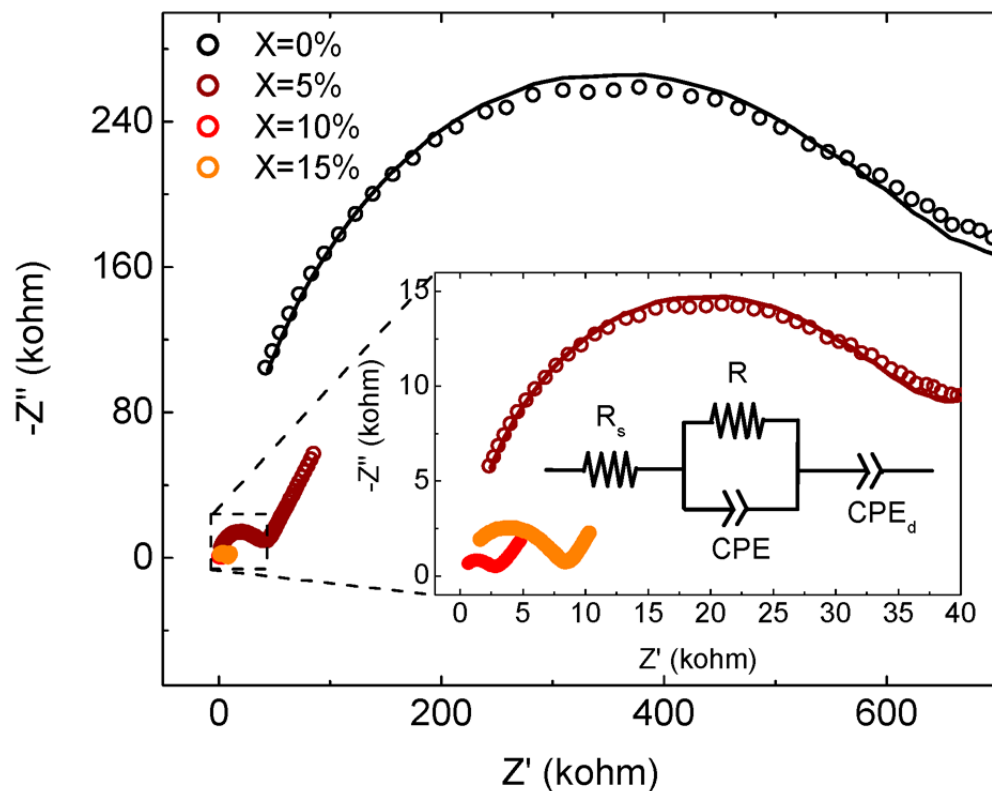


Table 3. Impedance Spectroscopy Analysis for Li-PAN-HTNT-X with X = 0, 5, 10, and 15^a

	X = 0	X = 5	X = 10	X = 15
R (ohm)	$(6.13 \pm 0.12) \times 10^5$	$(3.39 \pm 0.07) \times 10^4$	$(2.53 \pm 0.12) \times 10^3$	$(7.93 \pm 0.25) \times 10^3$
CPE Q ₀ (F)	$(1.37 \pm 0.20) \times 10^{-12}$	$(2.48 \pm 0.37) \times 10^{-11}$	$(2.09 \pm 0.62) \times 10^{-9}$	$(4.53 \pm 1.00) \times 10^{-10}$
CPE n	0.860 ± 0.011	0.860 ± 0.012	0.685 ± 0.023	0.717 ± 0.018
σ (S·cm ⁻¹)	$(1.63 \pm 0.08) \times 10^{-6}$	$(2.95 \pm 0.15) \times 10^{-5}$	$(3.95 \pm 0.20) \times 10^{-4}$	$(1.26 \pm 0.64) \times 10^{-4}$

^aResistance (R) and constant phase element (CPE) parameters were calculated from the circuit model fittings shown in Figure 8b, inset. The lithium conductivity (σ) was calculated using $\sigma = 1/\rho$ using $\rho = R(A/d)$ with $A = 0.1 \text{ cm}^2$ as the electrode contact area and $d = 0.1 \text{ cm}$ as the pellet thickness. In all cases, the analysis was performed in triplicate.

5. Conclusiones Generales

- ❑ Se realizó la preparación de nanocompósitos polímero-nanopartícula
 - ❑ Se caracterizaron de forma Químico-Estructural
 - ❑ Se caracterizaron electroquímicamente, con valores en rangos aceptables, acorde al estado del arte.
- $\sigma_{total} \sim 3.95 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$

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Article

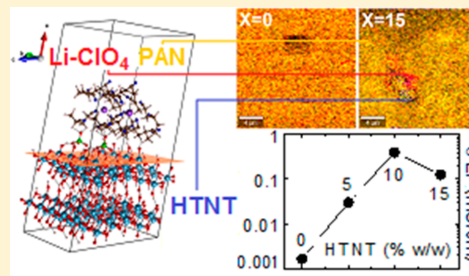
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Enhancement of Lithium-Ion Transport in Poly(acrylonitrile) with Hydrogen Titanate Nanotube Fillers as Solid Polymer Electrolytes for Lithium-Ion Battery Applications

Fernando Pignanelli, Mariano Romero,*[✉] Ricardo Faccio,*[✉] Luciana Fernández-Werner,[✉] and Alvaro W. Mombrú

Centro NanoMat/CryssMat/Física, DETEMA Facultad de Química, Universidad de la República, Montevideo, C.P. 11800, Uruguay

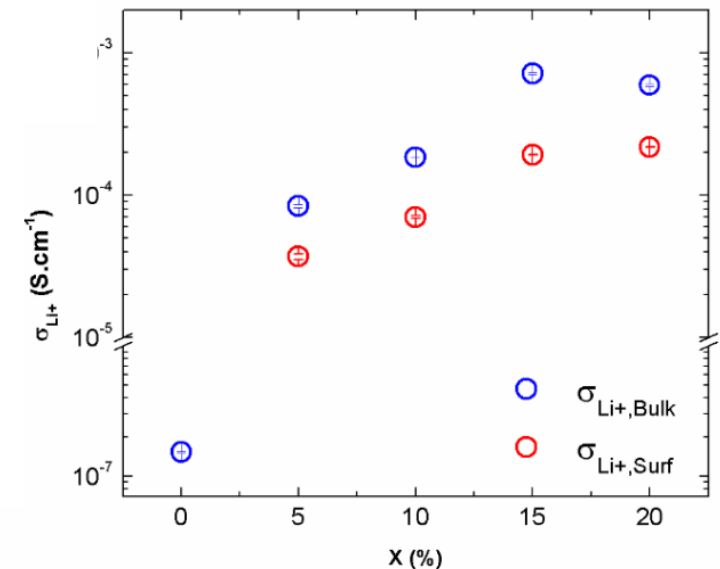
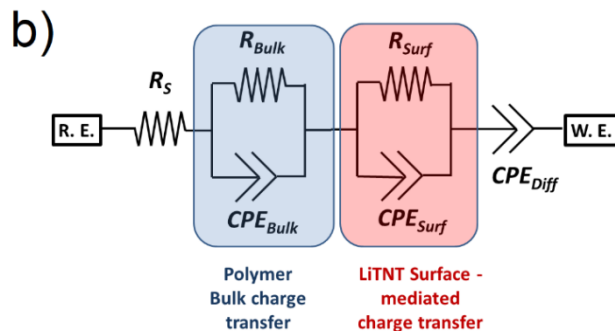
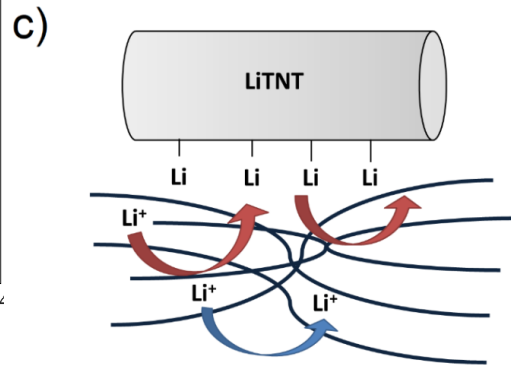
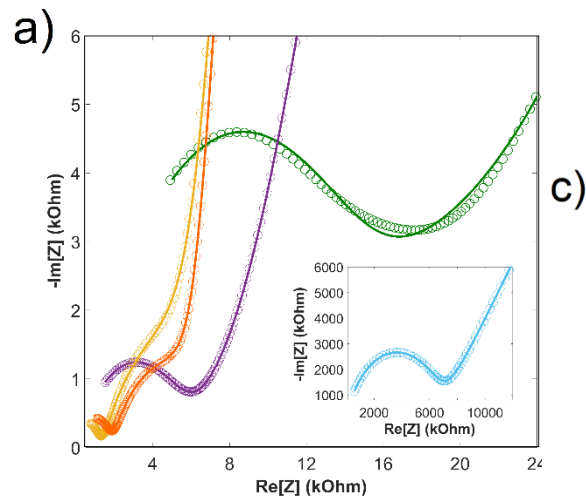
ABSTRACT: In the present work, we report the enhancement of lithium-ion dissociation and transport in poly(acrylonitrile) host promoted by the addition of hydrogen titanate nanotube fillers for solid polymer electrolytes. We show experimental and theoretical evidence of lithium perchlorate dissociation due to the presence of the acidic hydrogen titanate nanotubes embedded in the polymer matrix. We performed confocal Raman microscopy analysis to reveal the presence of lithium perchlorate dissociation at the interface of polymer and nanotube fillers. The large affinity of perchlorate anions at the hydrogen titanate nanotube surface, as envisaged from the ab initio molecular dynamics simulations, could be responsible for the enhancement of more than 2 orders of magnitude in the lithium conductivity, reaching $\sim 4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for a certain amount of nanotube fillers addition.



5. Perspectivas

Seguir con el trabajo con Fillers activos:

■ LiTNT y NaTNT



$$\sigma_{\text{total}} \sim 7 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$$

F. Pignanelli et al, submitted (2018)