Clase 1
Operaciones numéricas básicas
Ordenes de tamaño del Universo

Clase 1- Operaciones numéricas básicas en Biología
(biological numeracy)

Base de datos CONFIABLES en Biologia : BioNumbers website (http://bionumbers.hms.harvard.edu/)

BNID

Estimados rápidos de ordenes de magnitud en Biologia:

limite inferior Xi

limite superior Xs

guess reasonable upper and lower bounds to within a factor of 10.

media geometrica $X_{estimada} : \sqrt{xi.xs}$

media aritmética :resultados dominados por el limite superior-sobreestimación

Clase 1 Orden de magnitud vs aproximacion

"Order of magnitude" ~ means so only to **within a factor of 10** (or in a different context it means "proportional").

"Approximately" is indicated by the symbol **≈**, and loosely means accurate to **within a factor of 2** or so.

We usually write <u>approximately</u> because we know the property value indeed roughly but to better than a factor of 10 so ≈ is the correct notation and not ~.

In the cases where we only know the order of magnitude we will write the value only as an exponent 10^x without extraneous significant digits.

 Grandes aproximaciones

1 Dalton (Da) = 1 g/mol ≈ 1,6 x 10^{-24} g

1 nM aproximadamente 1 molécula por volumen bacteriano (1 μm^3 = 1 fl= 10^{-15} l) o 10-10^2 para levaduras, 10^3-10^4 para células HeLa

1M aproximadamente 1/nm^3

2-4 x 10^6 proteínas /volumen celular

1ppm proteoma celular ≈ 5 nM

1 mg ADN ~ 1 pmol segmentos de 1 kb longitud ≈ 10^{12} moléculas

En condiciones estándar **1M partículas** están ≈ 1 nm distancia entre si

Densidad del aire ≈ 1kg/m3

Densidad del agua [55 M] ≈ 1000 x densidad del aire ≈ 1000 kg/m^3

50 mM osmolitos ≈ 1 atm presión osmotica

1k_bT ≈ 2,5 KJ/mol ≈ 0,6 kcal/mol ≈ 25meV ≈ 4pN nm ≈ 4x 10^{-21}J

~ 6kJ/mol sostienen una diferencia de concentración de 1 orden de magnitud [k_bT ln (10) ≈ 1,4 kcal/mol]

El movimiento a través de membrana esta asociado a 10-20 kJ/mol por cada carga neta debido a potencial de membrana

Hidrolisis de ATP en condiciones fisiológicas libera 20 k_bT ≈ 50 kJ/mol ≈ 12 kcal/mol ≈ 10^{-19} J

1litro O_2 libera ≈ 20kJ durante la respiración

Un pequeño metabolito difunde 1 nm en ~ 1 ps

Las cifras significativas (o dígitos significativos) de un numero son aquellas que tienen un significado real o aportan alguna información

Cifras significativas de un número

Para conocer el número de cifras significativas de un número decimal, se siguen las siguientes reglas:

- Cualquier dígito distinto de cero es significativo. Por ejemplo, 438 tiene tres cifras significativas.
- Los ceros situados en medio de números diferentes de cero son significativos. Por ejemplo, 402 tiene tres cifras significativas, y 30002 tiene cinco cifras significativas.
- Los ceros a la izquierda del primer número distinto de cero no son significativos. Por ejemplo, 0,0023 tiene dos cifras significativas.
- Los ceros que se encuentran después de la coma y después de un dígito distinto de cero, son significativos. Por ejemplo 10,00 tiene 4 cifras significativas, y 0,0030 tiene dos cifras significativas.
- En los números enteros, los ceros situados después de un dígito distinto de cero pueden ser o no significativos. Por ejemplo, 600 puede tener una cifra significativa (6), dos (60), o tres (600). Para conocer el número correcto de cifras significativas necesitamos conocer más información acerca de cómo fué generado el número (por ejemplo, si el número es una medición, necesitamos conocer la precisión del instrumento de medición empleado). También podemos conocer el número correcto de cifras significativas si expresamos el número en notación científica. Por ejemplo, 6×10^2 tiene una cifra significativa, $6,0 \times 10^2$ tiene dos cifras significativas, y $6,00 \times 10^2$ tiene tres cifras significativas.

La precisión de la medida esta dada por su repetibilidad
La repetibilidad está dada por la desviación estándar o error estándar

El numero de cifras significativas serian indicativas de precisión. La incerteza de la ultima cifra seria indicativa de exactitud

La incerteza se reporta con 1 solo digito

Los errores sistemáticos no causan imprecisión, pero si inexactitud

it is usually a reasonable choice in reporting numbers in biology to use 2 significant digits

Clase 1 Cifras significativas

Cuando están expresados en notación científica, todos los dígitos se interpretan como significativos.

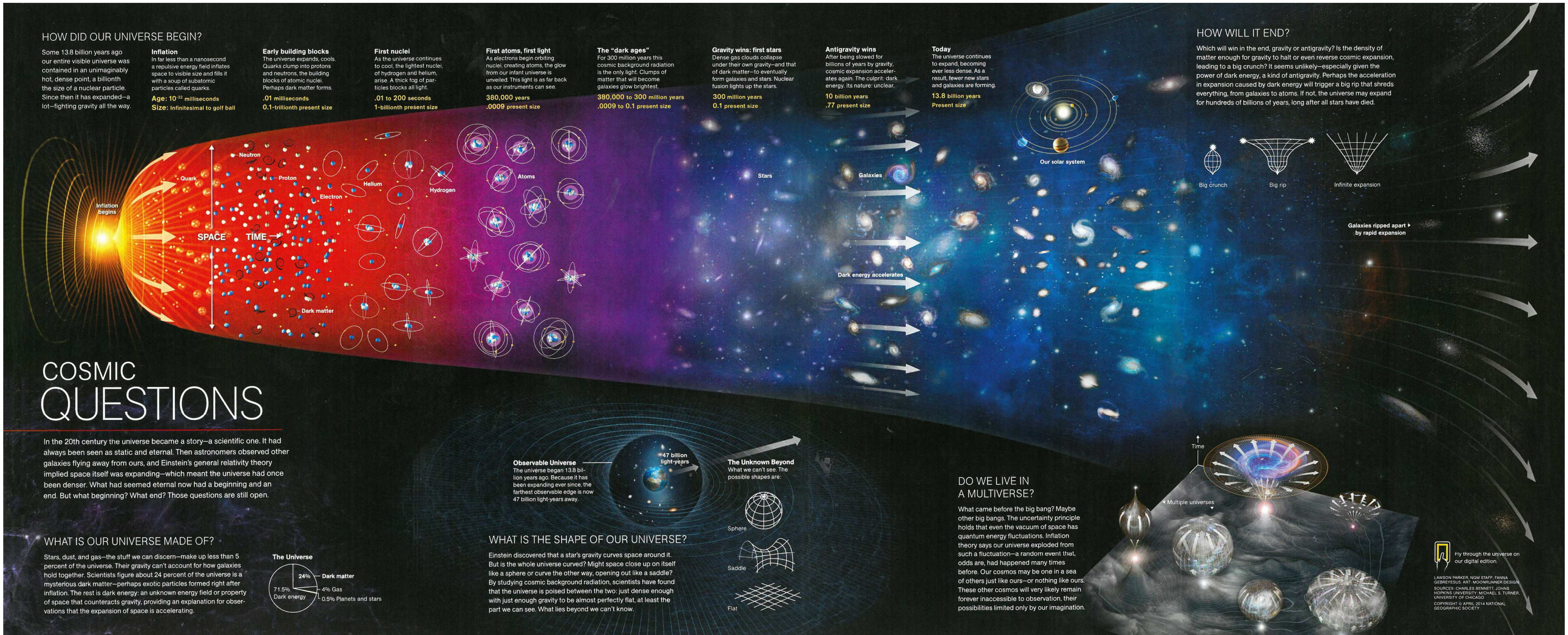
Número	***Cantidad de cifras significativas***
4.2×10^4	2
4.20×10^4	3
4.200×10^4	4
7×10^{-3}	1
7.0×10^{-3}	2

Big numbers at your disposal

- Seconds in a year ≈ ⍰⍰x10^7 (yes, pi, just a nice coincidence and easy way to remember)
- Seconds in a day ≈ 10^5
- Hours in a year ≈ 10^4
- Avogadro's constant ≈ 6×10^{23}
- Cells in the human body ≈ 4×10^{13}

- Water molecule volume ≈0.03 nm^3, (≈0.3 $nm)^3$
- A base pair has a volume of ≈1 nm^3
- A base pair has a mass of ≈600 Da
- Lipid molecules have a mass of ≈500 -1000 Da
- 1 k_BT ≈ 2.5 kJ/mol ≈ 0.6 kcal/mol ≈ 25 meV ≈ 4 pN nm ≈ 4×10^{-21} J
- ≈6 kJ/mol sustains one order of magnitude concentration difference (=RT ln(10) ≈ 1.4 kcal/mol)
- Movement across the membrane is associated with 10-20 kJ/mol per one net charge due to membrane potential
- ATP hydrolysis under physiological conditions releases 20 k_BT ≈ 50 kJ/mol ≈ 12 kcal/mol ≈ 10^{-19} J
- One liter of oxygen releases ≈20 kJ during respiration
- A small metabolite diffuses 1 nm in ~1 ns
- 1 OD_{600} ≈0.5 g cell dry weight per liter
- ≈10^{10} carbon atoms in a 1 μm^3 cell volume

Clase 1- Ordenes de tamaño en el Universo



NATIONAL GEOGRAPHIC

HOW DID OUR UNIVERSE BEGIN?

Some 13.8 billion years ago our entire visible universe was contained in an unimaginably hot, dense point, a billionth the size of a nuclear particle. Since then it has expanded—a lot—fighting gravity all the way.

Inflation
In far less than a nanosecond a repulsive energy field inflates space to visible size and fills it with a soup of subatomic particles called quarks.
Age: 10^{-32} **milliseconds**
Size: Infinitesimal to golf ball

Early building blocks
The universe expands, cools. Quarks clump into protons and neutrons, the building blocks of atomic nuclei. Perhaps dark matter forms.
.01 milliseconds
0.1-trillionth present size

First nuclei
As the universe continues to cool, the lightest nuclei, of hydrogen and helium, arise. A thick fog of particles blocks all light.
.01 to 200 seconds
1-billionth present size

First atoms, first light
As electrons begin orbiting nuclei, creating atoms, the glow from our infant universe is unveiled. This light is as far back as our instruments can see.
380,000 years
.0009 present size

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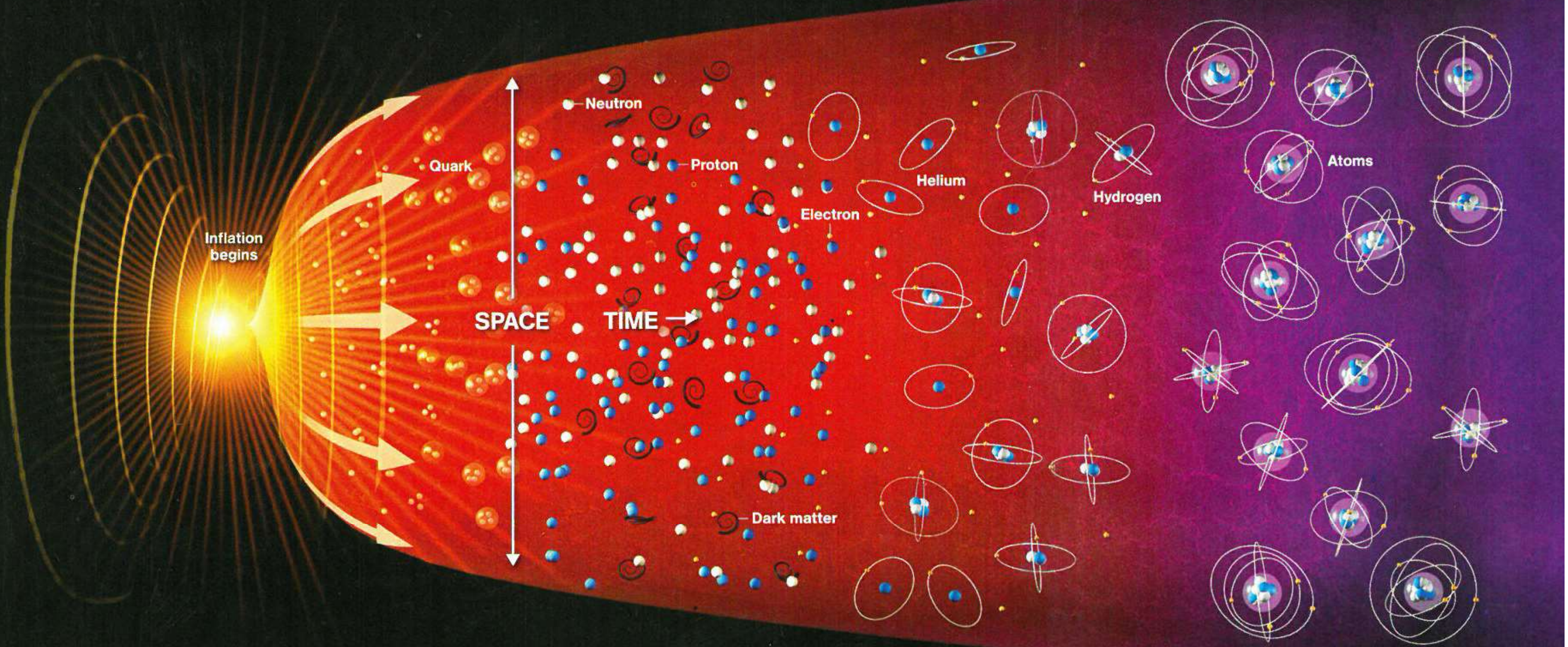
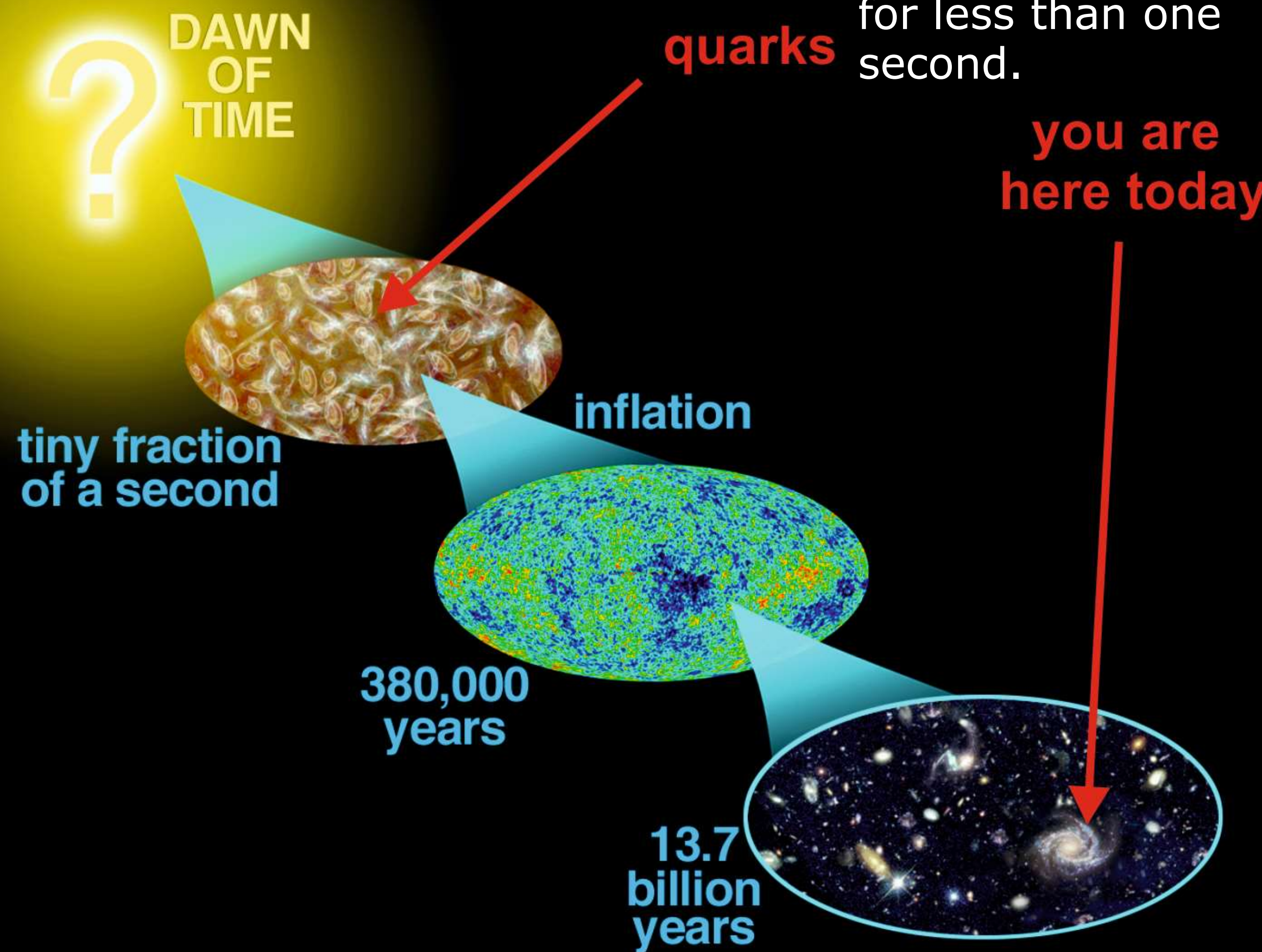


COSMIC QUESTIONS

In the 20th century the universe became a story—a scientific one. It had always been seen as static and eternal. Then astronomers observed other galaxies flying away from ours, and Einstein's general relativity theory

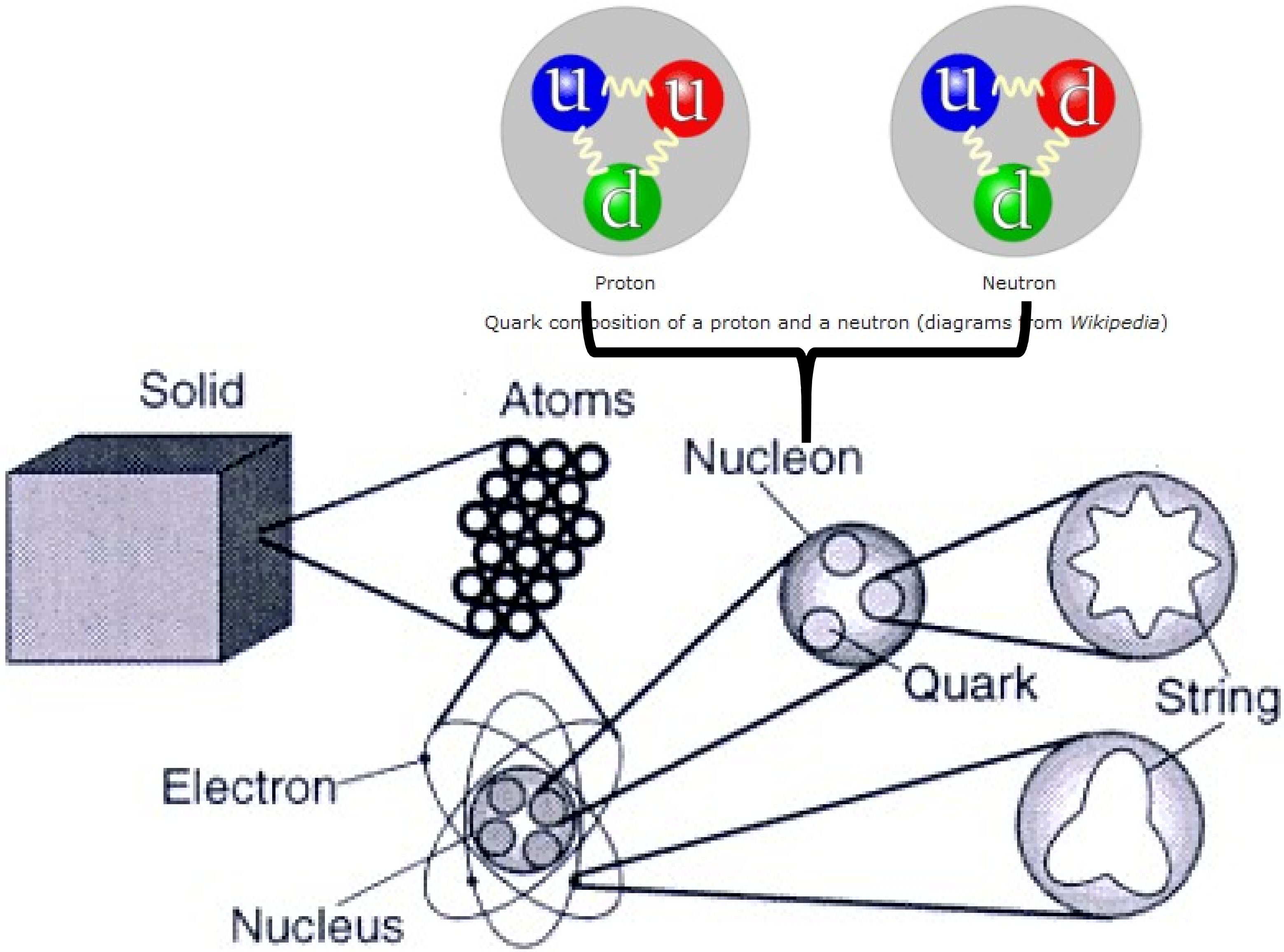
Observable Universe

Quarks – came into existence when the Universe has existed for less than one second.



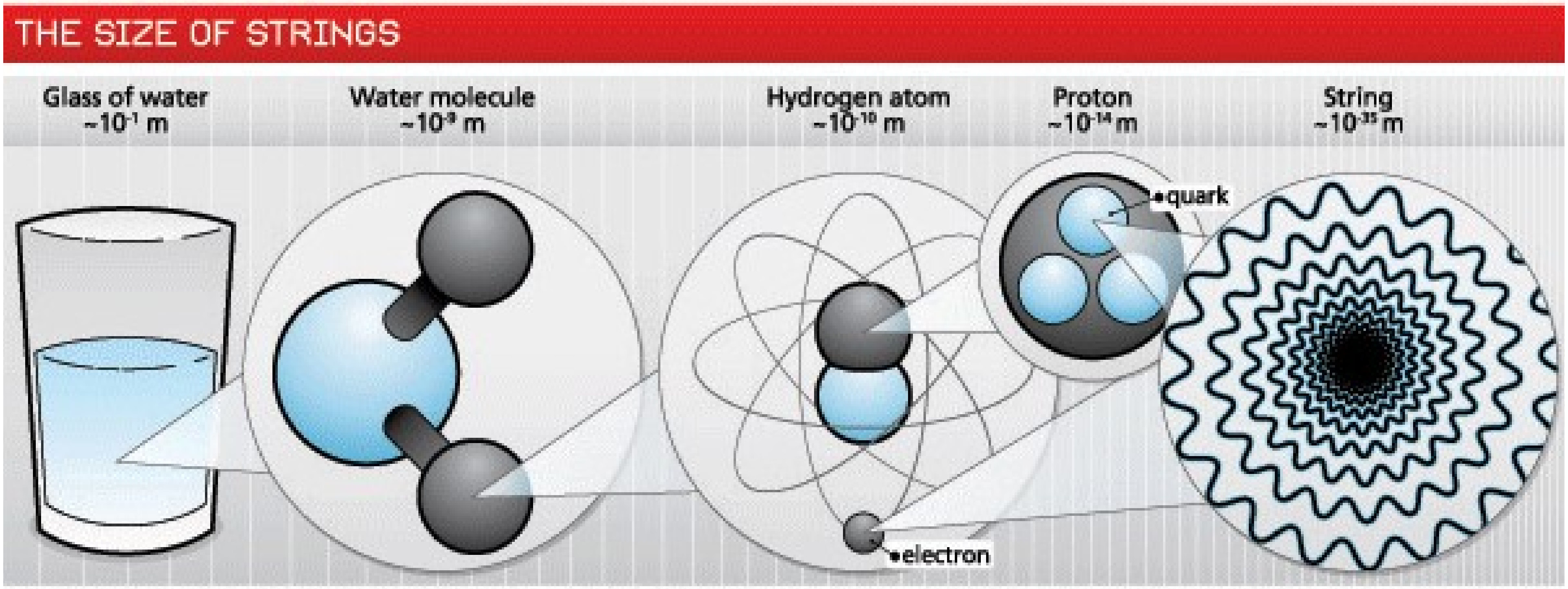
http://www.derekscope.co.uk/the-universe-20th/atoms/

Clase 1 Elementos de estructura atómica



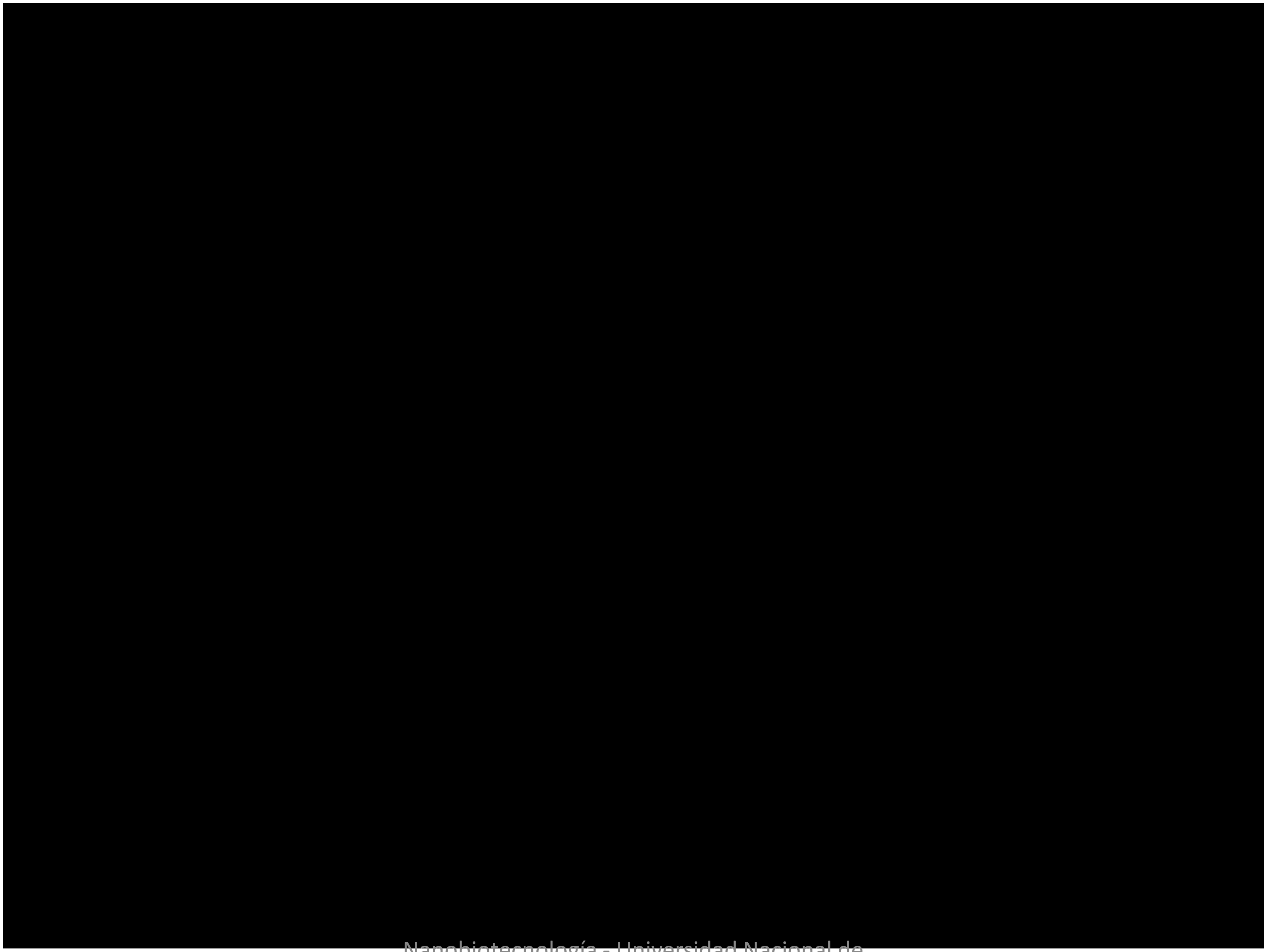
http://www.columbia.edu/cu/record/23/18/14.html

Clase 1 Elementos de estructura atómica: orígenes y una perspectiva de tamaño



itrings are the smallest, least accessible objects known to physics. Here, a progressive zoom into a glass of water reveals the relative scales of a wate nolecule, a hydrogen atom, a proton, an electron, a quark, and a string. The sizes of these objects ranges across thirty-four orders of magnitude. Fo erspective, if an atom were the size of our solar system, a string would be somewhat larger than an atomic nucleus.

Clase 1 Orígenes y una perspectiva de tamaño



Clase 2

Introducción a la Nanotecnología. Nuevos fenómenos asociados a la nanoescala (eléctricos, ópticos y químicos).

Clase 2. Introducción a la Nanotecnología. **Definiciones básicas**

Definición de **Nanociencia:**
"Estudio de los fenómenos y manipulación de materiales a escala atómica, molecular y macromolecular, donde las propiedades de los materiales difieren significativamente de aquellas a mayor escala" [evolución de disciplinas científicas mas tradicionales]
(Nanoscience and Nanotechnologies: opportunities and uncertainties, report by the Royal Society and The Royal Academy of Engineering, 2004, http://www.nanotec.org.uk)

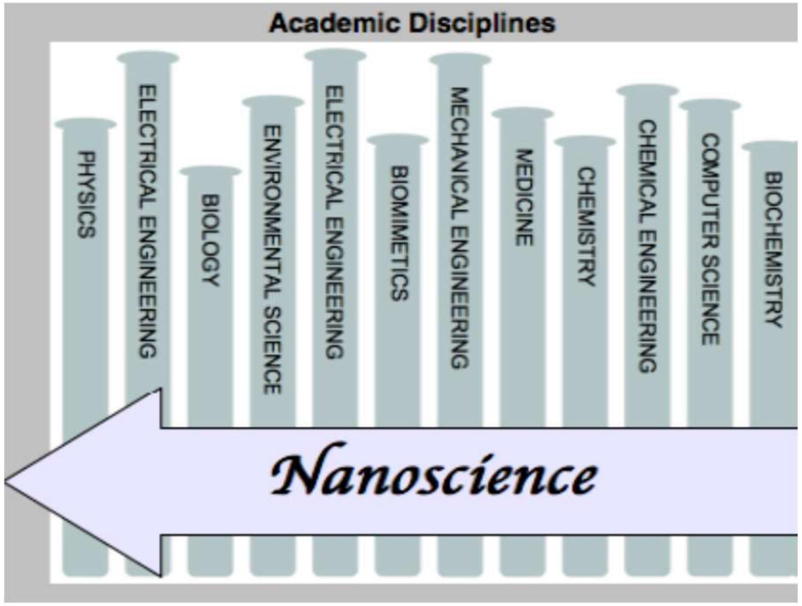
Materiales *"bulk"* (macro y micro escala): poseen propiedades físicas **continuas**

Materiales en la nano-escala: sus propiedades no se describen mediante física clásica
deben aplicarse principios de mecánica cuántica
sus propiedades pueden diferir considerablemente de aquellas en fase *"bulk"*

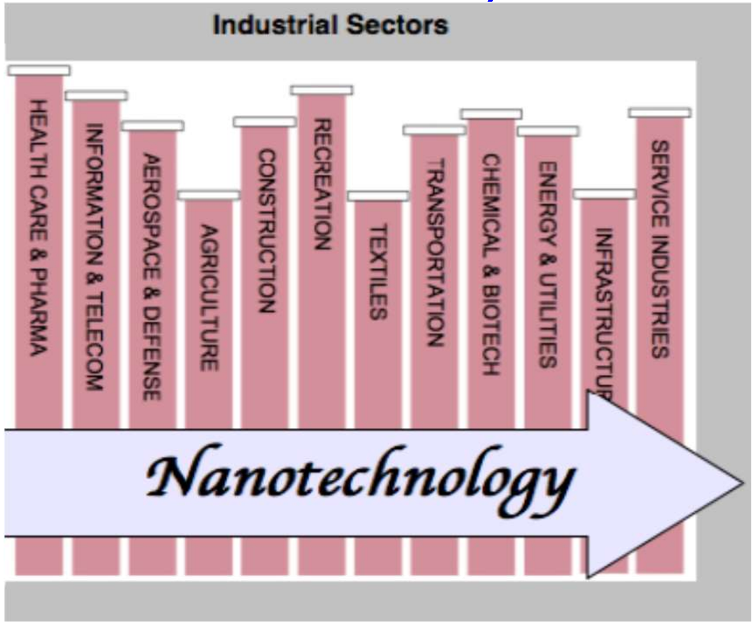
Definición de **Nanotecnologías:**
"Diseño, caracterización, producción y aplicación de estructuras, dispositivos y sistemas, cuya forma y tamaño están controladas en la nano escala"

Clase 2. Introducción a la Nanotecnología. Definiciones básicas

Nanotecnologías: Aplicación de nanociencia a la resolución de cuestiones practicas. Objetivos industriales y comerciales. **Todos los materiales podrían mejorarse con nanotecnología (costo/beneficio adicionado)**



Ciencia interdisciplinaria:
horizontal e integrativa,
cruza a las ciencias e ingenierías verticales



Tecnologías *enabling* (proveen las plataformas y herramientas para desarrollar productos) **horizontales convergentes** (juntan sectores previamente separados) que cruzan todos los sectores industriales verticales

G.L. Hornyak et al , Introduction to Nanoscience, CRC Press 2008

Clase 2 Nanotecnologia

Aun no existen consensos generales sobre la definición de términos básicos como "nanotecnología", "nanomaterial", "nanopartícula", "nanoescala" (**Bawa R. Regulating nanomedicine: can the FDA handle it? Curr Drug Deliv 2011;8(3):22734.**)

Ni siquiera sobre esto…!:

Prefijo "nano [unidad 10^{-9} m]": Latin (na**n**o= enano) y no Griego (na**nn**o= enano)

(11th General Conference on Weights and Measures, Sacha Loeve)

Por esta razón en este Curso tendremos en cuenta las siguientes definiciones:

De acuerdo al **U.S. National Science and Technology Council, Nanotecnología** es "la capacidad de controlar y re estructurar la materia a nivel atómico y molecular en el **rango aproximado** entre 1-100 nm, y de explotar aquellas propiedades y fenómenos a escala atómica o molecular, que sean diferentes a aquellas en fase bulk o de átomos por separado." Idéntica definición emplean la U.S. **National Nanotechnology Initiative (NNI)** (http://www.nano.gov/), **la Food and Drug Administration (FDA) y el National Cancer Institute (NCI).**

De acuerdo a la **European Comission** (https://ec.europa.eu/programmes/horizon2020/en/h2020-section/nanotechnologies), **Nanotecnología** es "la ciencia y tecnología, que mediante la manipulación de átomos y moléculas en la nanoescala, ayudara a enfrentar desafíos sociales clave, tales como cambio climático, reducción de emisión de carbono, desarrollo de energías renovables, uso mas eficiente de recursos y abordar las necesidades medicas de la población en envejecimiento.

Clase 2 Nanotecnologia

La **nanotecnología es habilitadora** *(“enabling”)*; esto significa que inicia otras tecnologías, procesos o productos. También los transforma en tecnologías con nuevas propiedades. Es una tecnología horizontal, lo que posibilita su aplicación a múltiples campos además de la industria. En términos generales no está encasillada en sectores industriales claramente distinguidos , ni se la identifica como un producto diferente, en la mayor parte de los mercados. **Poseer las condiciones necesarias para ser reconocida por el mercado, es imprescindible para promover su comercialización.**

Donde ocurre una excepción a la ausencia de reconocimiento de mercado, es justamente en sus aplicaciones a la medicina (nanomedicina)

Como tecnología disruptiva, la nanotecnología puede crear nuevos productos y mercados. Es, por lo tanto, proclive a la ocurrencia de un “ciclo de sobre expectación”, donde las expectativas suben para luego declinar en sub-estimación, antes de consolidarse . Durante ese camino, la nanotecnología puede ser la próxima “revolución industrial” o evolucionar hacia una decepción. En particular, el éxito en la comercialización y formación de mercado en nanomedicina, dependerá de como los participantes clave reaccionen a la variedad de retos que esta plantea.

Clase 2 Nanotecnologia

Retos a superar (ingreso al Mercado nanomedicina/nanobiotecnologia/nanobioingenieria)

(1) contar con definiciones consensuadas de alcance global
(2) contar con predicciones razonablemente confiables acerca del mercado nano y en particular del nanomedico
(3) identificar las métricas apropiadas para las evaluaciones del mercado nano
(4) conseguir adecuado retorno de inversión en nanomedicinas, durante el *market recovery*
(5) enfocar correctamente, y superar los retos técnicos impuestos por la nanomedicina
(6) obtener financiación durante y mas allá del *economic recovery*
(7) contar con solidas estructuras de negocios en el campo de la nanomedicina
(8) abordar adecuadamente los aspectos relativos a propiedad intelectual, regulatorios, legales, éticos, así como incertezas reglamentarias.

Estos retos pueden ser abrumadores, fundamentalmente porque muchos requieren sustanciales aportes de capital durante un tiempo en el que la recuperación económica de una recesión importante, es lento. A nivel global, y a pesar de los retos arriba señalados sin embargo, las inversiones en nanotecnologia y nanomedicina continúan creciendo.

Alencar MSM, Porter AL, Antunes AMS. Nanopatenting patterns in relation to product life cycle. Technol Forecast Soc Change 2007;74:166180.
Market Considerations for Nanomedicines and Theranostic Nanomedicines. Archie A. Alexander and Fabrice Jotterand. Chapter 25. X. Chen and S. Wong (Eds): Cancer Theranostics. © 2014 Elsevier Inc. All rights reserved.

Clase 2. Introducción a la Nanotecnología. **Definiciones básicas**

Escala nanométrica (nano-escala):

Extremo inferior: 1 nm (10^{-9}m) (> que el tamaño atómico) = 3.5 átomos de Au ($r_{covalente}$ 0.144 nm) (8 átomos H) (1 molécula glucosa)

Extremo superior: "fluido": 100- 200-300 nm: **lo importante es la aparición de nuevos fenómenos [cuánticos y biológicos] determinados por su tamaño** (**!)

Por esta razón no se incluye un limite superior de tamaño en forma exacta

Los **átomos individuales** no son materiales en la nano-escala

Nanomaterial: objeto con al menos 1 dimensión en la nano-escala

Dimensión en la nano-escala	Tipo de nanomaterial
3	Nanopartículas
2	Nanotubos
1	Films, capas, coberturas

Clase 2 Definición de nanomaterial

"**Nanomaterial:** material natural, incidental o manufacturado conteniendo partículas, en estado no-asociado, o como agregado, o aglomerado y donde mas del 50 % de las partículas en distribución de tamaño de numero, se hallan entre 1-100 nm".European Commission (EU)'s definition of Nanomaterials (European Commission 2011).

Principales elementos de la definición:

1. La presencia de partículas define a un material como "nanomaterial": >50% de las partículas deben tener al menos 1 dimensión entre 1-100 nm.
2. Alternativamente, será un nanomaterial aquel que tenga mas de 60 m2/cm3 superficie especifica por unidad de volumen
3. Se incluye específicamente al grafeno
4. Se incluyen materiales naturales e incidentales, así como partículas manufacturadas .
5. Se incluyen agregados o aglomerados de tales partículas.

No se especifican métodos de medición; se recomiendan seleccionar los mas adecuados para cada ocasión.

Definición de nanomaterial

La definición de nanomaterial es la piedra angular de toda legislación, y si bien la misma no tiene carácter regulatorio, los fundamentos que sustentan su autoridad están descriptos por el Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) en la publicación "Scientific Basis for the Definition of the Term "Nanomaterial". En el mismo también se describen ambigüedades y dificultades pertinentes a esta definición. **Las mismas pertenecen casi exclusivamente al ámbito biológico.** Por ejemplo: definir un **nanomaterial** en función de poseer una o mas dimensiones en la **nanoescala comprendida entre 1 y 100 nm**, es **insuficiente** porque:

a) los nanomateriales pueden cambiar su forma (bajo radiación UV, o en el interior celular), o al interactuar con otros materiales en el entorno medioambiental.
b) **frecuentemente partículas >100 nm exhiben propiedades "nano"** : por ejemplo, son reconocidas y procesadas endociticamente por células eucariotas. En el ámbito de las aplicaciones terapéuticas como sistemas *carriers* de drogas, el limite superior de la nanoescala se halla en los 300-400 nm

(**Kewal K. Jain, The Handbook of Nanomedicine, Third Edition 2017. Kewal K. Jain. Jain PharmaBiotech. Basel, Switzerland. Humana Press published by Springer Nature)**

Clase 2. Introducción a la Nanotecnología. **Definiciones básicas**

Nanomateriales

- **Nanomaterial natural**

  Origen no intencional **natural:**
  proteínas, AN, virus, nanopartículas producidas en erupciones volcánicas, etc.
- Origen no intencional **producidos por actividad humana:**
  nanopartículas de combustión diésel
- **Origen intencional**: mediante un proceso de fabricación
  [incluidos en la definición nanotecnologías]

Ordenes relativos de tamaños (super general)

Uñas: **1 nm/s**
Cabeza de alfiler: **10^6 nm**
Cabello humano: **$8x10^4$ nm**
ADN: **1-2 nm ancho**
Transistor Pentium Core Duo processor: **45 nm**

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala**

Cambios en las propiedades de la materia en la nano-escala (respecto de fase *"bulk"*)

1) Energía: aparición de efectos cuánticos

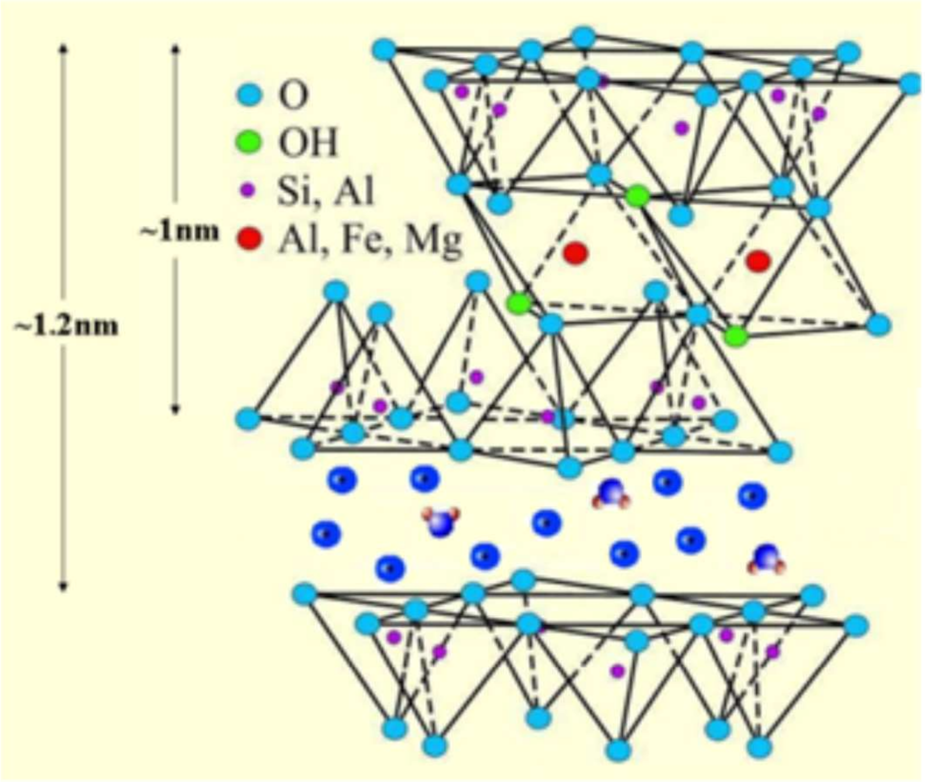
Conductividad eléctrica
Color
Rigidez
Peso

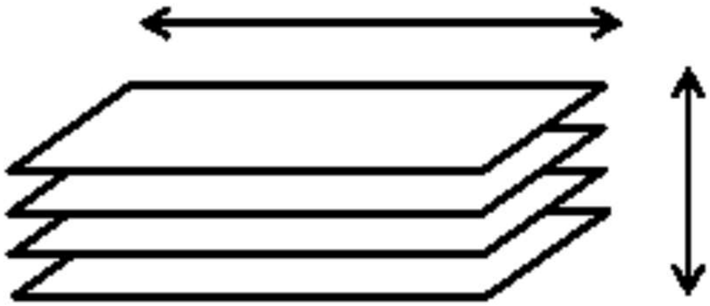
2) Posibilidad de fabricación de materiales "átomo por átomo": métodos *bottom-up* [autoensamblaje]

3) Elevada relación superficie/volumen

Los objetos de estudio de la **nanociencia** (base de la física, química, bioquímica) y los **nanomateriales** existen desde hace mucho tiempo. Lo novedoso es la aparición de poderosas **técnicas de caracterización** y de **producción,** que **posibilitan la aplicación de nuevos materiales [nuevas propiedades capacidades, funciones] en múltiples campos industriales**

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Nanomateriales naturales

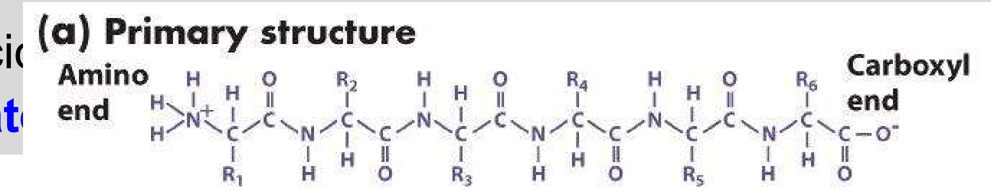




(1a) **(1b)**

Structure of montmorillonite (Figure 1a) and a scheme (Figure 1b) to highlight the significant difference in length with respect to thickness of the layers

Clase 2. Introducci... ateria en la nano-escala. Nanomat...



3) Coloides natura... ...gel):
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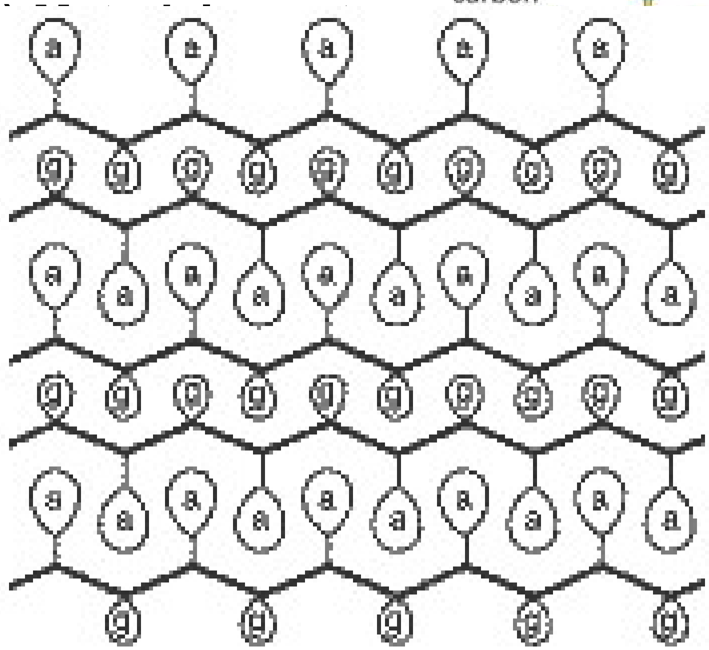
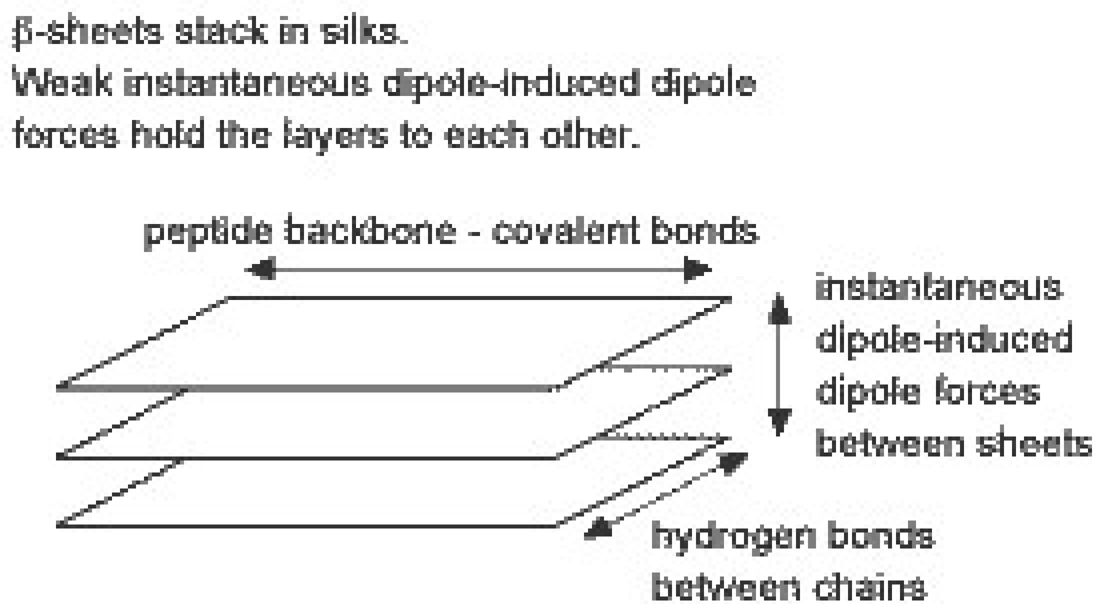




8) Tela de araña: h... ...nismo peso
[(... ...na]

9) Hoja de loto y s... ...estructura

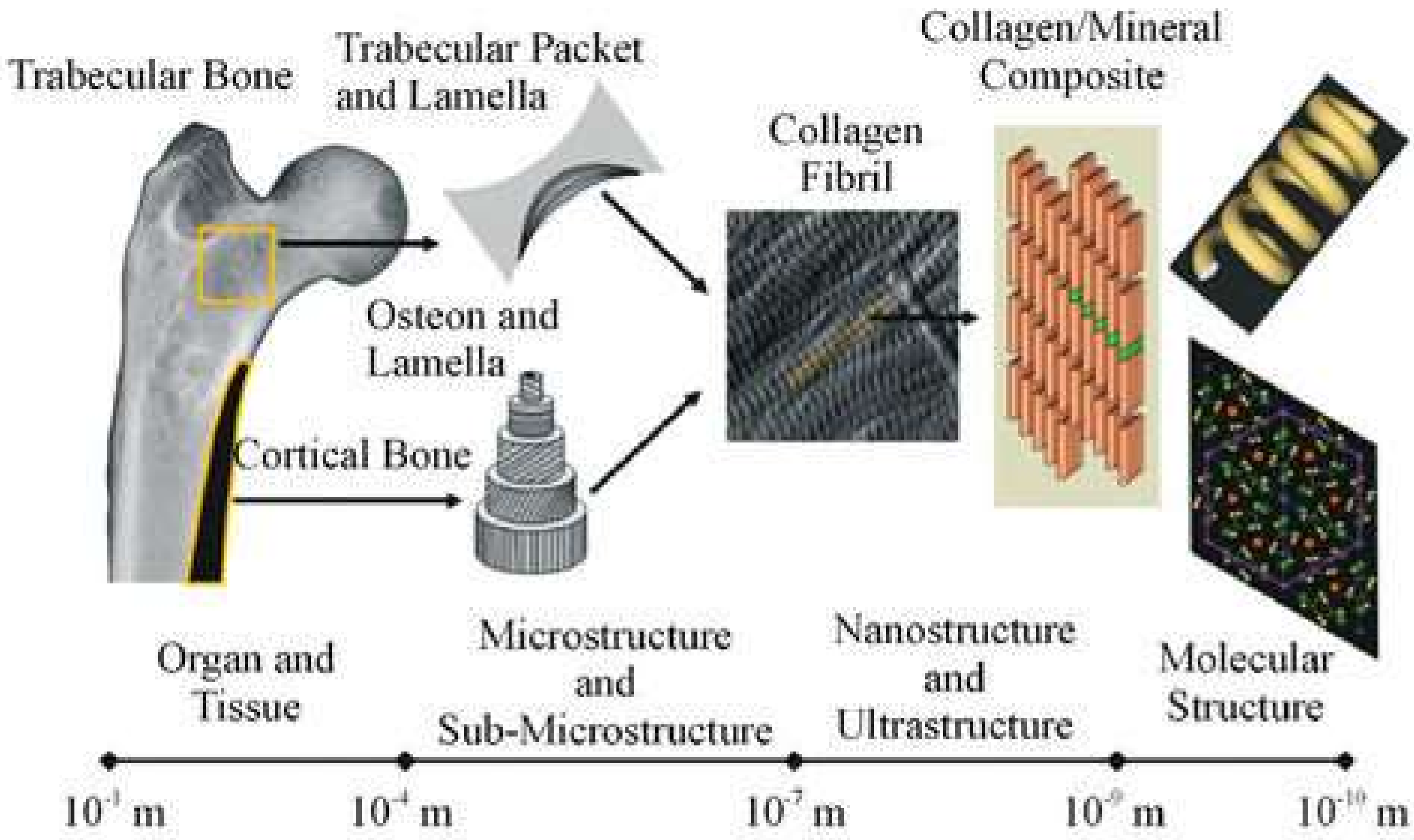
10) Pie de gecko: ... ...vertical

Figure 4-10 part 2 of 2 Essential Cell Biology, 2/e. (© 2004 Garland Science)

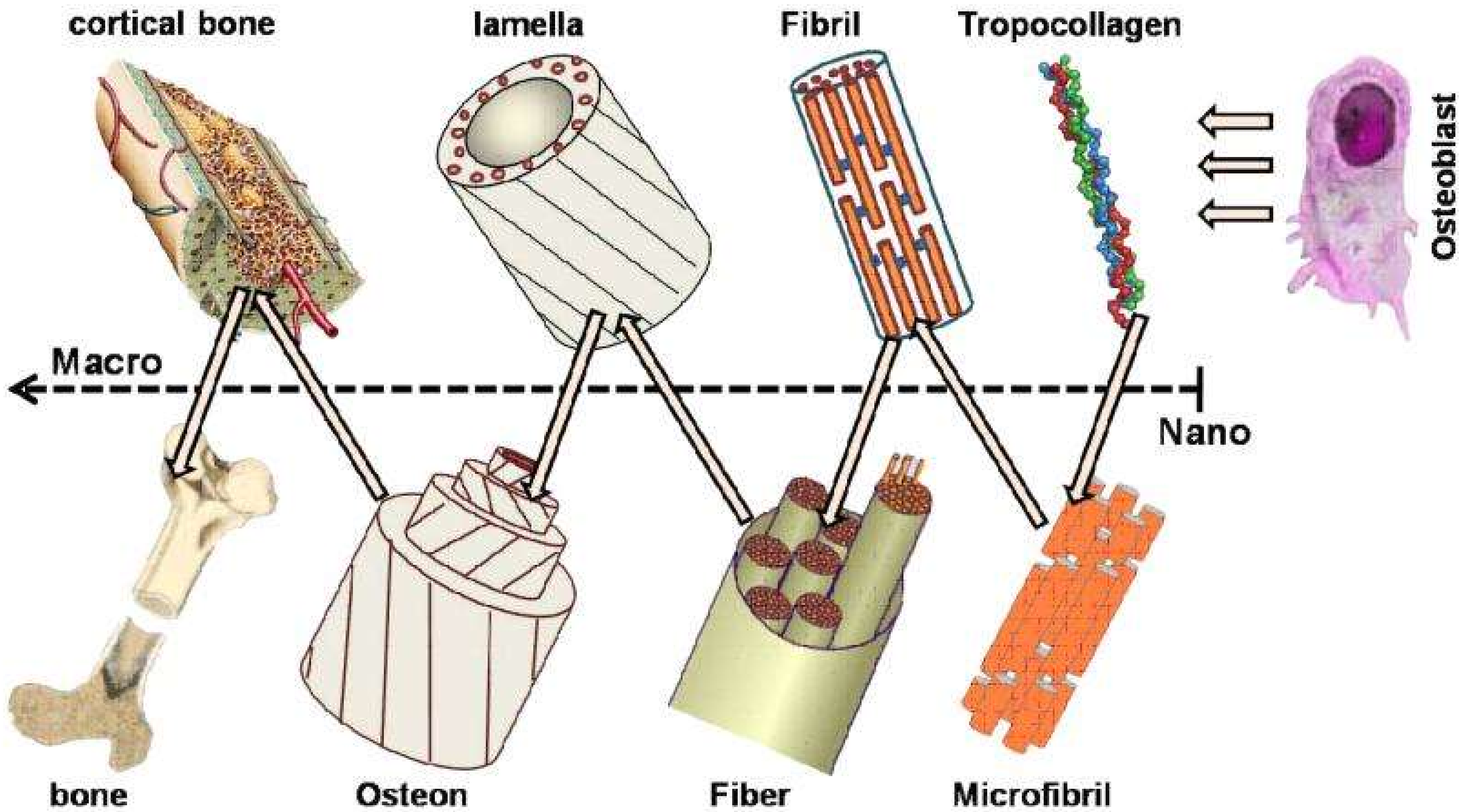
Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Nanomateriales naturales

4) Materiales naturales mineralizados: *shells*, corales, **huesos.**

Cristales de $CaCO_3$ auto-ensamblados con otros materiales naturales (polímeros), generando arquitecturas 3D en la nano-escala



Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Nanomateriales naturales



Finite element 3D modeling of Mechanical Behaviour of Mineralized collagen Microfibril Article · Dec 2011 · Journal of applied biomaterials & biomechanics (JABB)

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Nuevos efectos en la nano-escala

Las propiedades físicas en la macro y micro escala se determinan sobre **moles de moléculas, a las que se aplican las leyes newtonianas**. **En la nano-escala, las leyes newtonianas son reemplazadas por las leyes de la física cuántica: <u>las propiedades físicas dependen del tamaño del material</u>** (además de las composición química y enlaces)

Propiedades físicas relevantes en la nano-escala:

1) Escasa relevancia de fuerza gravitacional (pequeña masa), dominancia de fuerzas electromagnéticas

2) Dualidad onda [función de onda- probabilidad posición]-partícula (electrones): **a) Efecto túnel: penetración de e en regiones energéticas clásicamente prohibidas. E**n física cuántica, una nanopartícula tiene una probabilidad finita de atravesar una barrera de energía mayor (túnel virtual), siempre que la altura de la barrera (Energía potencial Ep) este en el orden de la λnanopartícula.

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nuevos efectos en la nano-escala**

a) The passage of a particle through a barrier in the **traditional world**: the particle does not pass if Ec < Ep and the particle passes if Ec > Ep.

b) The passage of a particle through a barrier in the **quantum world**: the probability of passage is not zero when Ec < Ep and the probability increases with Ec to reach 1 when Ec = Ep.

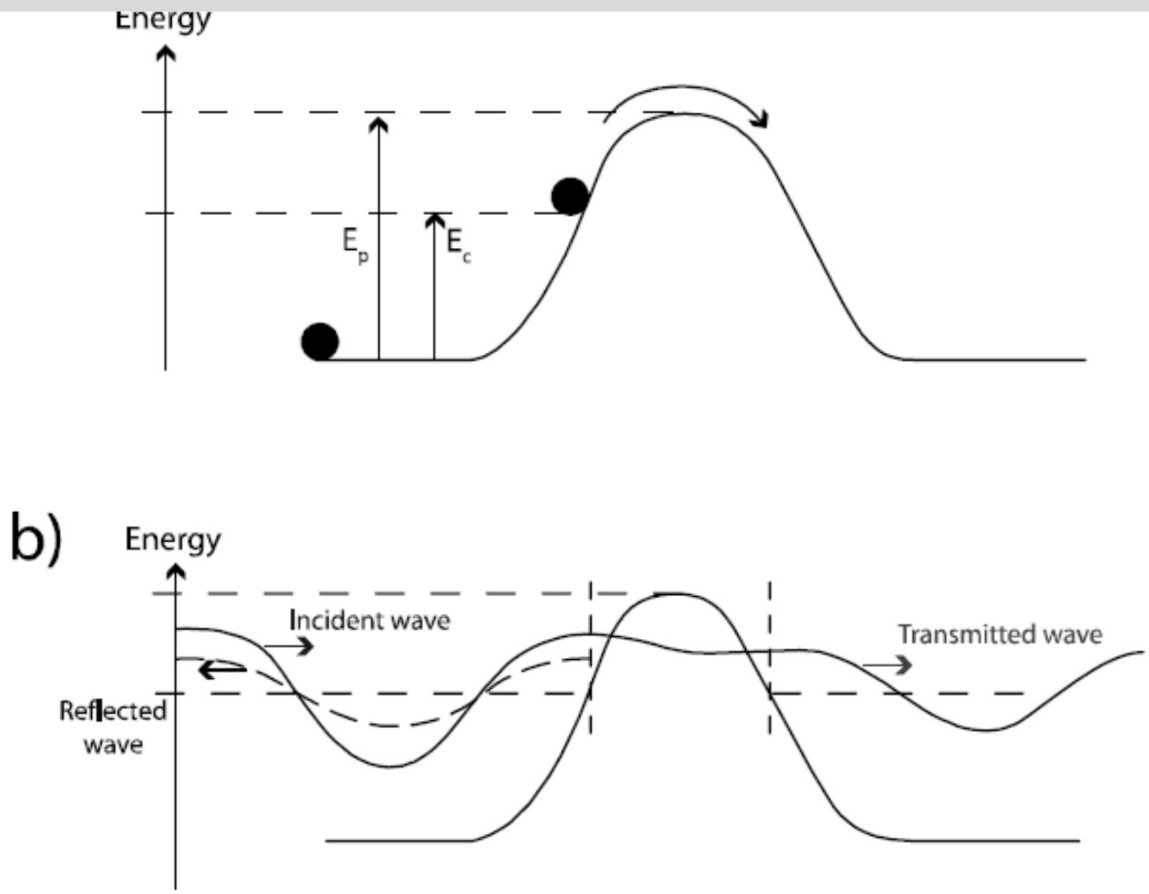


Figure 2.1. An effect of quantum physics: **the tunneling effect**

Chapter 2. Some Science to Get You Started. *The Necessary Toolkit*
An Introduction to Nanoscience and Nanotechnology. **Alain Nouailhat**

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nuevos efectos en la nano-escala**

El **efecto túnel** es la base del funcionamiento del **STM (Scanning Tunnelling Microscope,** microscopia de efecto túnel), que permite obtener imágenes de superficies nanoestructuradas; el STM se usa también como **instrumento de nanofabricación para mover átomos uno x uno**

b) Confinamiento cuántico: en nanomateriales, los electrones no se mueven libremente, sino que se hallan confinados

c) Cuantización de energía: los electrones únicamente pueden existir en niveles discretos de energía (Q-dots)

d) Movimientos moleculares al azar (r*andom*): los movimientos moleculares ocurren debido a la Energía cinética (asumiendo T>0K), son ominipresentes y pueden estar en la escala del tamaño de nanoparticulas. Ej: movimiento Browniano

En la macroescala estos movimientos no se perciben.

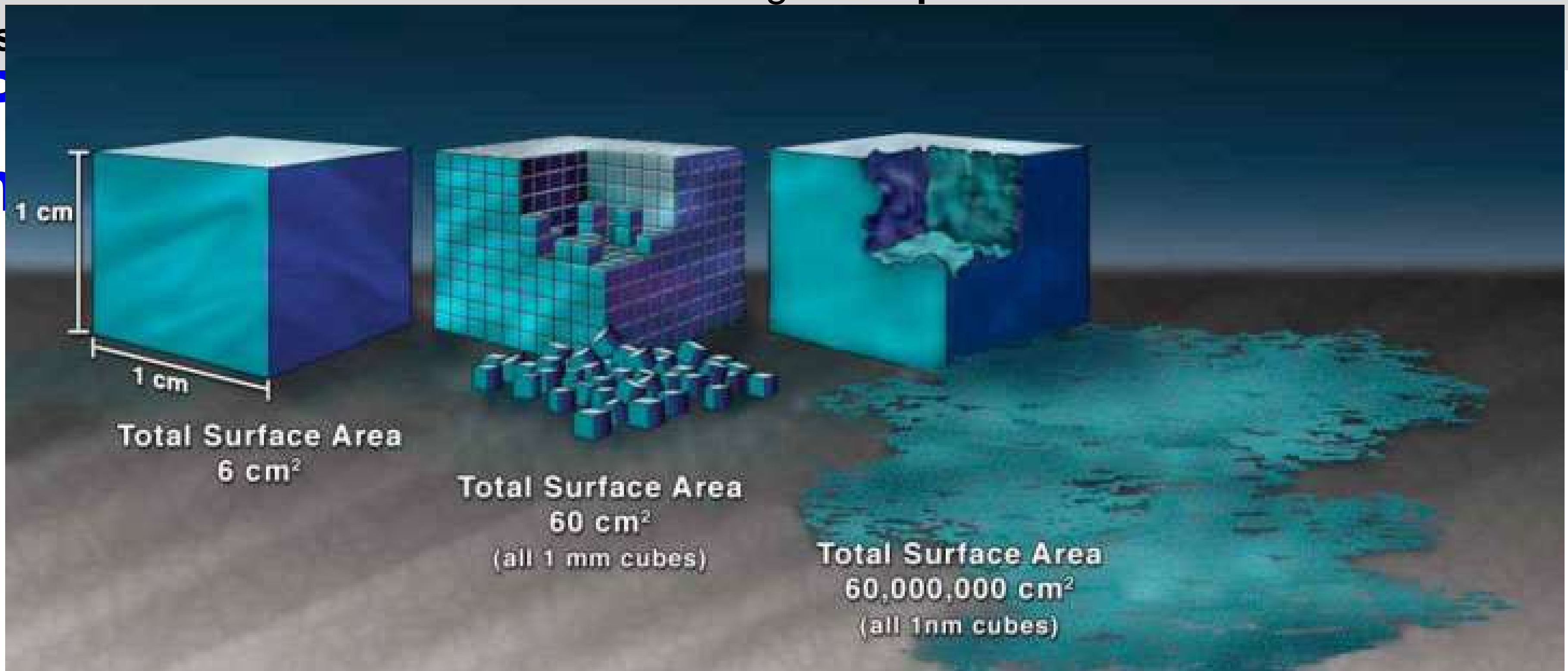
e) Elevada relación superficie/volumen

Propiedades químicas relevantes en la nano-escala:

Dado que los nanomateriales son *clusters* de átomos o moléculas, los enlaces químicos son relevantes

1) **Enlaces intramoleculares (uniones químicas):** iónicas, covalentes, metálicas
2) Enlaces intermoleculares (interacciones físicas/no introducen cambios en estructuras químicas): interacción ion-ion, ion-dipolo, Van der Waals, -H-, interacción hidrofóbica, fuerzas repulsivas (estéricas)

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-es**



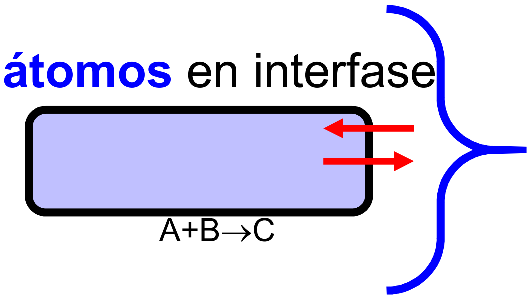
interfase

de cubo	cubos	superficial total
1 m	1	6 m^2
0.1 m	10^3	60 m^2
10^{-2}m	10^6	600 m^2
10^{-3}m	10^9	6000 m^2
10^{-9}m	10^{27}	6 x 10^9 m^2= 6000km^2

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nuevos efectos en la nano-escala**

Importancia de átomos en superficie

> átomos en interfase



Reactividad catalítica
Resistividad eléctrica
Adhesión
Almacenamiento gaseoso
Reactividad química/detección
Adsorción
Punto de fusión:
Pf (nanomateriales) < Pf (materiales bulk)

Forma: a = V, la forma determina la extensión de la interfase: cilindros, esferas, cubos

Energía superficial: los átomos o moléculas en la interfase son mas reactivos que los internos (inestables, > $E_{superficial}$, > tendencia a agregarse): los nanomateriales son inherentemente inestables: tenderán espontáneamente a minimizar su elevada $E_{superficial} = \gamma$

Agregación/aglomeración: una forma de reducir γ (aditiva)

Reacciones donde las propiedades superficiales son importantes:

Catálisis: excluyendo las enzimas, los catalizadores comunes son menos eficientes y consisten en su mayoría en partículas metálicas fijas en una superficie de oxido, sometidas a un flujo de reactivos a alta T (para reducir el envenenamiento catalítico causado por la ocupación de sitios activos por el CO atmosférico)

La superficie activa (SA) (área sobre la que ocurre la catálisis) es un parámetro critico [enorme para los nanomateriales]. A > SA, > reactividad

La organización espacial de los sitios activos es otro parámetro critico
Industrias: química, petróleo, automotor, farmacéutica, alimentos
Beneficios medioambientales

Au *bulk*: metal noble, no toxico, resistente a oxidación/ataques químicos
Nanopartículas Au: son catalíticas (usadas sobre soportes de óxidos) > metales de transición Pt*, Rh, Pd* [*convertidores catalíticos automóviles-tóxicos, raros, costosos]

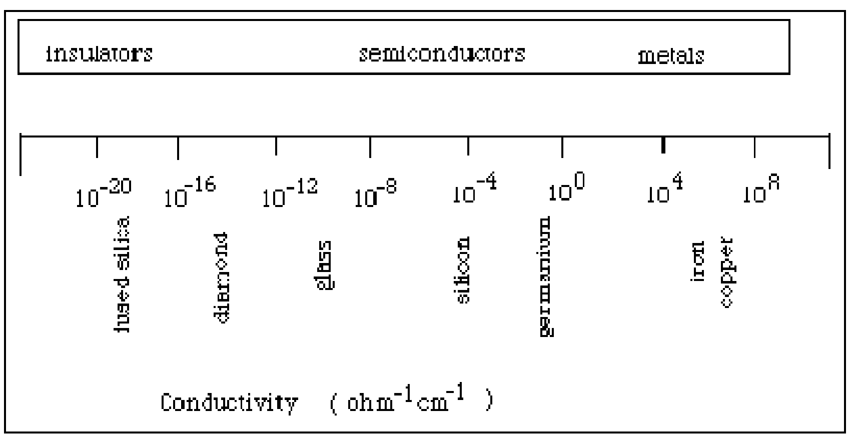
Detección de analitos en mezclas complejas (por sensores químicos, biosensores y *microarrays*): igual que en catálisis, la detección ocurre sobre interfases materiales.

nanomateriales en zona de detección:

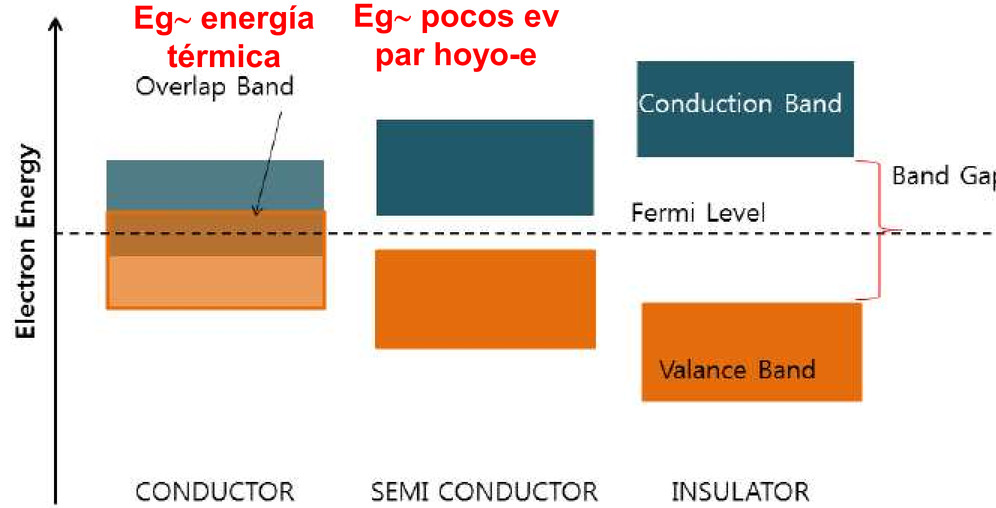
- ↑↑velocidad, selectividad, exactitud
- ↓↓limites de detección
- Propiedades (bioquímicas/químicas) superficiales especificas en sitios activos
- "Empaquetamiento" muchos sitios de detección en el mismo dispositivo: detección de múltiples analitos: ***multiplex-detection devices***

Propiedades eléctricas relevantes en la nanoescala

Materiales
- Conductores
- Semiconductores
- Aislantes



http://matse1.matse.illinois.edu/sc/prin.html



Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala. Nuevos efectos en la nano-escala Confinamiento cuántico**

Confinamiento cuántico:

↑↑ Eg
overlap entre bandas metálicas→ *bandgap*

metales (BULK)
↓
Semimetales (NANO)

Semiconductor
Quantum dot
Atomo

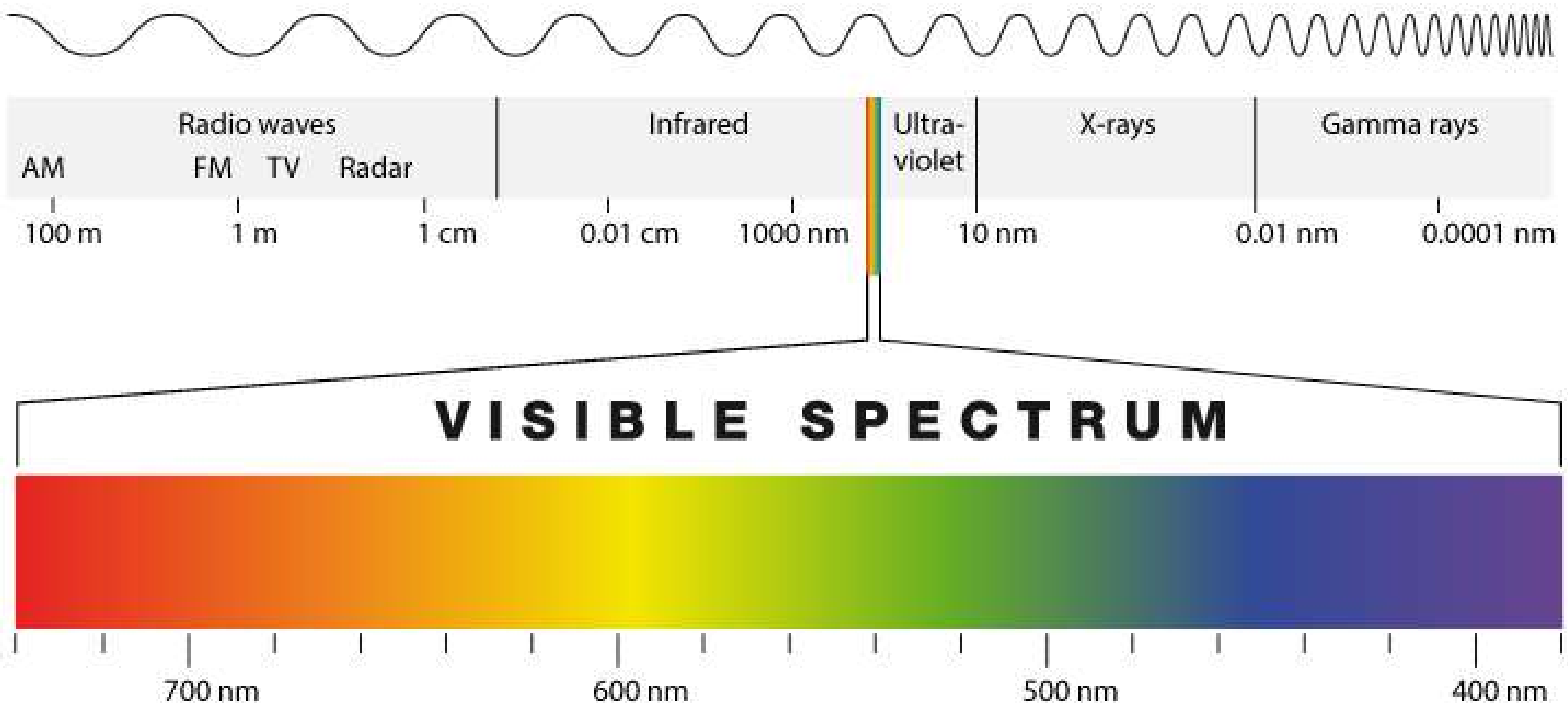
NANO: Corrimiento al azul en absorción de luz y en fluorescencia emitida

Las propiedades ópticas de semiconductores en la nano-escala pueden regularse de acuerdo al tamaño de nanopartícula

Materiales con propiedades eléctricas excepcionales:

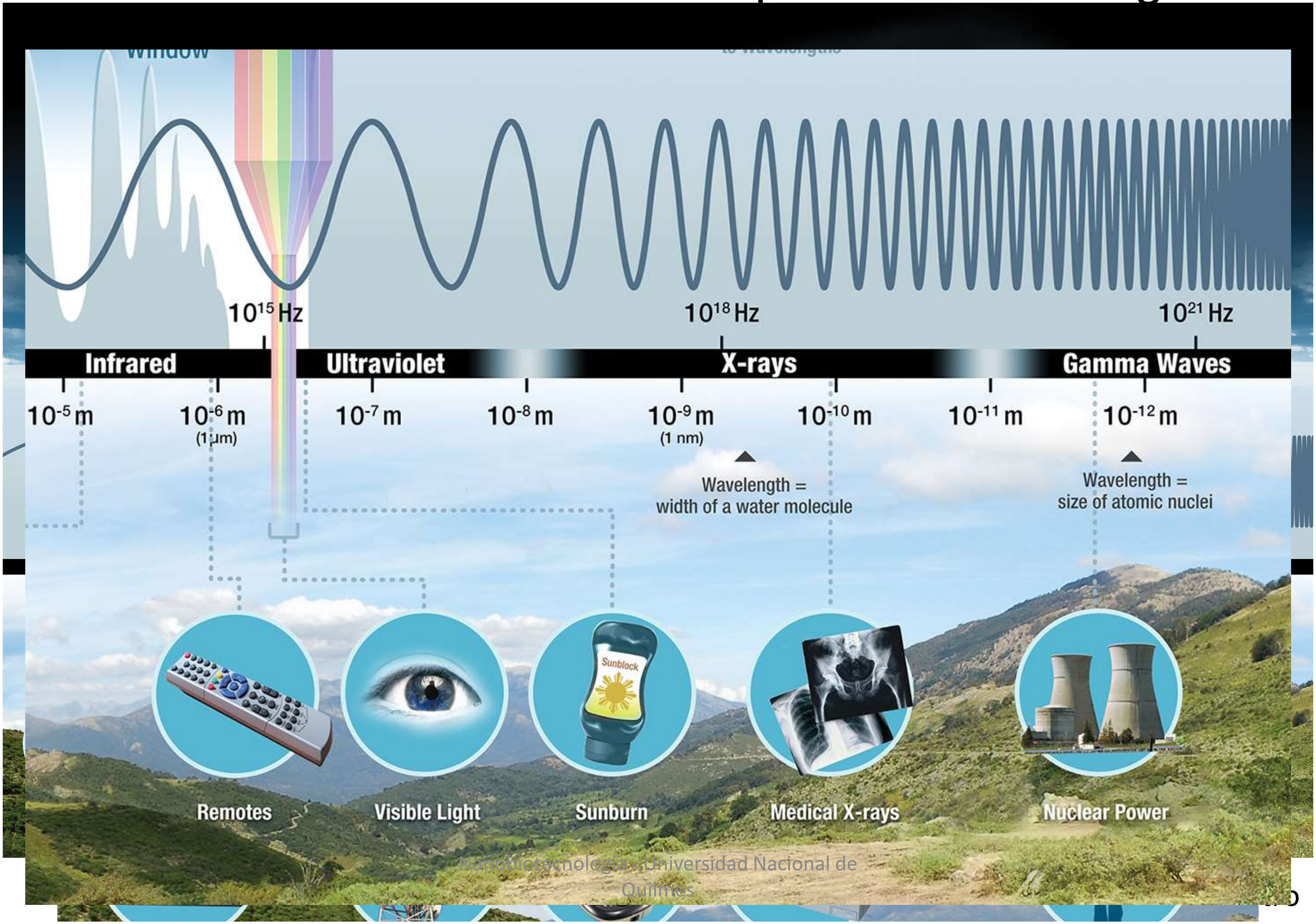
fullerenos y nanotubos de C, supercapacitores [no siguen ley de Ohm]

Clase 2 Espectro electromagnético: la luz y su comportamiento



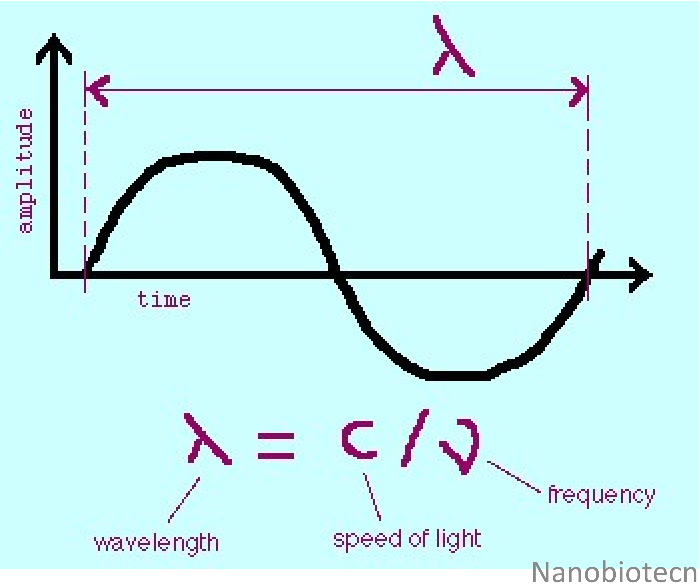
https://www.chromacademy.com/lms/sco736/02-The-Electromagnetic-Spectrum.html?fChannel=22&fCourse=97&fSco=736&fPath=sco736/02-The-Electromagnetic-Spectrum.html

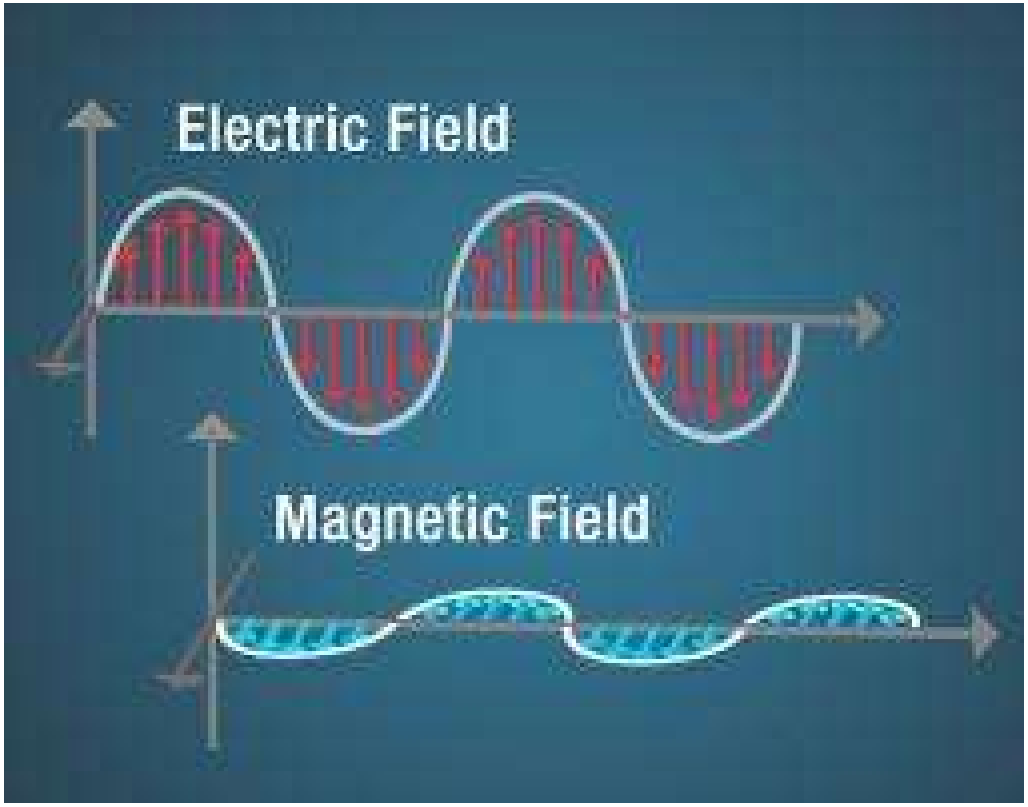
Clase 2 espectro electromagnético



Clase 2 Anatomía de las ondas electromagnéticas

Electromagnetic waves differ from mechanical waves in that they do not require a medium to propagate. This means that electromagnetic waves can travel not only through air and solid materials, but also through the vacuum of space.

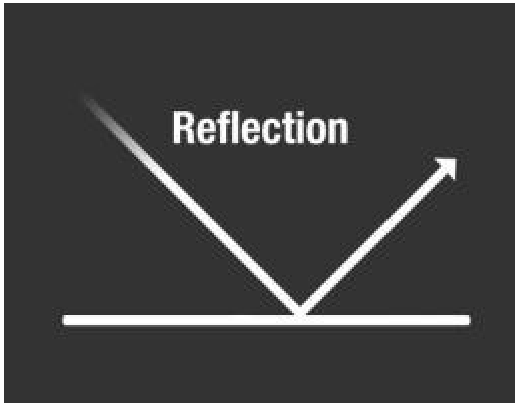




https://science.nasa.gov/ems/02_anatomy

reflexion

Reflection is when incident light (incoming light) hits an object and bounces off. Very smooth surfaces such as mirrors reflect almost all incident light.
The color of an object is actually the wavelengths of the light reflected while all other wavelengths are absorbed. Color, in this case, refers to the different wavelengths of light in the visible light spectrum perceived by our eyes. The physical and chemical composition of matter determines which wavelength (or color) is reflected.
This reflective behavior of light is used by lasers onboard NASA's Lunar Reconnaissance Orbiter to map the surface of the Moon. The instrument measures the time it takes a laser pulse to hit the surface and return. The longer the response time, the farther away the surface and lower the elevation. A shorter response time means the surface is closer or higher in elevation. In this image of the Moon's southern hemisphere, low elevations are shown as purple and blue, and high elevations are shown in red and brown.

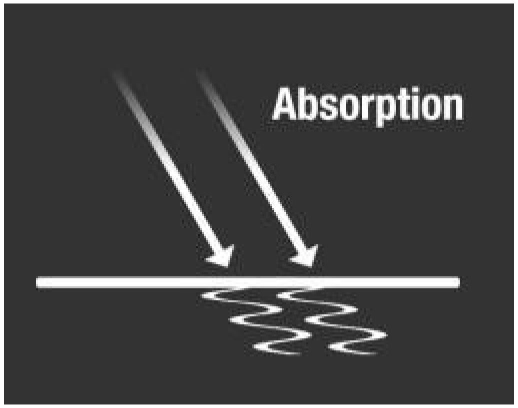


absorcion

Absorption occurs when photons from incident light hit atoms and molecules and cause them to vibrate. The more an object's molecules move and vibrate, the hotter it becomes. This heat is then emitted from the object as thermal energy.

Some objects, such as darker colored objects, absorb more incident light energy than others. For example, black pavement absorbs most visible and UV energy and reflects very little, while a light-colored concrete sidewalk reflects more energy than it absorbs. Thus, the black pavement is hotter than the sidewalk on a hot summer day. Photons bounce around during this absorption process and lose bits of energy to numerous molecules along the way. This thermal energy then radiates in the form of longer wavelength infrared energy.

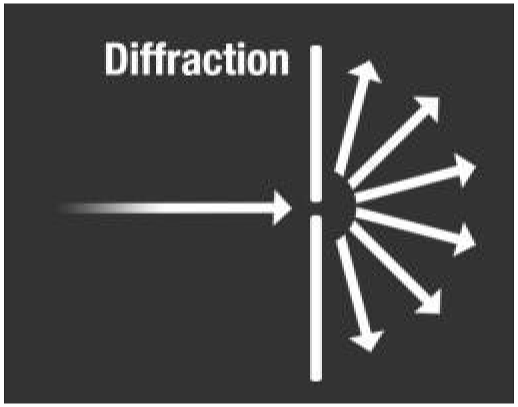
Thermal radiation from the energy-absorbing asphalt and roofs in a city can raise its surface temperature by as much as 10° Celsius. The Landsat 7 satellite image below shows the city of Atlanta as an island of heat compared to the surrounding area. Sometimes this warming of air above cities can influence weather, which is called the "urban heat island" effect.



difraccion

Diffraction is the bending and spreading of waves around an obstacle. It is most pronounced when a light wave strikes an object with a size comparable to its own wavelength. An instrument called a spectrometer uses diffraction to separate light into a range of wavelengths—a spectrum. In the case of visible light, the separation of wavelengths through diffraction results in a rainbow.

A spectrometer uses diffraction (and the subsequent interference) of light from slits or gratings to separate wavelengths. Faint peaks of energy at specific wavelengths can then be detected and recorded. A graph of these data is called a spectral signature. Patterns in a spectral signature help scientists identify the physical condition and composition of stellar and interstellar matter.

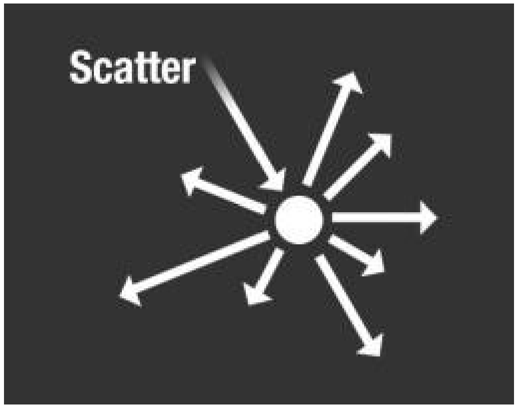


scattering

Scattering occurs when light bounces off an object in a variety of directions. The amount of scattering that takes place depends on the wavelength of the light and the size and structure of the object.

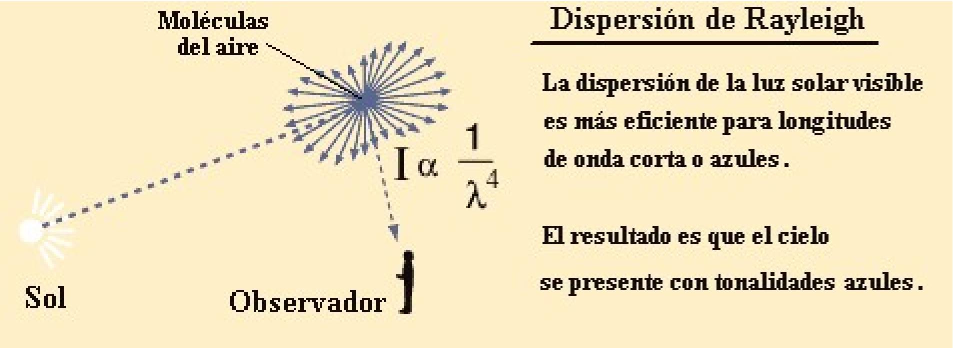
The sky appears blue because of this scattering behavior. Light at shorter wavelengths—blue and violet—is scattered by **nitrogen** and **oxygen** as it passes through the atmosphere. Longer wavelengths of light—red and yellow—transmit through the atmosphere. This scattering of light at shorter wavelengths illuminates the skies with light from the blue and violet end of the visible spectrum. Even though violet is scattered more than blue, the sky looks blue to us because our eyes are more sensitive to blue light.

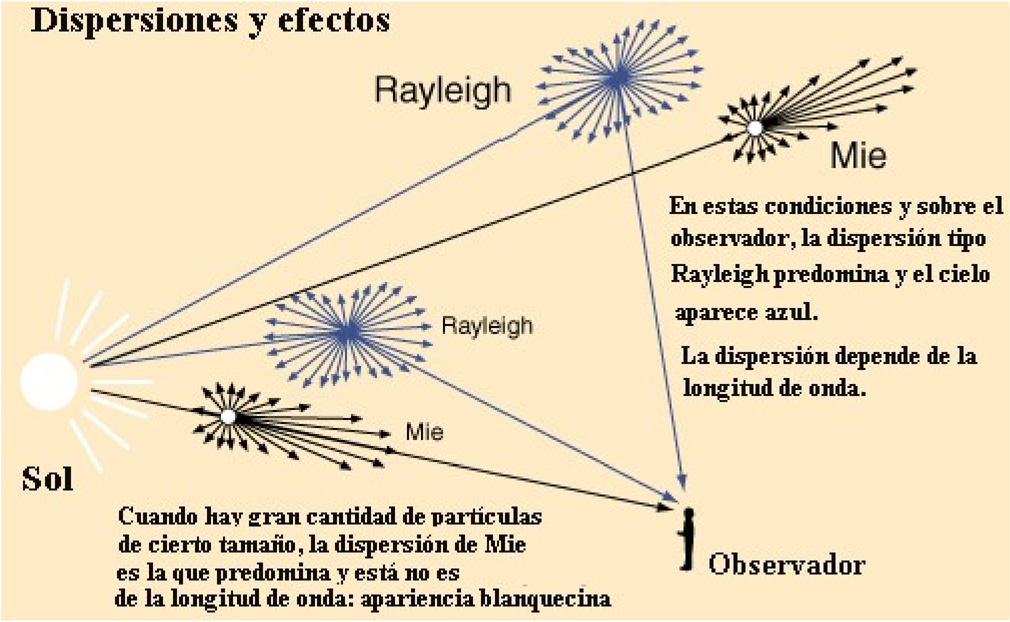
Aerosols in the atmosphere can also scatter light. NASA's Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite can observe the scattering of laser pulses to "see" the distributions of aerosols from sources such as dust storms and forest fires. The image below shows a volcanic ash cloud drifting over Europe from an eruption of Iceland's Eyjafjallajökull Volcano in 2010



Clase 2 Comportamientos de la luz

scattering





Cielo azul más arriba del horizonte (dispersión de Rayleigh) frente a cielo blanquecino y nubes blancas (dispersión de Mie).

http://hyperphysics.phy-astr.gsu.edu/hbasees/atmos/blusky.html

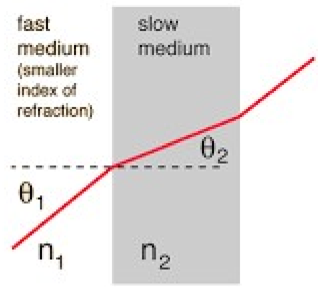
Clase 2 Comportamientos de la luz

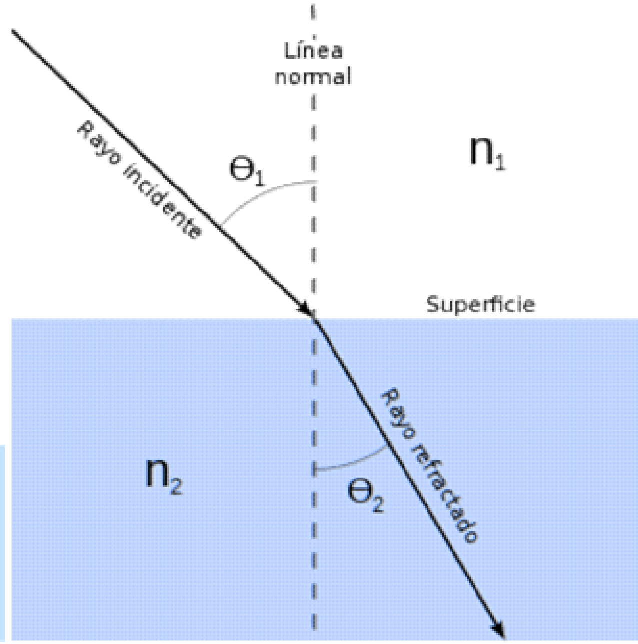
refraccion

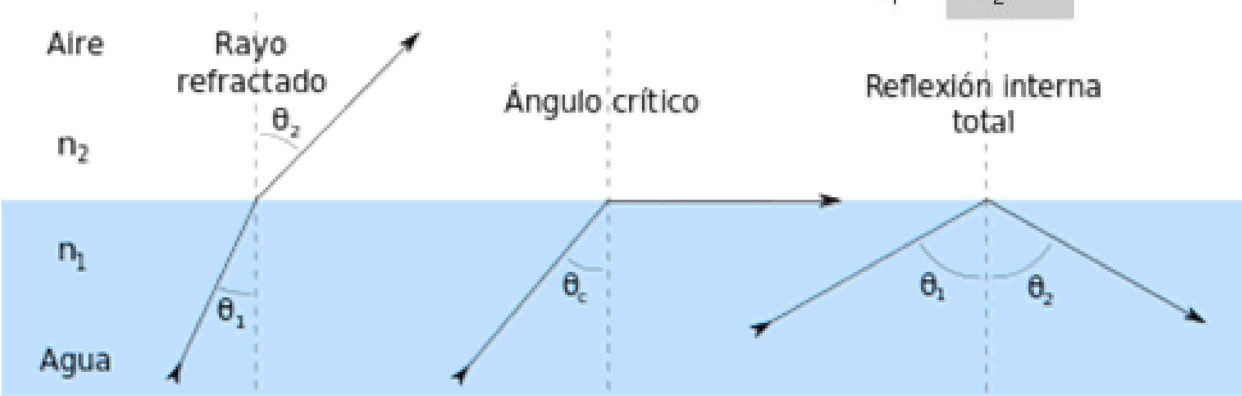
Refraction is when light wav
from one medium to another.
vacuum, and even slower in w
medium, the change in s
wavelengths of light are slow
them to bend at different angle

Snell's Law

$$\frac{n_1}{n_2} = \frac{\sin\theta_2}{\sin\theta_1}$$







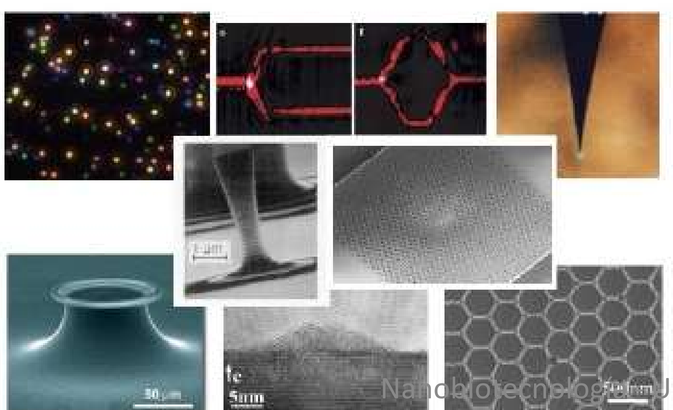
Confinamiento cuántico de la luz y de electrones

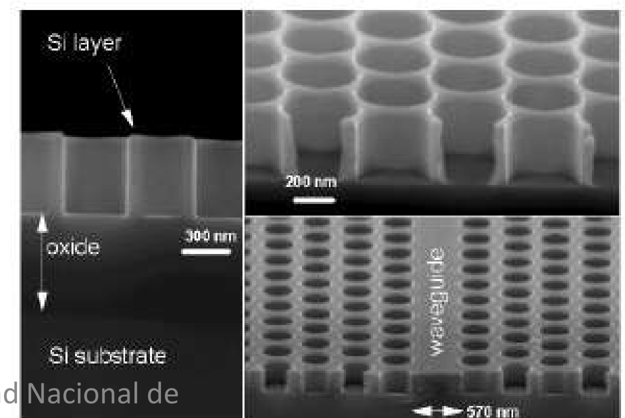
What is Nanophotonics?

Nanophotonics deals with the interaction of light with matter at a nanometer scale

increased control over the flow of light at length scales smaller than the wavelength

---National Academy of Science





Logan Liu. Micro and Nanotechnolgy Lab

Clase 2 . Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nuevos efectos en la nano-escala** **Confinamiento cuántico**

Confinamiento cuántico de la luz y de electrones

Confinamiento cuántico

- Fotones: cristales fotónicos: **confinamiento 1D (pueden existir 2 y 3 D también)**
- *Coupling* fotones-electrones: localized-SPR
- Electrones (u hoyos+): Qdots: **confinamiento 3D**

Clase 2 . Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala. Nuevos efectos en la nano-escala Confinamiento cuántico**

Confinamiento cuántico de la luz y de electrones

Los materiales que presentan confinamiento cuántico son aquellas estructuras con 1, 2 o 3 dimensiones en la nanoescala X, de acuerdo a:

$$X < \lambda = \frac{h}{mv}$$

[λ:Longitud de onda de ***de Broglie***]

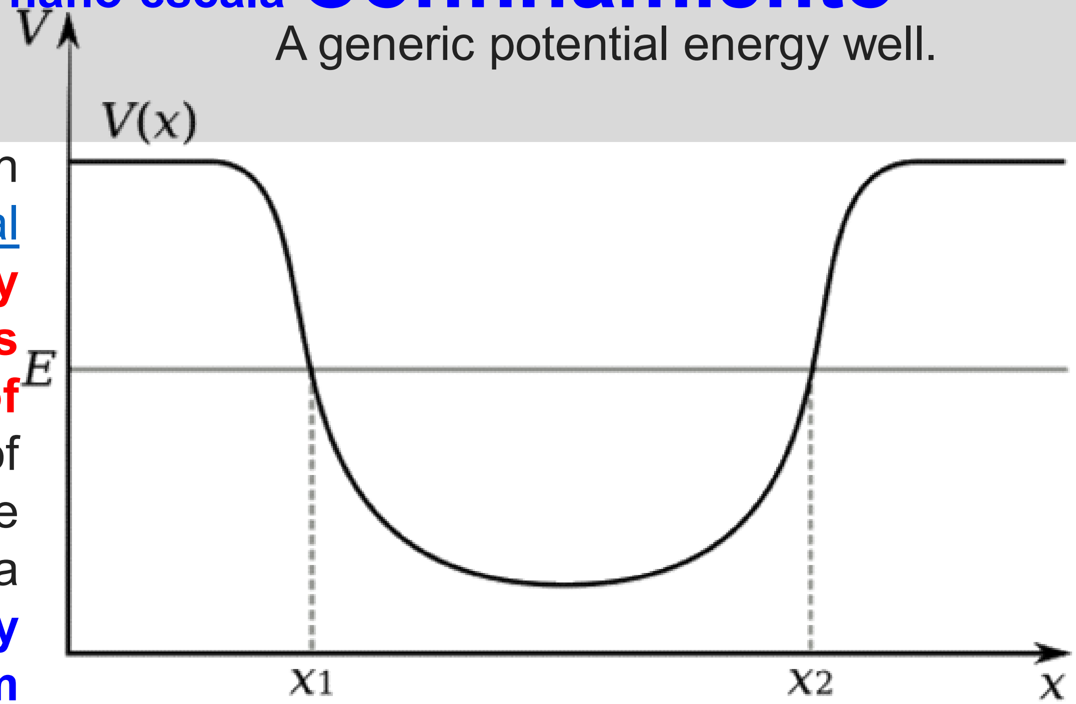
Energía térmica $= E = \frac{mv^2}{2} = kT$

$$\lambda = h/\sqrt[2]{2mkT}$$

Confinamiento cuántico efectivo: X < 10 nm

Clase 2 . Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Nuevos efectos en la nano-escala **Confinamiento cuántico**

A generic potential energy well.



A **potential well** is the region surrounding a local minimum of potential energy. **Energy captured in a potential well is unable to convert to another type of energy** (kinetic energy in the case of a gravitational potential well) because it is captured in the local minimum of a potential well. **Therefore, a body may not proceed to the global minimum of potential energy, as it would naturally tend to due to entropy.**

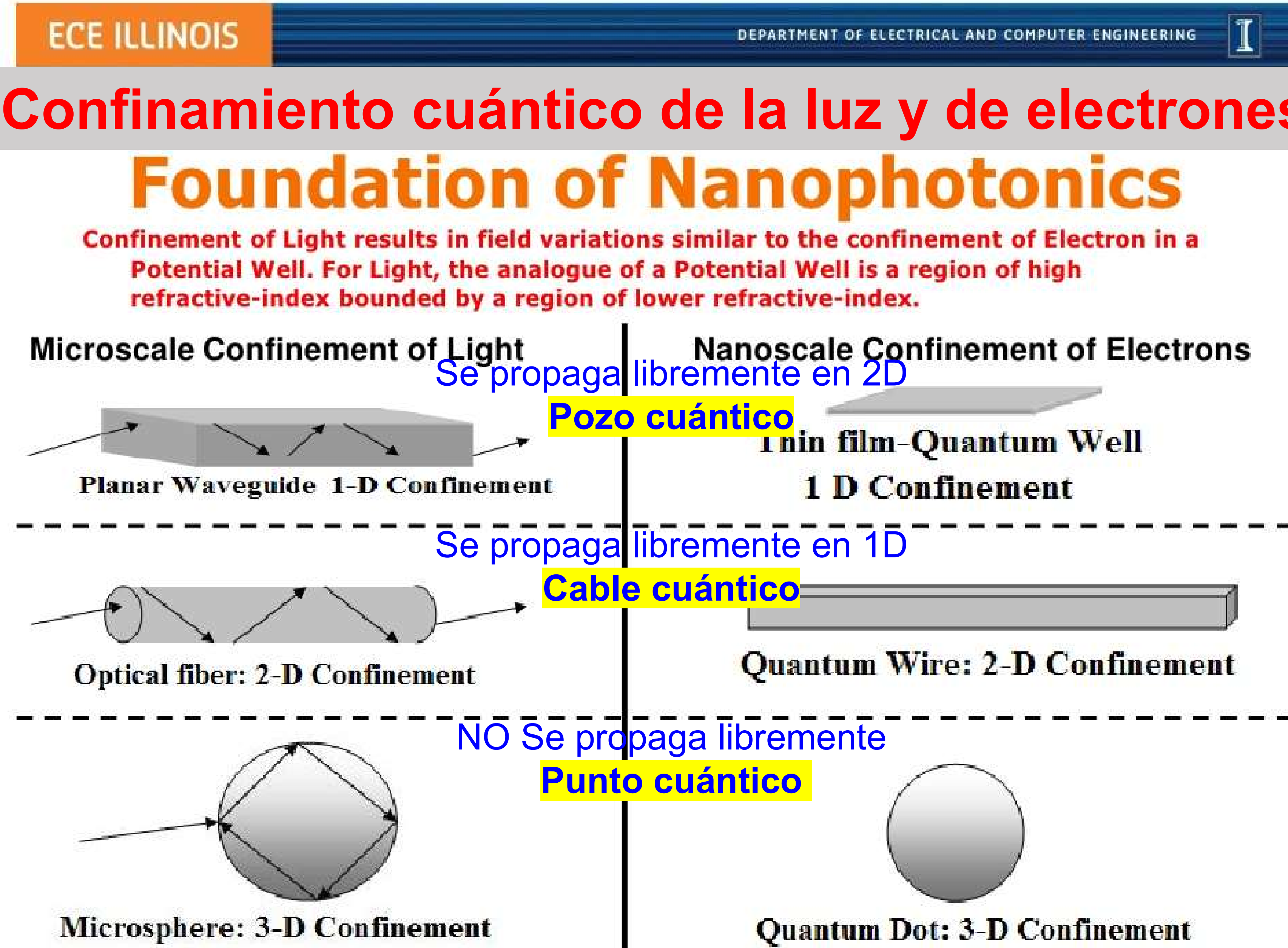
Energy may be released from a potential well if sufficient energy is added to the system such that the local maximum is surmounted. In quantum physics, potential energy may escape a potential well without added energy due to the probabilistic characteristics of quantum particles; in these cases a particle may be imagined to tunnel *through* the walls of a potential well.

The graph of a 2D potential energy function is a potential energy surface that can be imagined as the Earth's surface in a landscape of hills and valleys. Then a potential well would be a valley surrounded on all sides with higher terrain, which thus could be filled with water (e.g., be a lake) without any water flowing away toward another, lower minimum (e.g. sea level).

In the case of gravity, the region around a mass is a gravitational potential well, unless the density of the mass is so low that tidal forces from other masses are greater than the gravity of the body itself.

A potential hill is the opposite of a potential well, and is the region surrounding a local maximum.

Confinamiento cuántico de la luz y de electrones



Se propaga libremente en 2D
Pozo cuántico

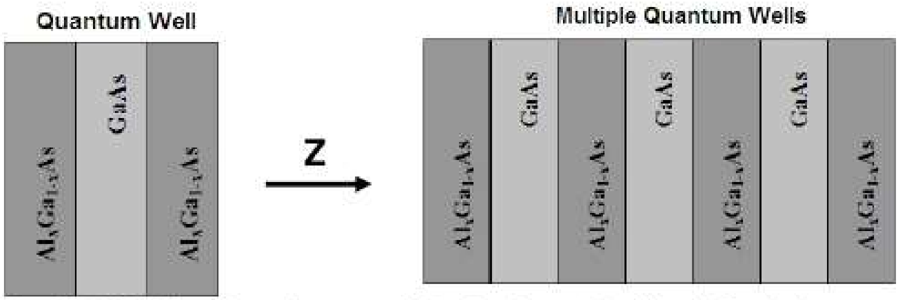
Se propaga libremente en 1D
Cable cuántico

NO Se propaga libremente
Punto cuántico

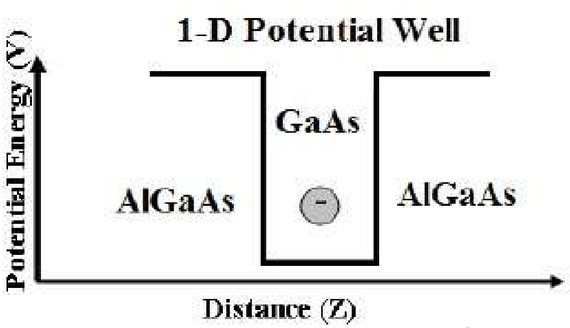
Confinamiento cuántico de la luz y de electrones

Quantum Confinement

Nanoscale Confinement in 1-Dimension results in a "Quantum Well"



At 300 K, The band gap of GaAs is 1.43 eV while it is 1.79 eV for AlxGa1-xAs (x=0.3). Thus the electrons and holes in GaAs are confined in a 1-D potential well of length L in the Z-direction.



Quantization of energy into discrete levels has applications for fabrication of new solid-state lasers. Two or more Quantum wells side-by-side give rise to Multiple Quantum Wells (MQM) structure.

Motion is confined only in the Z-direction. For electrons and holes moving in the Z-direction in low bandgap material, their motion can be described by Particle in a Box. If the depth of Potential Well is V, for energies E<V, we can write,

$$E_{n,k_x,k_y} = E_C + \frac{n^2h^2}{8m_e^*L^2} + \frac{h^2(k_x^{\ 2}+k_y^{\ 2})}{8\pi^2 m_e^*}$$

n = 1, 2, 3,.....

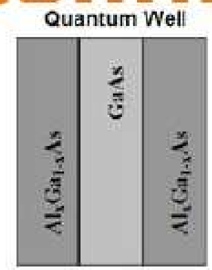
$p_x = (h/2\pi)k_x$ and $p_y = (h/2\pi)k_y$ can take continuous value and m_e^* is the effective mass of electron

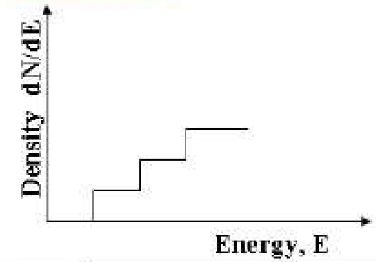
Quantum Confinement

Quantum Well: 1D Confinement

Due to 1-D confinement, the number of continuous energy states in the 2-D phase space satisfy

$$2mE_{2D} = p_x^2 + p_y^2$$



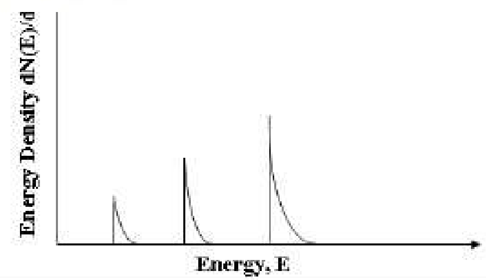


Quantum Wire: 2D Confinement

Quantum Wire: 2-D Confinement

2D confinement in X and Z directions. For wires (e.g. of InP, CdSe). with rectangular cross-section, we can write:

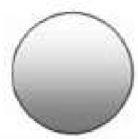
$$E_{n_1,n_2,k_y} = E_C + \frac{n_1^2 h^2}{8m_e^* L_x^2} + \frac{n_2^2 h^2}{8m_e^* L_z^2} + \frac{h^2 k_y^2}{8\pi^2 m_e^*}$$



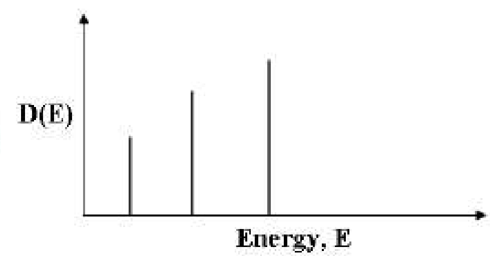
Quantum Dot: 3D Confinement

For a cubical box with the discrete energy levels are given by:

$$E_{n_1,n_2,n_3} = E_C + \frac{h^2}{8m_e^*}\left(\frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2} + \frac{n_3^2}{L_z^2}\right)$$



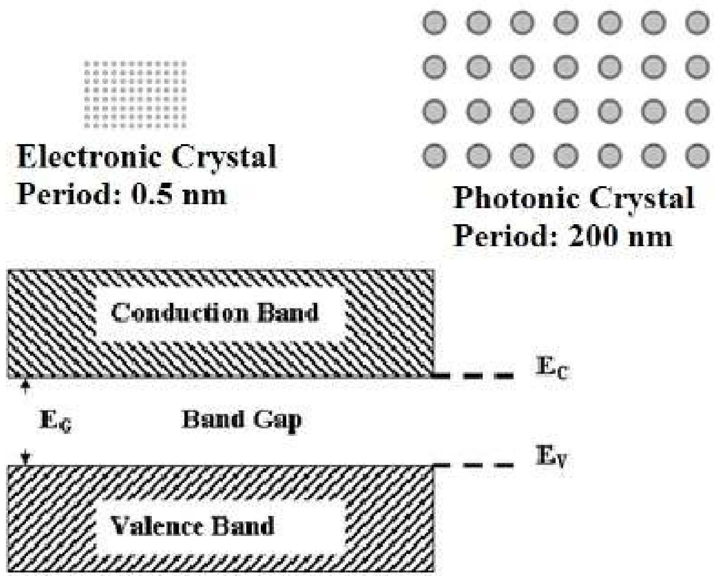
Quantum Dot: 3-D Confinement

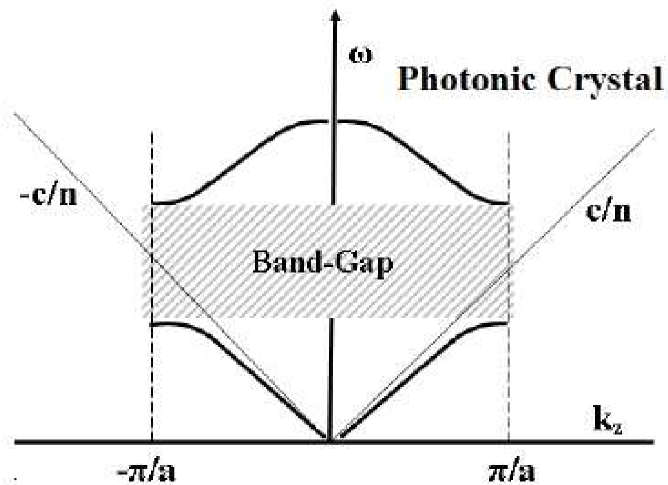


ECE ILLINOIS — DEPARTMENT OF ELECTRICAL AND COMPUTER ENGINEERING

Confinamiento cuántico de la luz: aparición de band gap y de estados discretos

The most striking similarity is the Band-Gap within the spectra of Electron and Photon Energies





Electronic Crystal

Solution of Schroedinger's equation in a 3D periodic coulomb potential for electron crystal forbids propagation of free electrons with energies within the Energy Band-Gap.

Likewise, diffraction of light within a Photonic Crystal is forbidden for a range of frequencies which gives the concept of Photonic Band-Gap. The forbidden range of frequencies depends on the direction of light with respect to the photonic crystal lattice. However, for a sufficiently refractive-index contrast (ratio n1/n2), there exists a Band-Gap which is omni-directional.

Bio-inspired sensors based on photonic structures of Morpho butterfly wings: a review Qingsong Li,a Qi Zeng,a Lei Shi,b Xiaohua Zhangc and Ke-Qin Zhang*Journal of Materials Chemistry C2016

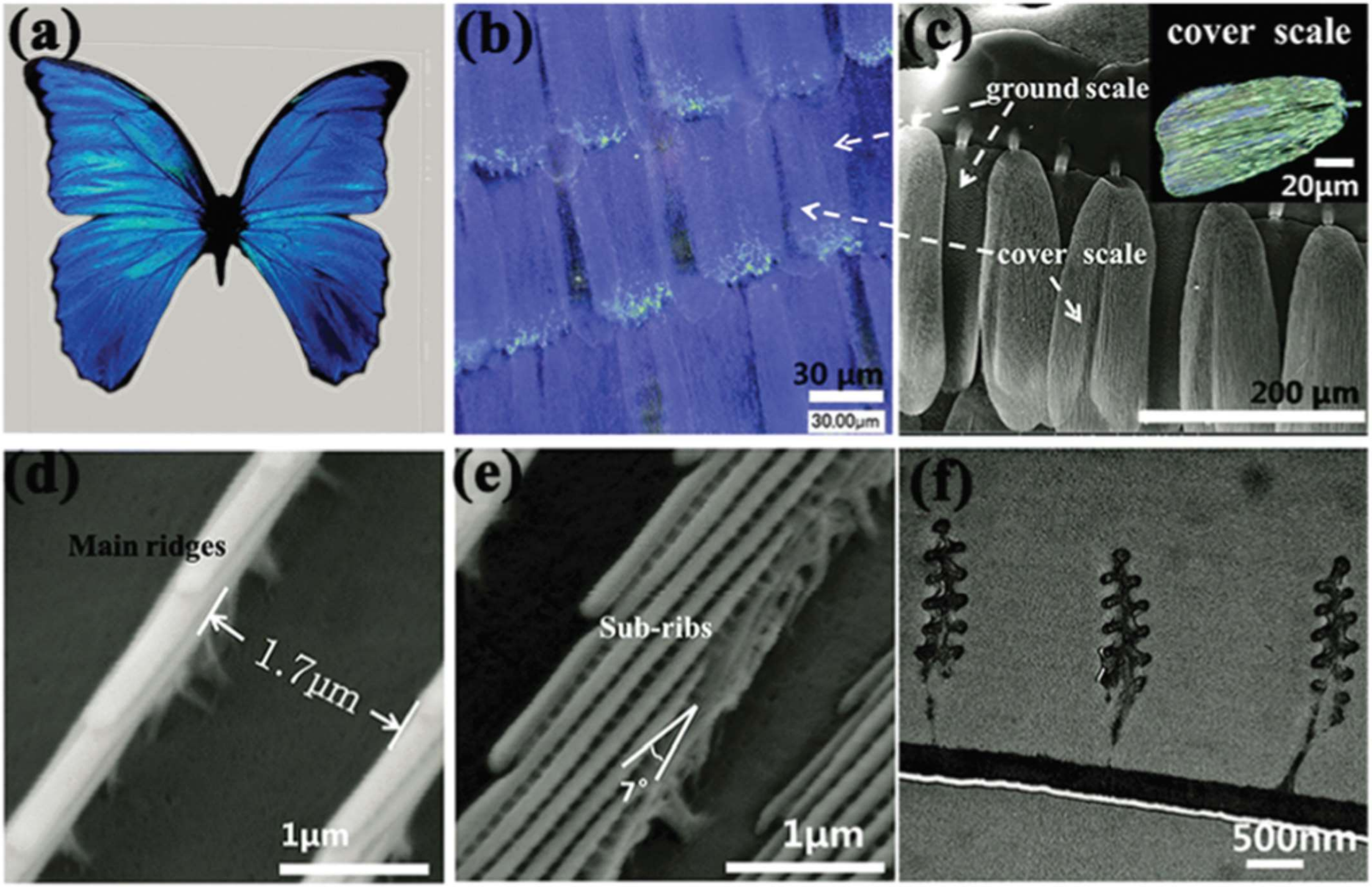


Fig. 1 (a) The image of a typical Morpho didius butterfly, (b) optical image of the scales, (c) the cover scale and the ground scale. Inset: The optical image of a single cover scale, (d) SEM image from the top view of a cover scale, (e) the SEM image of the ground scale, and (f) the TEM image of the ground scale.

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nanomateriales naturales**

Colores estructurales ≠ colores pigmentarios

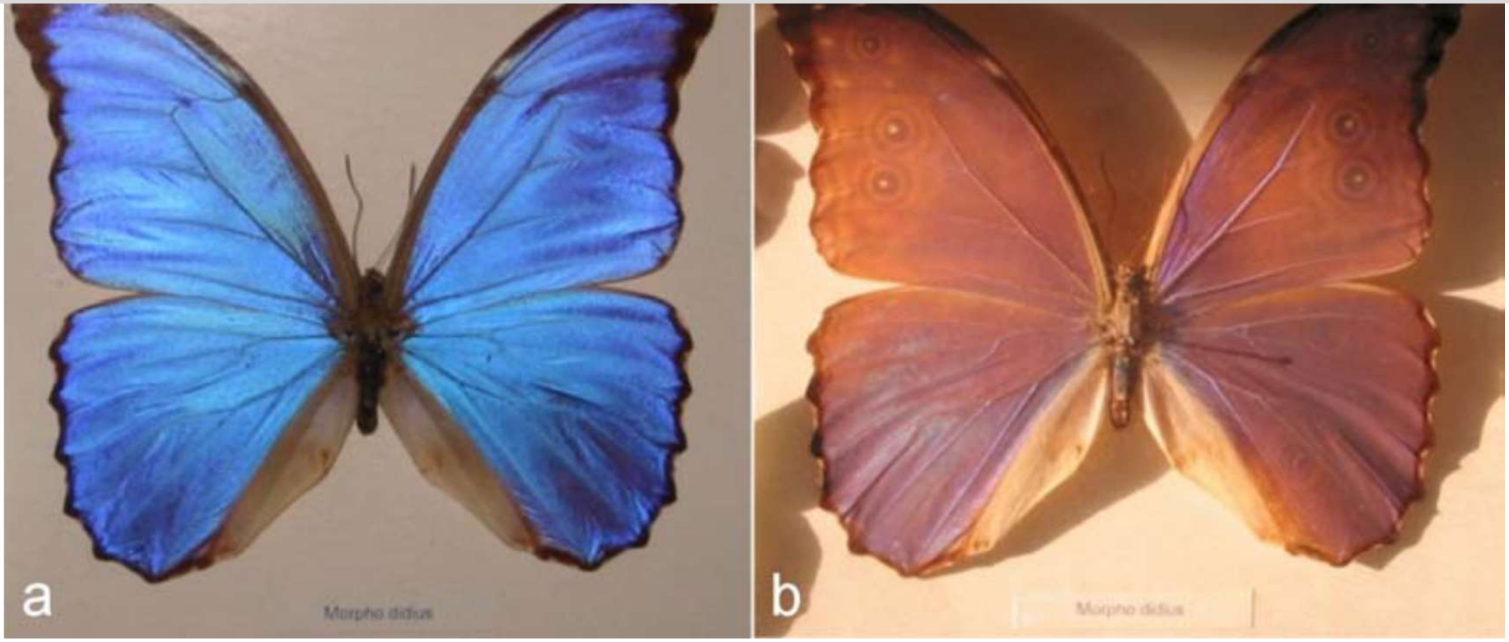
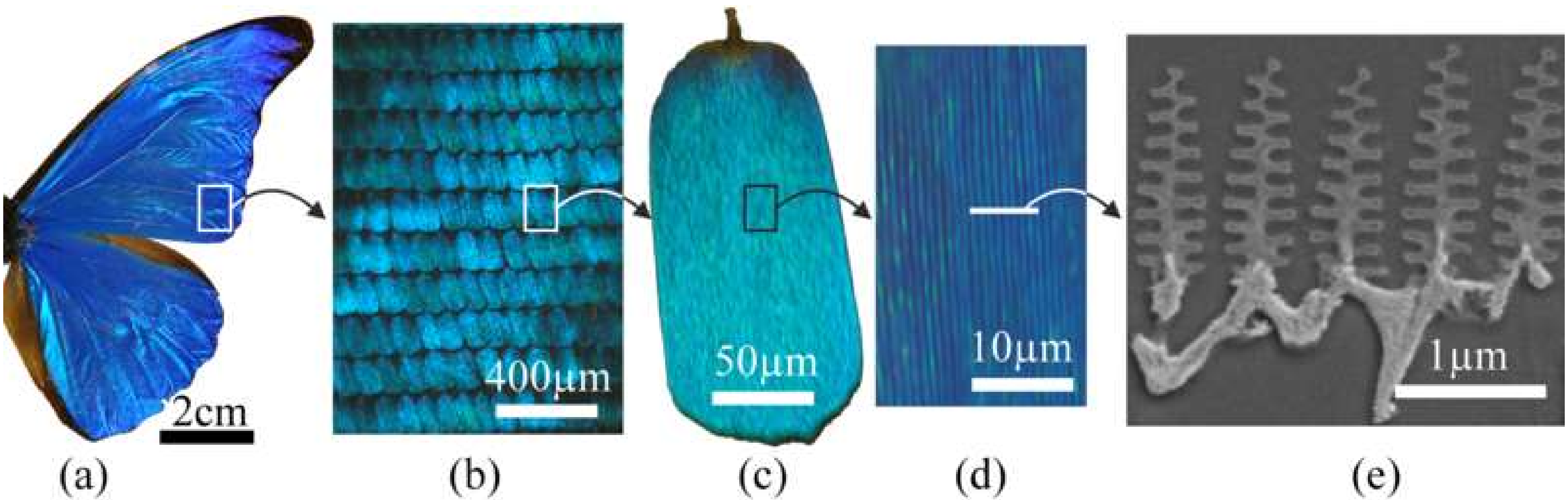


Fig. 7. The dorsal wings of the tropical butterfly *Morpho didius* have a striking blue color (**a**) due to multilayer interference reflection. Upon oblique illumination (**b),** outside the angle of interference reflection, a light brown pigmentation in the wing scales becomes visible; note the so-called eyes at the under wings, which are often quite marked in other butterflies, but with natural, wide-angle illumination they are completely swamped by the interference reflection in Morpho butterflies

Clase 2 Colores estructurales ≠ colores pigmentarios

La periodicidad (alternancia zonas de distinto índice de refracción) del cristal fotónico debe estar en el orden de $\lambda/2$ [para el visible entre 200 y 350 nm]



The nanostructures are mainly responsible for the scattering of the light in Blue Morpho butterfly

All structurally coloures species [butterflies and moths (Lepidoptera)] are appropriately nanostructured to produce visible colours by **coherent scattering**, i.e. differential interference and reinforcement of scattered, visible wavelengths.

Habrá λ "prohibidas"= gaps fotónicos

https://asknature.org/strategy/wing-scales-cause-light-to-diffract-and-interfere/#.Wp_gGujOXIU

SCIENTIFIC REPORTS

Nanofabrication and coloration study of artificial *Morpho* butterfly wings with aligned lamellae layers

Sichao Zhang & Yifang Chen Published: 18 November 2015

:ly seen in butterflies1–5, beetles6 , and sea
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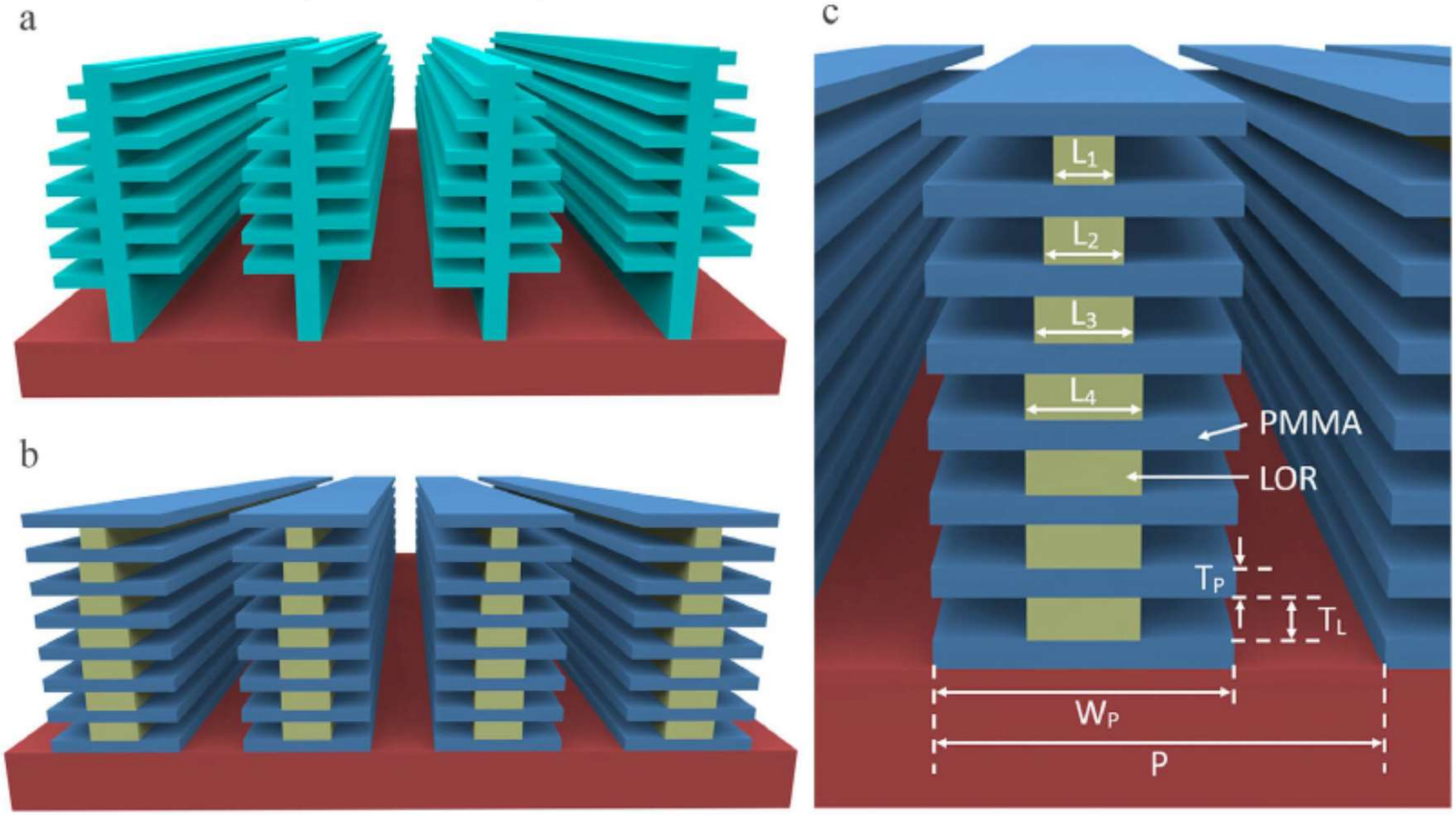
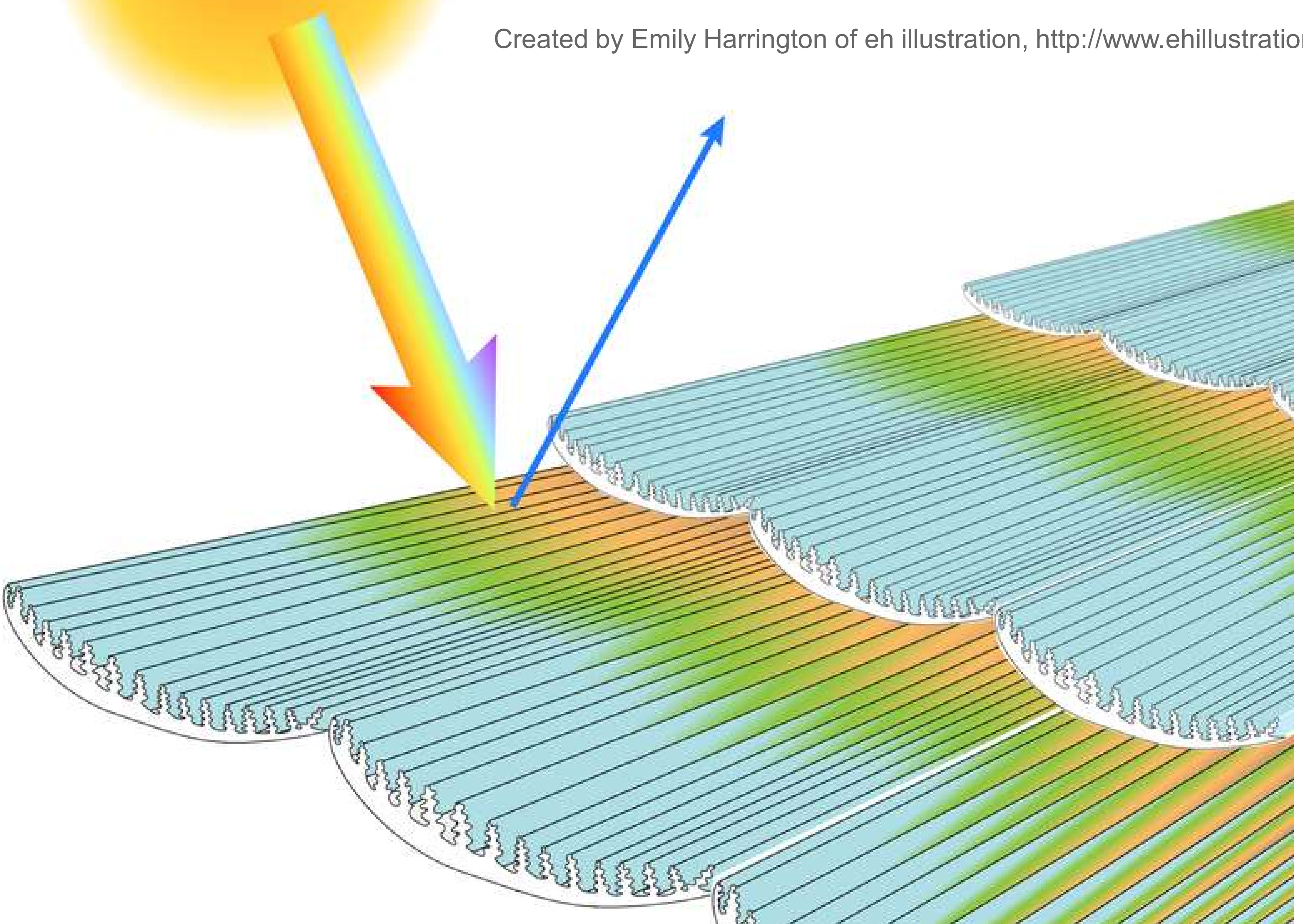


ecture of the periodical structure on the micro-
wing scale, which is also an inevitable step
aily life. As schematically shown by the original

Clase 2 Colores estructurales ≠ colores pigmentarios



Created by Emily Harrington of eh illustration, http://www.ehillustration.com.

https://asknature.org/strategy/wing-scales-cause-light-to-diffract-and-interfere/#.Wp_gGujOXIU

Clase 2 . Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Nanomateriales naturales**

Colores estructurales ≠ colores pigmentarios

Fo … rflies:
ph … tment
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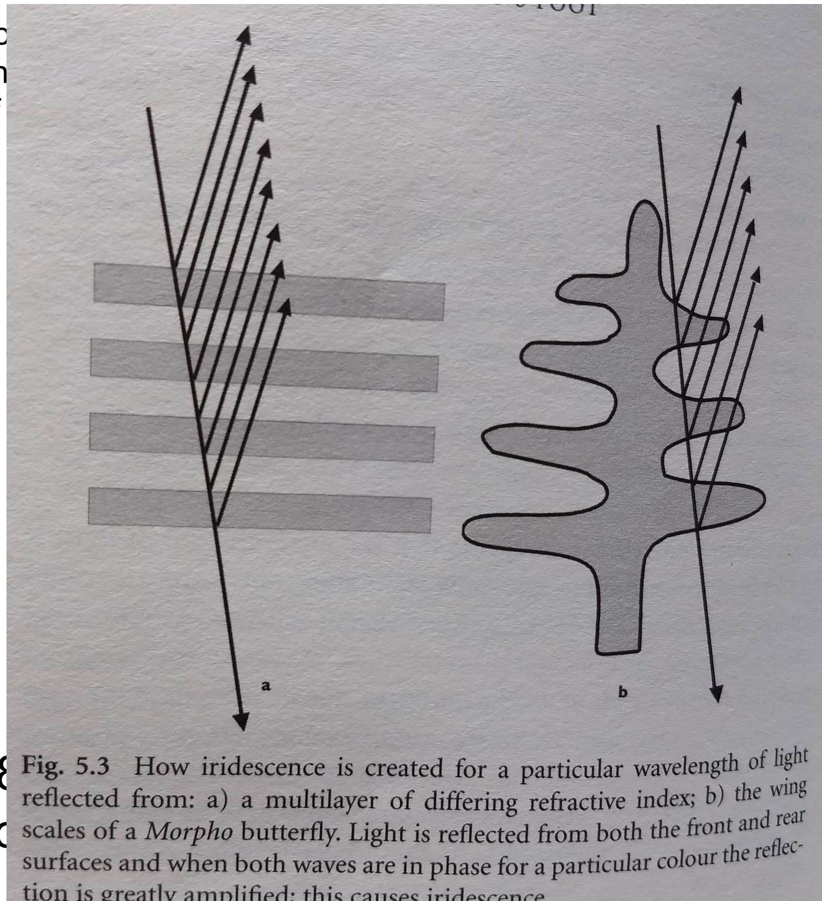


Fig. 5.3 How iridescence is created for a particular wavelength of light reflected from: a) a multilayer of differing refractive index; b) the wing scales of a *Morpho* butterfly. Light is reflected from both the front and rear surfaces and when both waves are in phase for a particular colour the reflection is greatly amplified; this causes iridescence.

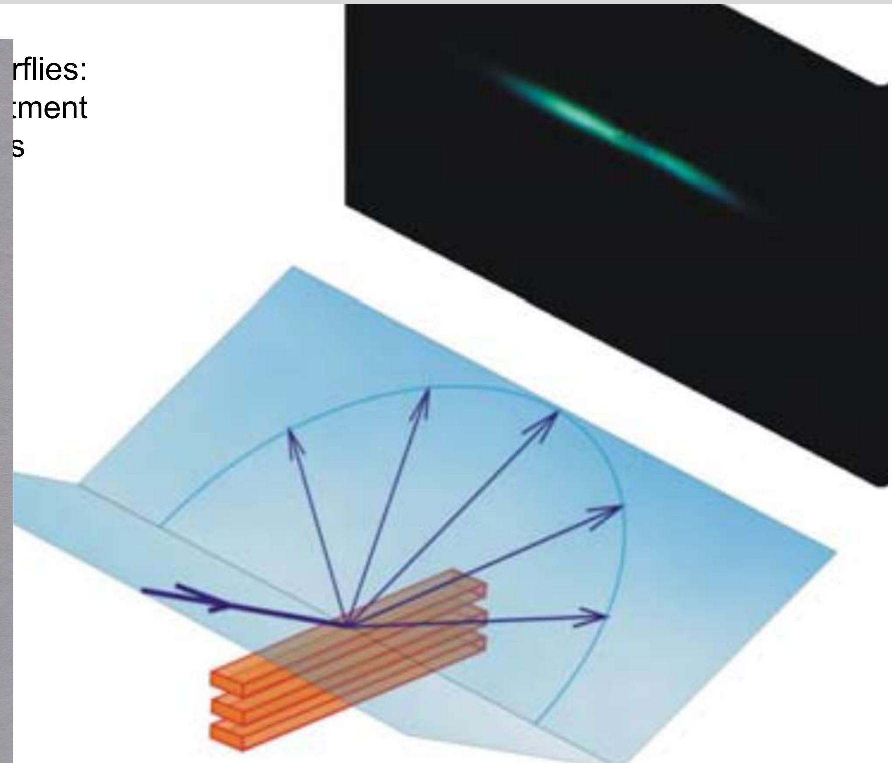


Fig. 8 … scent coloration of Morpho wings (similar pheno… raviolet). A scale ridge forming a multilayer stack … ciple according to Snell's law, but the light wave is diffracted in a plane, because the width of the ridge is in the order of the wavelength of light.

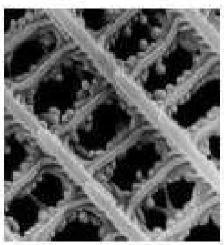
Clase 2 Colores estructurales ≠ colores pigmentarios

https://asknature.org/strategy/wing-scales-cause-light-to-diffract-and-interfere/#.Wp_hZOjOXIU

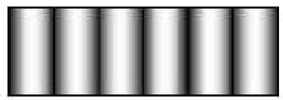
<iframe width="800" height="450" src="https://www.youtube.com/embed/x4I9mmd-2Rc" frameborder="0" allow="autoplay; encrypted-media" allowfullscreen></iframe>

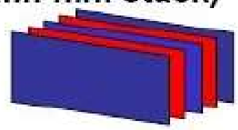
Photonic Crystal

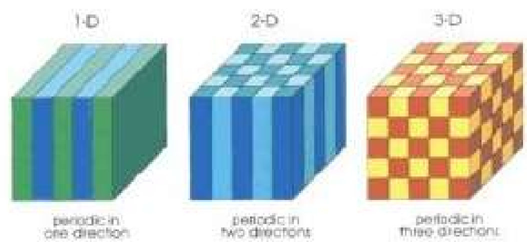
NATURAL



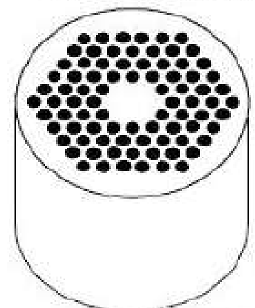
1D Photonic Crystal
(Bragg grating and thin film stack)

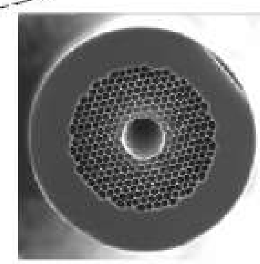




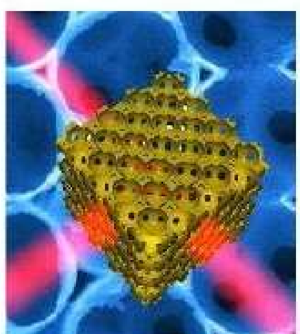


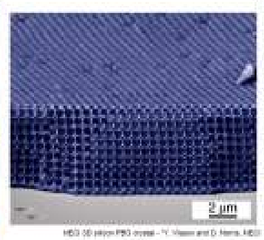
2D Photonic Crystal
MICROSTRUCTURED OPTICAL FIBER



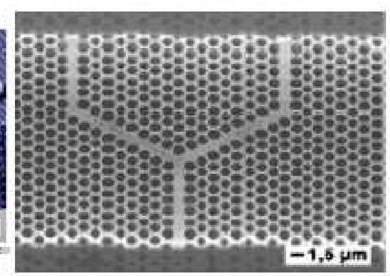


3D PHOTONIC CRYSTAL

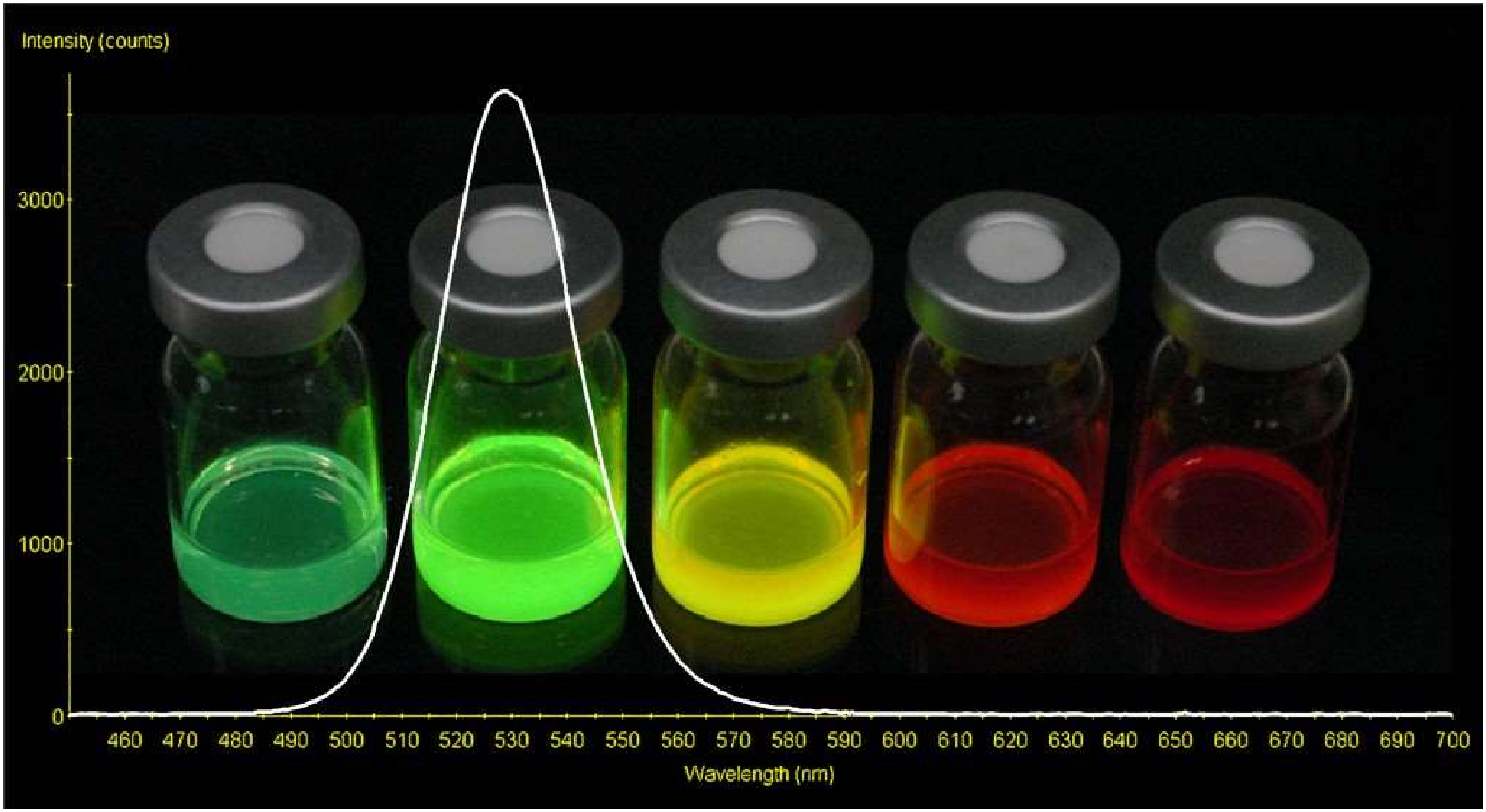




2D Photonic Crystal
PLANAR WAVEGUIDE

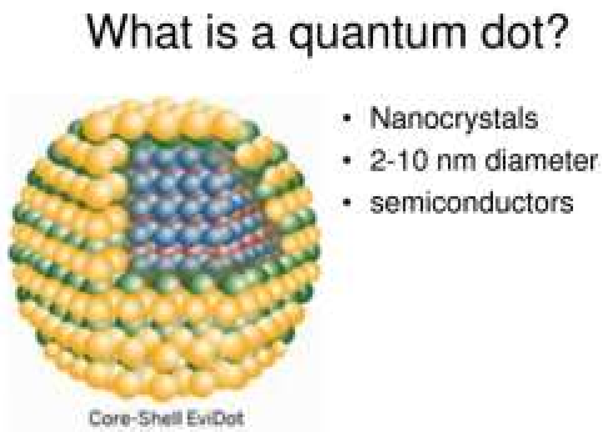


Clase 2 Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Quantum dots**



http://physicsopenlab.org/2015/11/20/quantum-dots-a-true-particle-in-a-box-system/

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Quantum dots**



A **quantum dot** (**QD**) is a crystal of semiconductor material whose diameter is on the order of several nanometers – a size which results in its free charge carriers experiencing "quantum confinement" in all three spatial dimensions. The electronic properties of quantum dots are intermediate between those of bulk semiconductors and of discrete molecules and closely related to their size and shape. This allows properties such as the band gap, emission color, and absorption spectrum to be highly tuneable, as the size distribution of quantum dots can be controlled during fabrication. For example, the band gap in a quantum dot, which determines the frequency range of emitted light, is inversely related to its size. In fluorescent dye applications, the frequency of emitted light increases as the size of the quantum dot decreases, shifting the color of emitted light from red to violet.

The small quantum dots, such as nanocrystalline semiconductors in a colloidal solution, have dimensions between 2 and 10 nanometers, corresponding to about 10-50 atoms in diameter, and may reach a total of 100-100000 atoms for each quantum dot .

The self-assembled quantum dots have a size of 10-50 nanometers; while those defined by means of electronic lithography have larger sizes around 100 nm.

Besides confinement in all three dimensions (i.e., a quantum dot), other quantum confined semiconductors include:

•Quantum wires, which confine electrons or holes in two spatial dimensions and allow free propagation in the third.

•Quantum wells, which confine electrons or holes in one dimension and allow free propagation in two dimensions.

The Quantum Dot which contain electrons can also be compared to atoms: both have discrete energy levels and contain a small number of electrons, but unlike the atoms, the confinement potential of Quantum Dot not necessarily show spherical symmetry. Moreover the electrons do not move in the limited space, but inside the semiconductor crystal that hosts them.

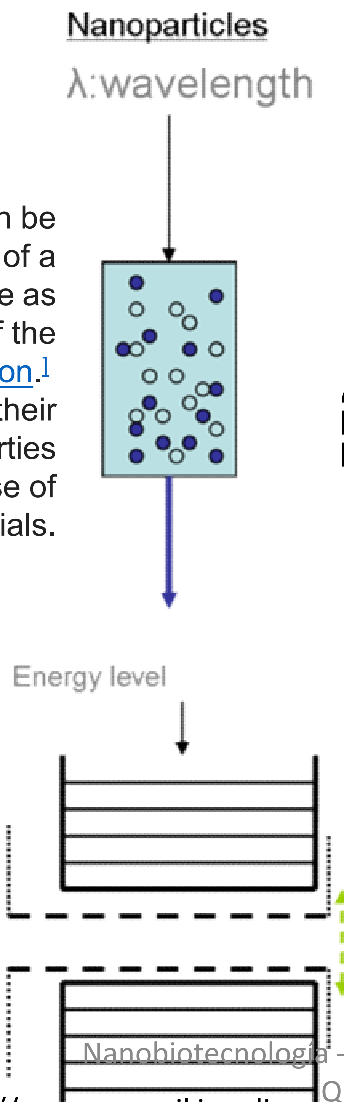
Researchers have studied applications for quantum dots in transistors, solar cells, LEDs, and diode lasers. They have also investigated quantum dots as agents for medical imaging and as possible qubits in quantum computing. The small size of quantum dots allows them to be suspended in various solvents and thus compatible with solution processing techniques such as spin coating and inkjet printing.

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Confinamiento cuántico

Quantum confinement can be observed once the diameter of a material is of the same magnitude as the de Broglie wavelength of the electron wave function.[1] When materials are this small, their electronic and optical properties deviate substantially from those of bulk materials.

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mkT}}$$

Specifically, the effect describes the phenomenon resulting from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement, called the **exciton Bohr radius**.

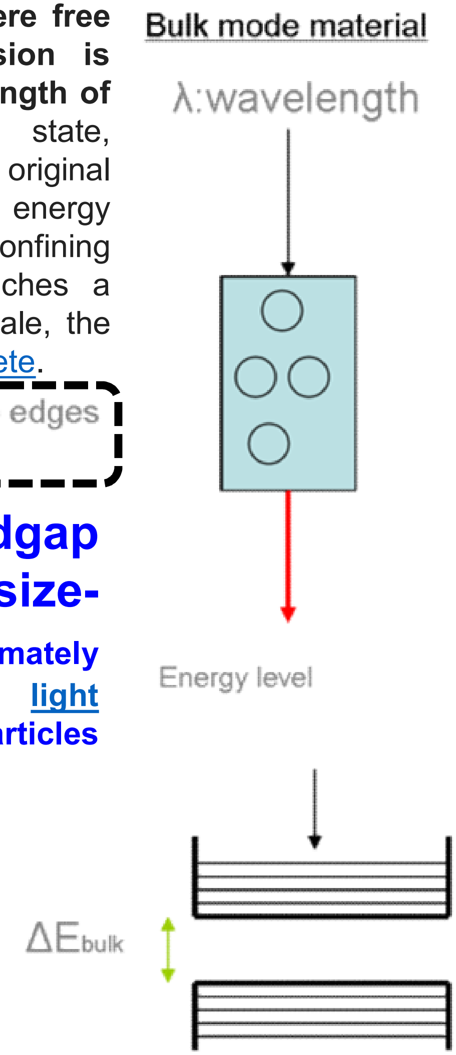


A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, the bandgap remains at its original energy due to a continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in nanoscale, the energy spectrum becomes discrete.

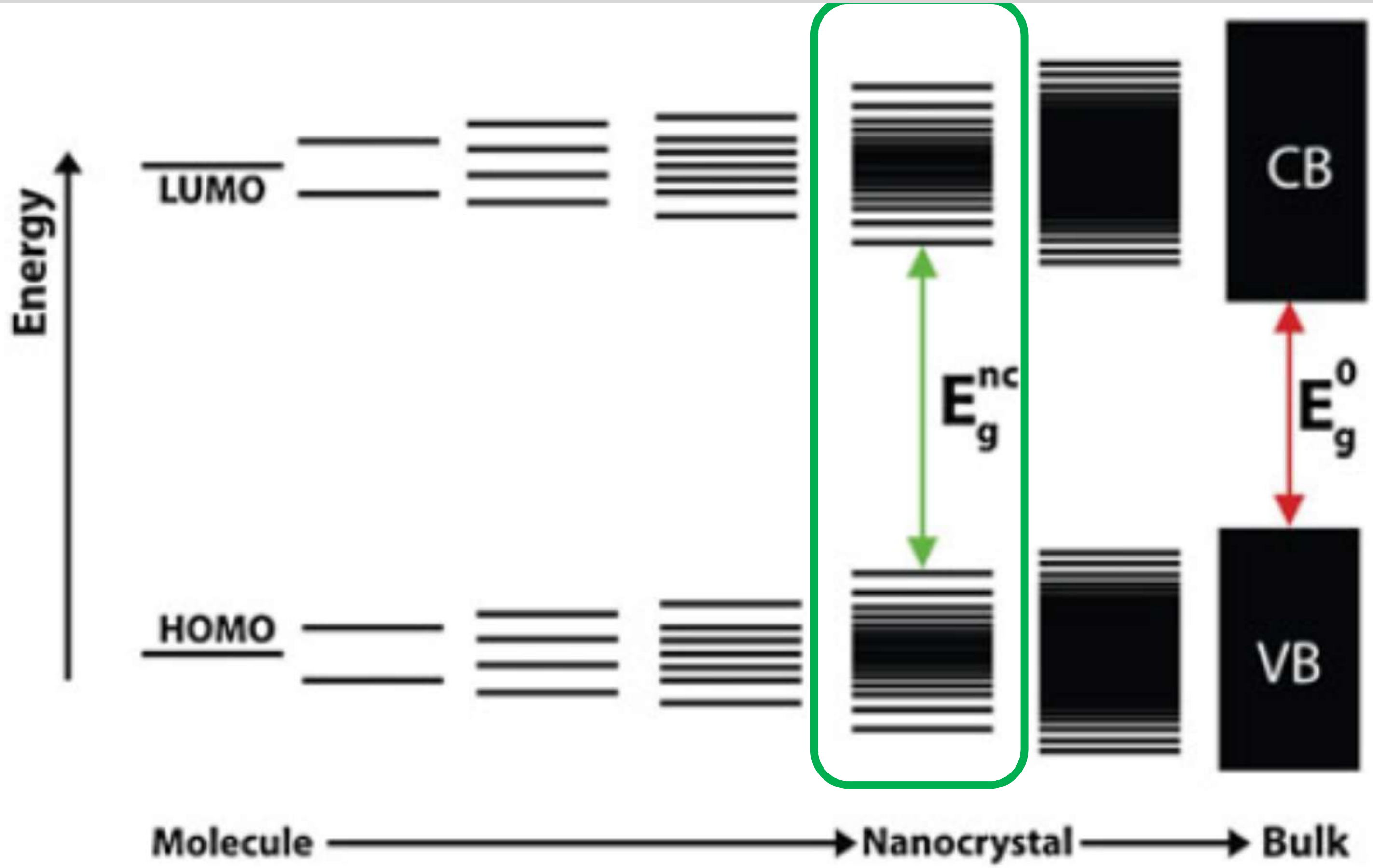
Radiation shift between the two edges of visible spectra

As a result, the bandgap becomes size-dependent. This ultimately results in a blueshift in light emission as the size of the particles decreases.

$\Delta E_{nano} > \Delta E_{bulk}$



Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Quantum dots**

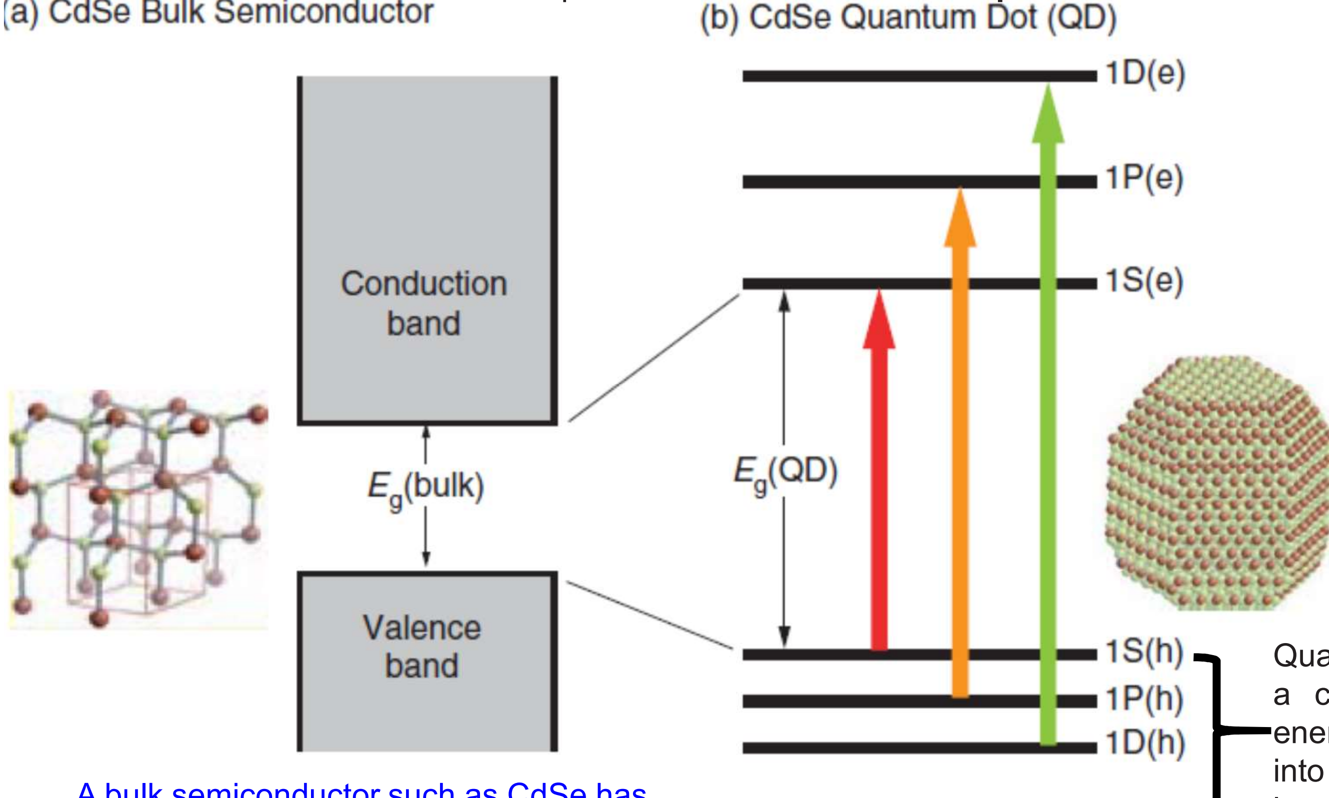


Evolution of the energy level structure from a hypothetical diatomic molecule (extreme left) to a bulk semiconductor (extreme right). Eg nc and Eg 0 indicate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for a nanocrystal and bulk, respectively (CB = conduction band, VB = valence band).

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Quantum dots

Size ~ λ De Broglie è:

As a result of these "geometrical" constraints, electrons "feel" the presence of the particle boundaries and respond to changes in particle size by adjusting their energy. This phenomenon is known as the **quantum-size effect**



(c) The expression for the size dependence separation between the lowest electron and hole QD states—Eg(QD), the QD energy gap—was obtained with the spherical "quantum box" model.

(c)

$$E_g(\mathrm{QD}) \approx E_{g0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

$$m_{eh} = \frac{m_e m_h}{m_e + m_h}$$

m_e = effective electron mass

m_h = effective hole mass

Quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic like energy levels.

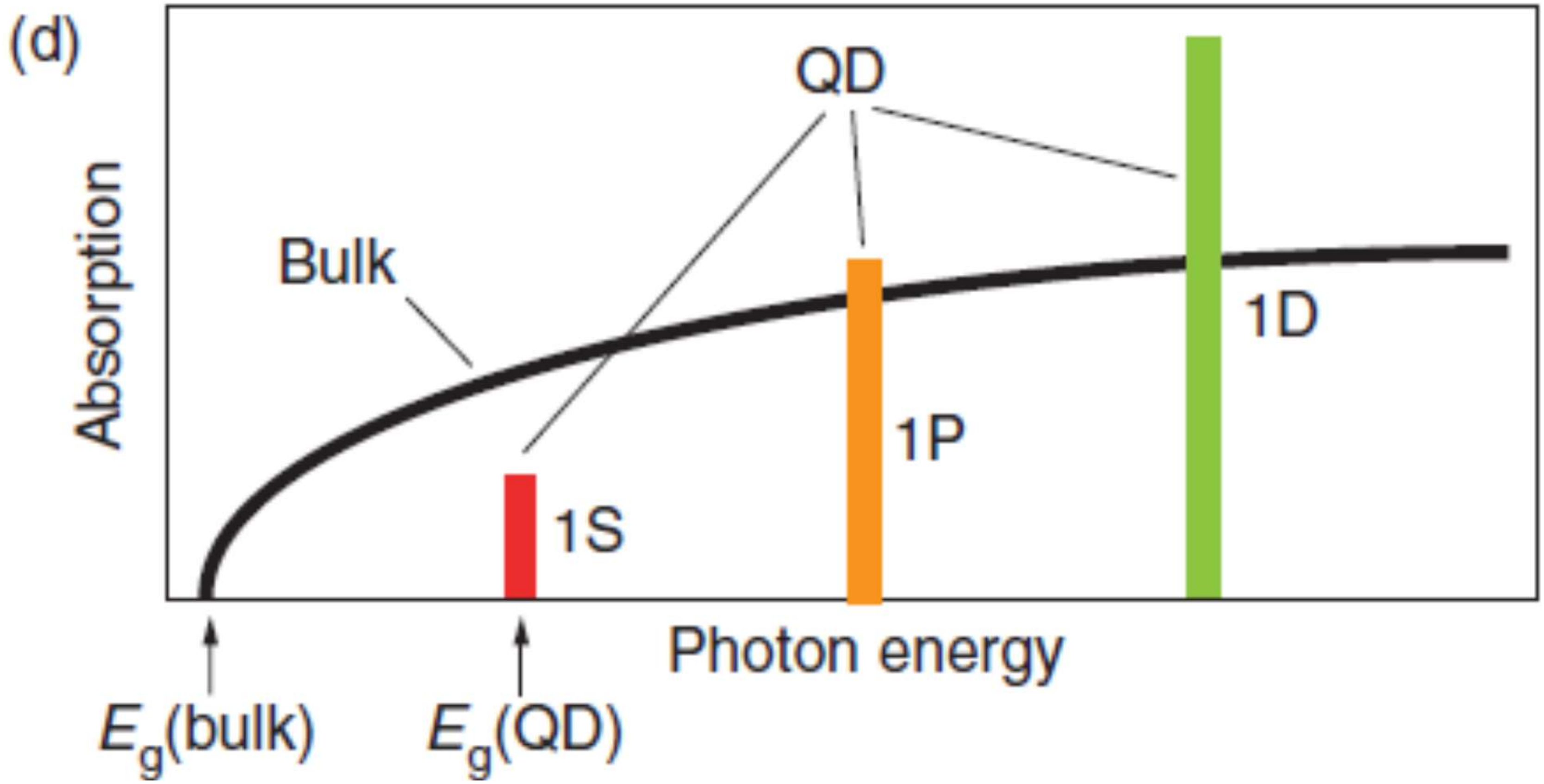
A bulk semiconductor such as CdSe has continuous conduction and valence energy bands separated by a "fixed" energy gap, Eg(bulk). Electrons normally occupy all states up to the edge of the valence band, whereas states in the conduction band are empty

A QD is characterized by discrete atomic-like states with energies that are determined by the QD radius R. These well-separated QD states can be labeled with atomic-like notations, such as 1S, 1P, and 1D.

Nanocrystal Quantum Dots *From fundamental photophysics to multicolor lasing Victor I. Klimov* Number 28 2003 *Los Alamos Science*

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Quantum dots

This schematic represents the continuous absorption spectrum of a bulk semiconductor (black line) compared with a discrete absorption spectrum of a QD (colored bars).

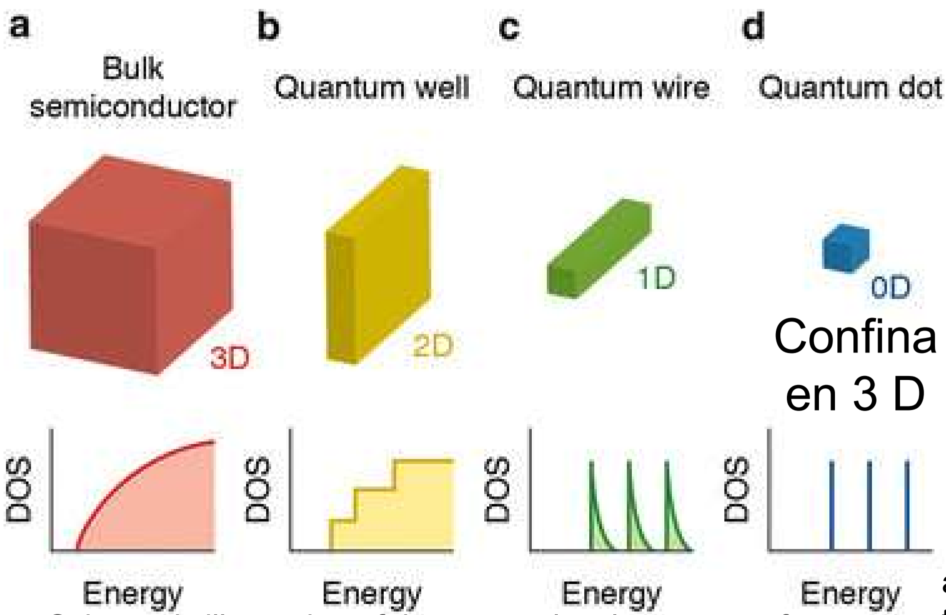


The excitons in the quantum dot are confined to a distance smaller than the Bohr exciton radius, **5.4 nm in bulk CdSe** [6, 8]. Previous work on CdSe nanocrystals observed emission maxima ranging from blue (490 nm) to orange (580 nm) with estimated dot radii from 0.9 nm to 2.4 nm, which fall within the strong confinement region [1],[3]

Seminario1. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** **Confinamiento cuántico**

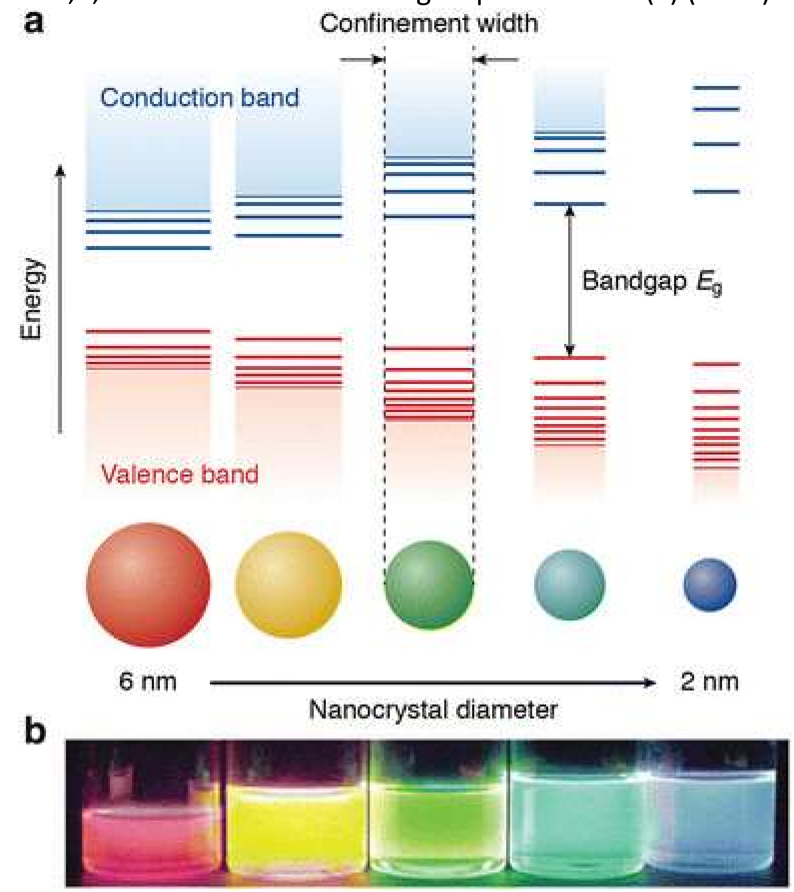
Excited-State Dynamics in Colloidal Semiconductor Nanocrystals Freddy T. Rabouw1,2,3 • Celso de Mello DonegaTop Curr Chem (Z) (2016) 374:58

In current application, a quantum dot such as a small sphere confines in three dimensions, a quantum wire confines in two dimensions, and a quantum well confines only in one dimension. **These are also known as zero-, one- and two-dimensional potential wells**, respectively. In these cases they refer to the number of dimensions in which a confined particle can act as a free carrier.



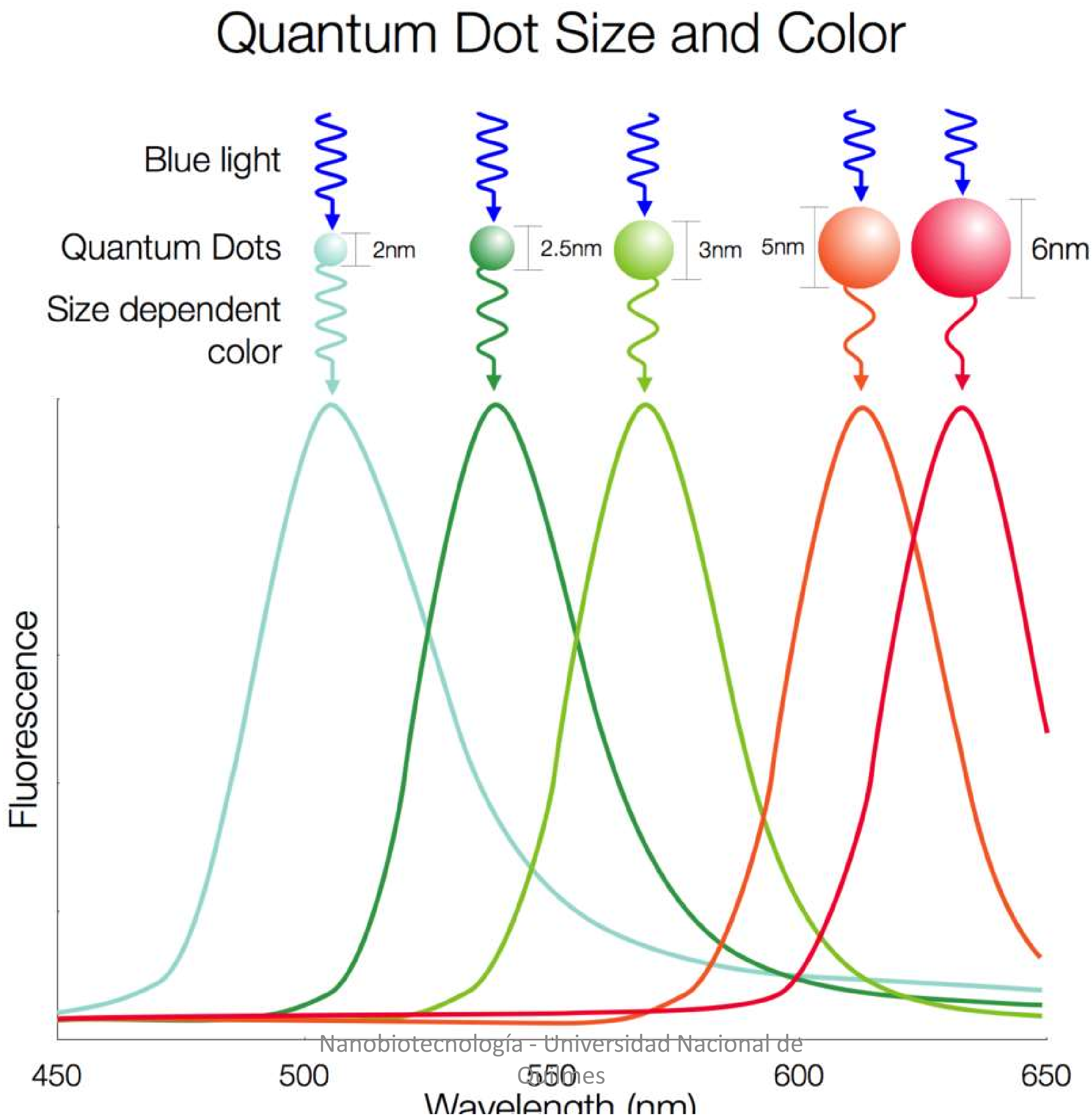
Confina en 3 D

Schematic illustration of the energy level structure of a **bulk semiconductor (a)**, and **semiconductor nanostructures (b–d)** with reduced dimensionality.
b 2D semiconductor nanostructure or quantum well.
c 1D semiconductor nanostructure or quantum wire.
d 0D semiconductor nanostructure or quantum dot.
DOS represents the density of electronic states



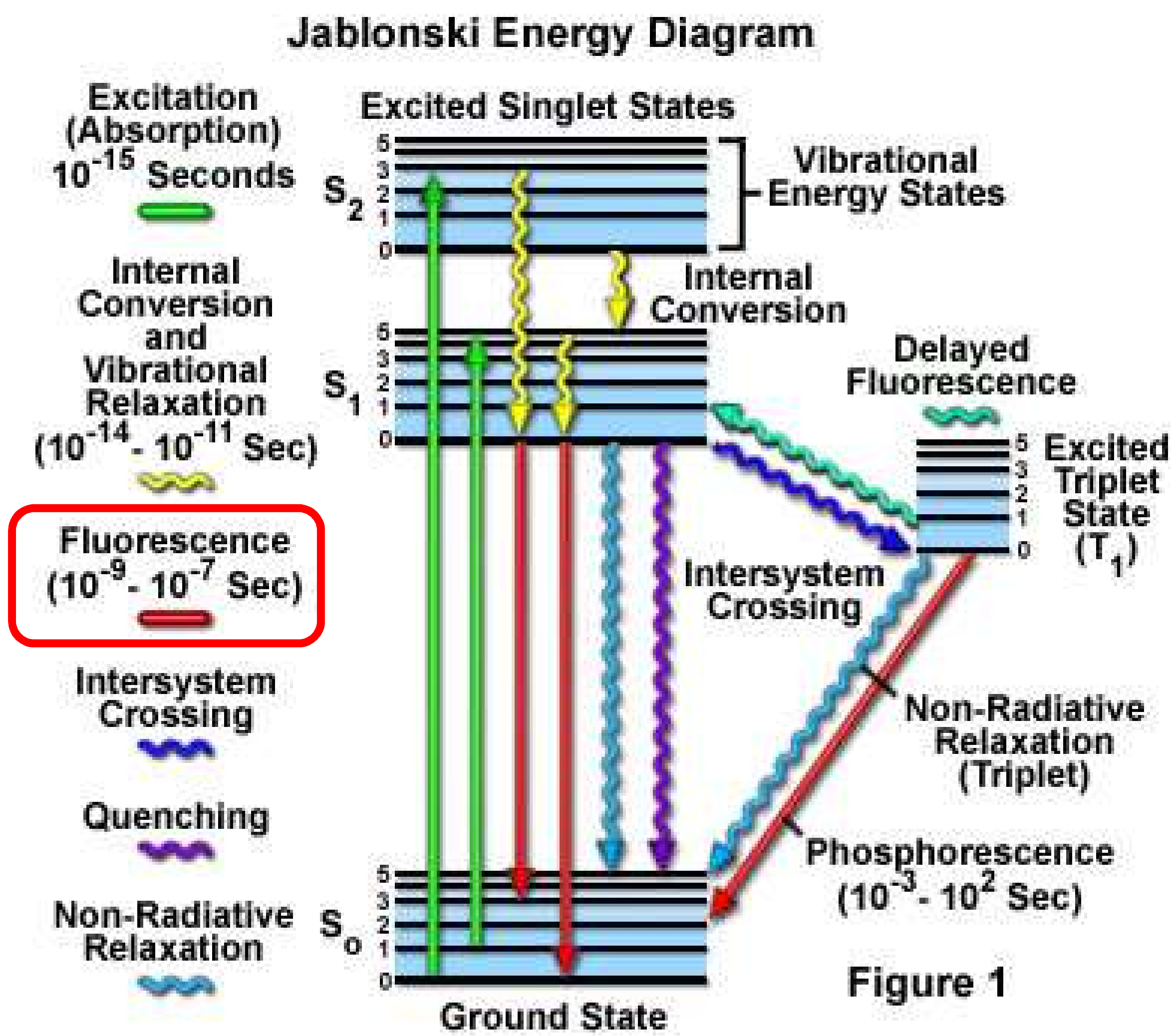
a Schematic representation of the quantum confinement effects: the bandgap (or HOMO–LUMO gap) of the semiconductor nanocrystal increases with decreasing size, **while discrete energy levels arise at the band-edges.** The energy separation between the band-edge levels also increases with decreasing size.
b Photograph of five colloidal dispersions of CdSe QDs with different sizes, under excitation with a UVlamp in the dark. The color of the photoluminescence changes from red to blue as the QD diameter is reduced from 6 to 2 nm

Clase ... **n la nano-escala.**



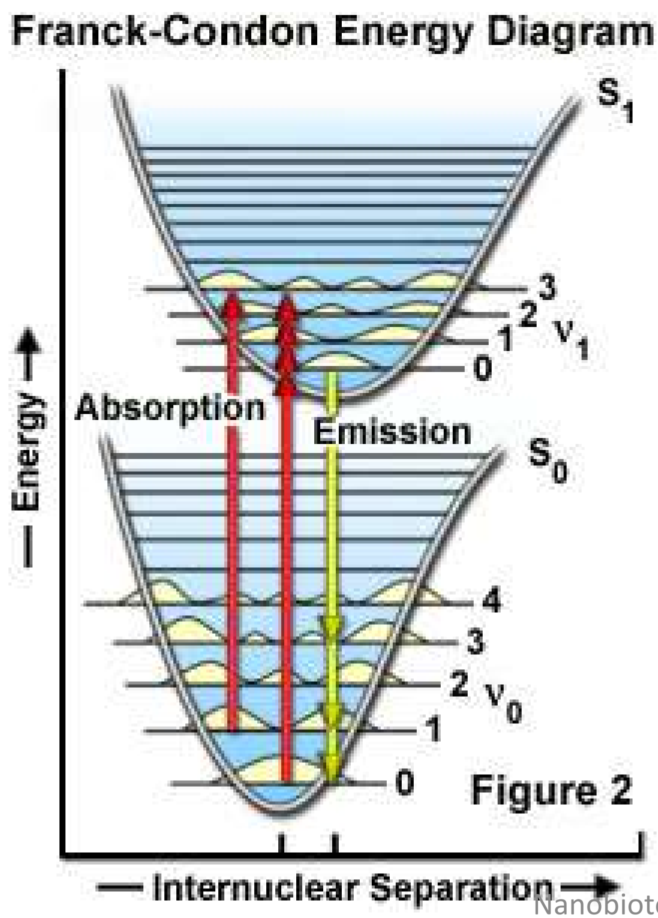
Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia**

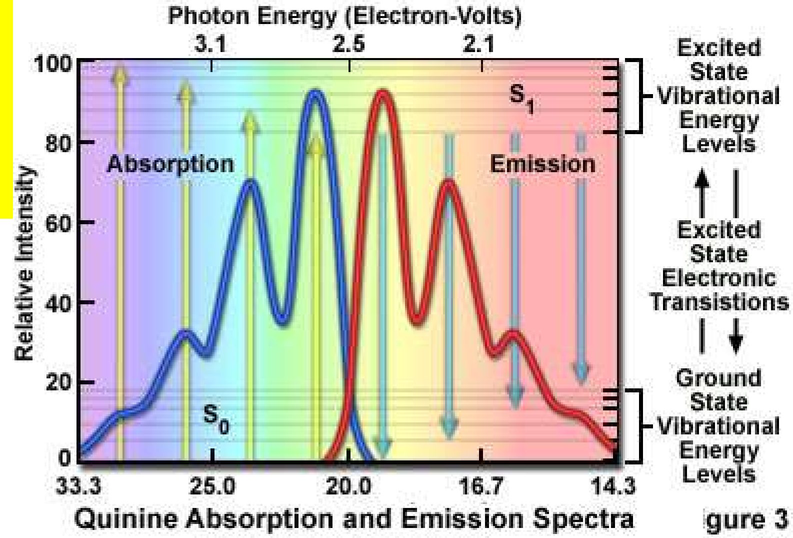
Fluorescence is a member of the ubiquitous **luminescence** family of processes in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical mechanism. Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed **photoluminescence**, which is formally divided into two categories, **fluorescence** and **phosphorescence**, depending upon the electronic configuration of the excited state and the emission pathway. **Fluorescence is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval, termed the fluorescence lifetime**. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime.

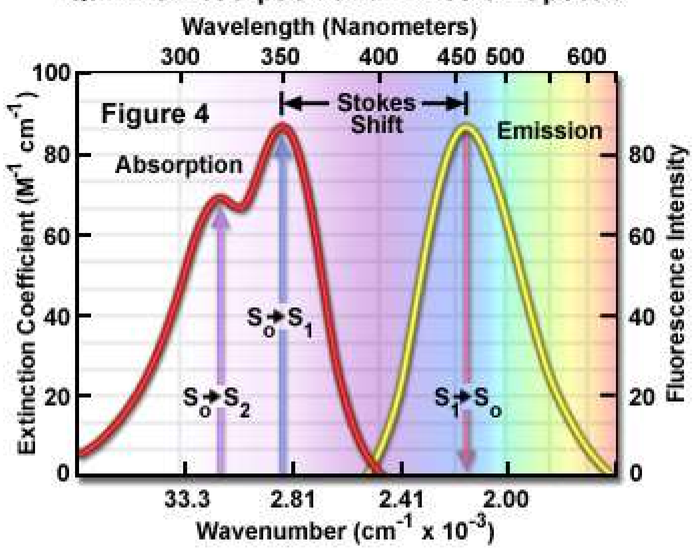


http://www.olympusmicro.com/primer/techniques/fluorescence/fluorescenceintro.html

Because the emitted photon usually carries less energy and therefore has a longer wavelength than the excitation photon, the emitted fluorescence can be distinguished from the excitation light. The excitation and photon emission from a fluorophore is cyclical, and until the fluorophore is irreversibly damaged (Photo bleaching), it can be repeatedly excited. Fluorophores can thus emit numerous photons through this cycle of excitation and emission and fluorescent molecules are therefore used for a broad range of research applications.

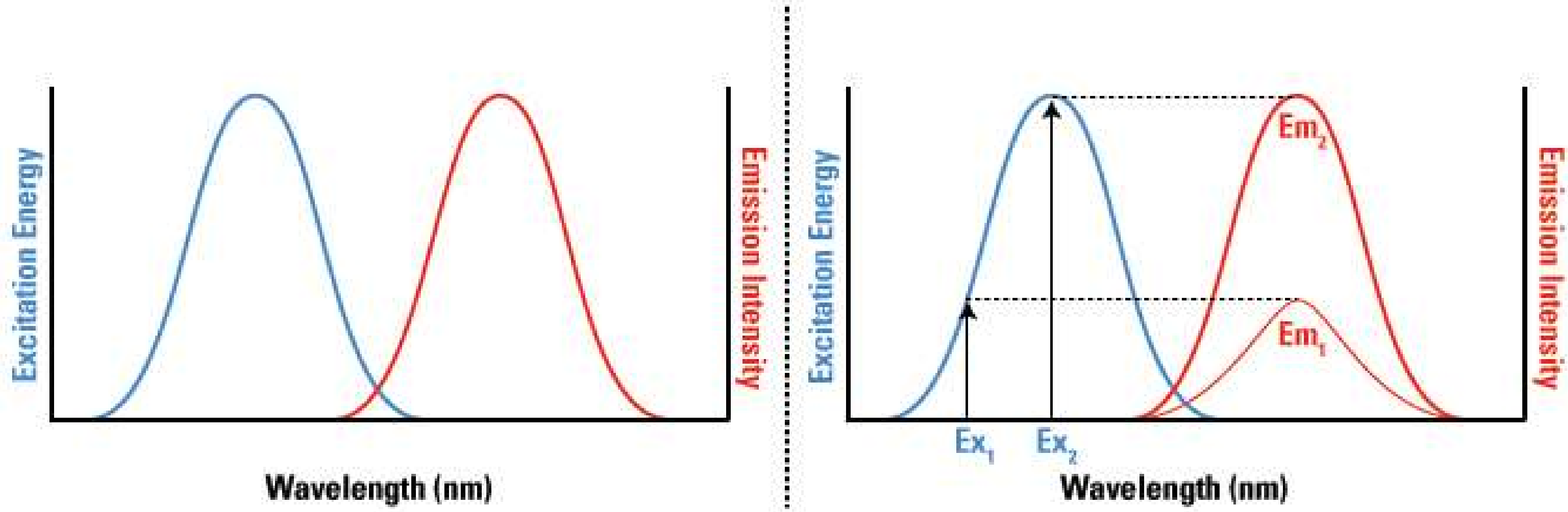






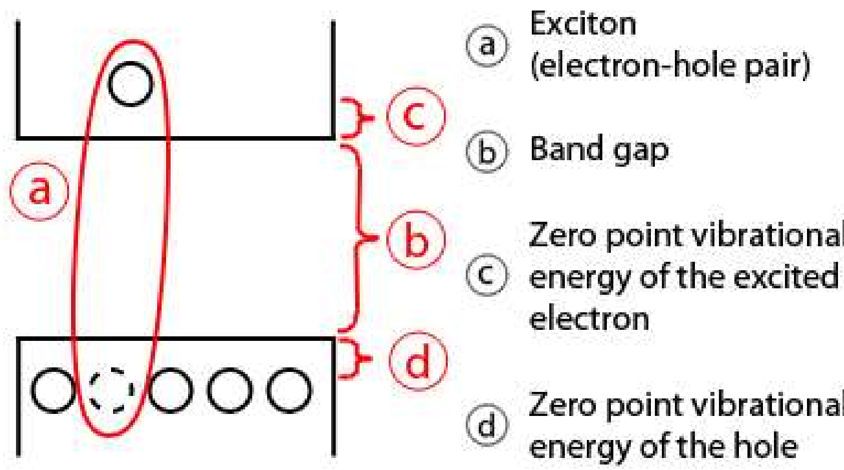
http://www.olympusmicro.com/primer/techniques/fluorescence/fluorescenceintro.html

Both the excitation and emission wavelengths are specific characteristics for each fluorophore, and while these wavelengths are discrete for monoatomic fluorophores, polyatomic fluorophores exhibit broad excitation and emission spectra. The spectra for fluorescent molecules (both mono- and polyatomic) are graphed on x,y plots that indicate the wavelengths that correspond to the maximum and minimum excitation and emission signal intensity for each fluorophore, as shown below (left panel). It is important to note that while the emission wavelength is independent of the excitation wavelength due to partial loss of energy prior to emission (as shown above), the emission intensity is proportional to the amplitude of the excitation wavelength, as indicated by the excitation energies (Ex1 and Ex2) and their corresponding emission intensities (Em1and Em2, respectively) in the graph below (right panel) (2).



https://www.thermofisher.com/ar/es/home/life-science/protein-biology/protein-biology-learning-center/protein-biology-resource-library/pierce-protein-methods/fluorescent-probes.html

Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia**



As the confinement energy depends on the quantum dots size, both absorption onset and fluorescence emission can be tuned by changing the size of the quantum dot during its synthesis. The larger the dot, the redder (lower energy) its absorption onset and fluorescence spectrum. Conversely , smaller dots absorb and emit bluer (higher energy) light. Furthermore, it was shown that the lifetime of fluorescence is determined by the size of the quantum dot. Larger dots have more closely spaced energy levels in which the electron-hole pair can be trapped. Therefore, electron-hole pairs in larger dots live longer causing larger dots to show a longer lifetime.

To improve fluorescence quantum yield, quantum dots can be made with “shells” of a larger bandgap semiconductor material around them. The improvement is suggested to be due to the reduced access of electron and hole to non-radiative surface recombination pathways in some cases, but also due to reduced auger recombination in others.

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala.** Quantum dots vs fluoroforos convencionales

Quantum dots (QDs), nanosized crystals made of **pure metals** and/or three-dimensional **semiconductor alloys**, ranging in size from **1 to 20 nm**. Depending on its size, a QD may consist of **hundreds or thousands of atoms**. **Most of these atoms lie on the surface** (i.e., have a high area-to-volume ratio).

Most QDs used in analytical applications are synthesized as core/shell structures, in which **the core of the nanocrystal is coated with another semiconductor material to protect and improve its properties**, among which we can mention:

(i) excellent optical performance with good photo stability, high-quantum yield (QY), and a long fluorescent lifetime,

(ii) excitation of multiple QDs by a single light source,

(iii) narrow, symmetric, and adjustable- size emission spectrum coupled to the absorption spectrum wave

(iv) wide spectral windows spanning from the ultraviolet region to the infrared region.

Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales**

Quantum confinement effects give rise to unique optical and electronic properties in QDs, giving them numerous advantages over current fluorophores, such as organic dyes, fluorescent proteins and lanthanide chelates

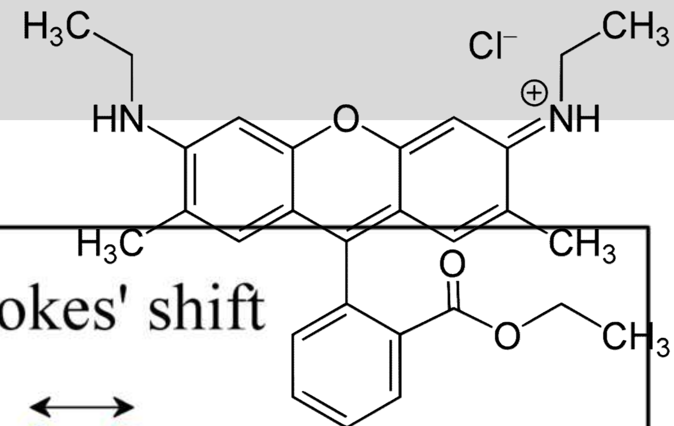
Properties that particularly influence fluorophore behaviour, and therefore applicability to different situations, include

1. **width of the excitation spectrum,**
2. **width of the emission spectrum,**
3. **photostability,**
4. **decay lifetime**

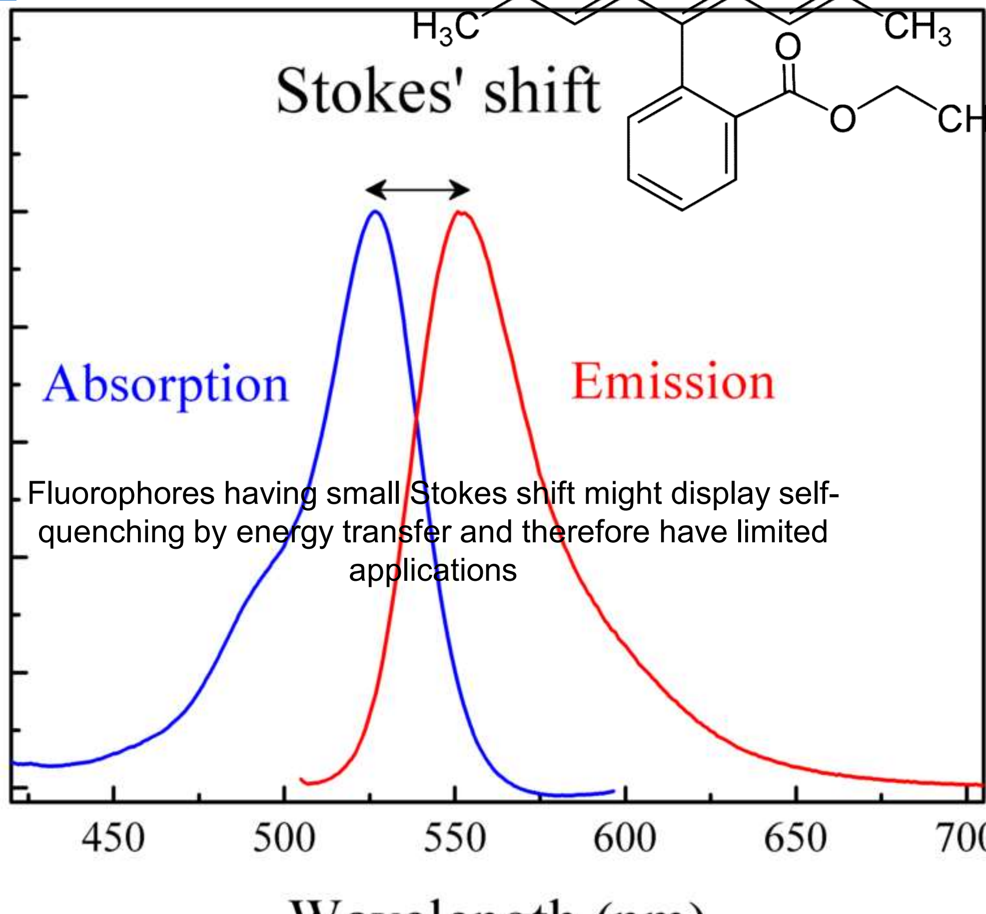
Biological applications of quantum dots Timothy Jamiesona , Raheleh Bakhshia , Daniela Petrovaa , Rachael Pococka , Mo Imanib , Alexander M. Seifalian Biomaterials 28 (2007) 4717–4732

Clase 2. Introducción a la Nanotecnología. Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales

Absorption and emission spectra
of Rhodamine 6G with ~25 nm Stokes shift



The distance between the excitation and emission wavelengths is called the Stokes Shift (see below) and is a key aspect in the detection of the emitted fluorescence in biological applications. Stokes shift is also a distinct characteristic of each fluorophore. For example, the detection of emitted fluorescence can be difficult to distinguish from the excitation light when using fluorophores with very small Stokes shifts (right panel), because the excitation and emission wavelengths greatly overlap. Conversely, fluorophores with large Stokes shifts (left panel) are easy to distinguish because of the large separation between the excitation and emission wavelengths. Stokes shift is especially critical in multiplex fluorescence applications, because the emission wavelength of one fluor may overlap, and therefore excite, another fluor in the same sample.



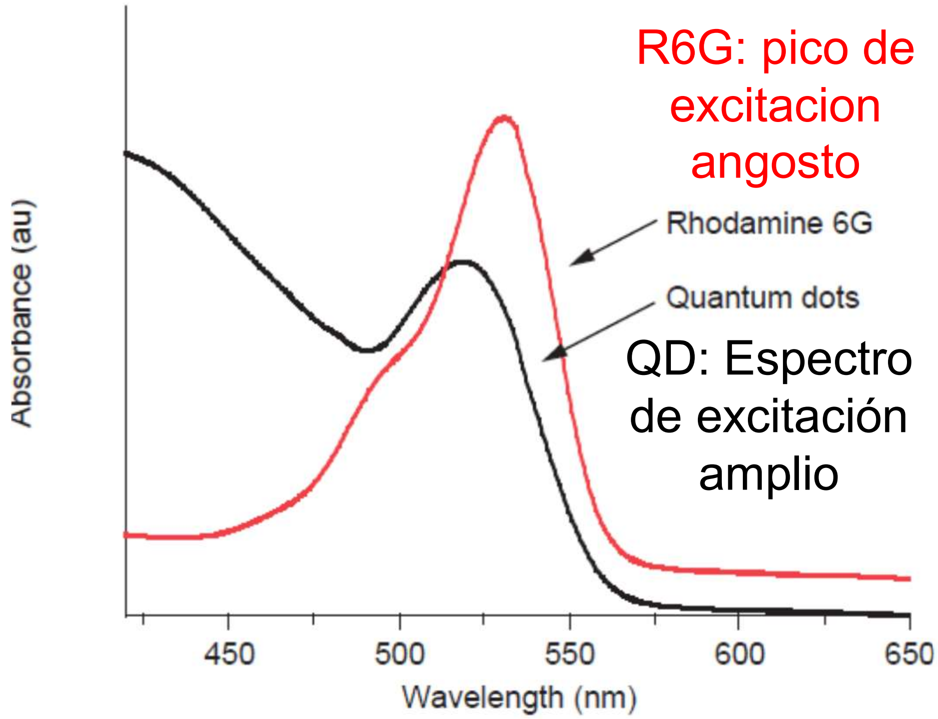
Fluorophores having small Stokes shift might display self-quenching by energy transfer and therefore have limited applications

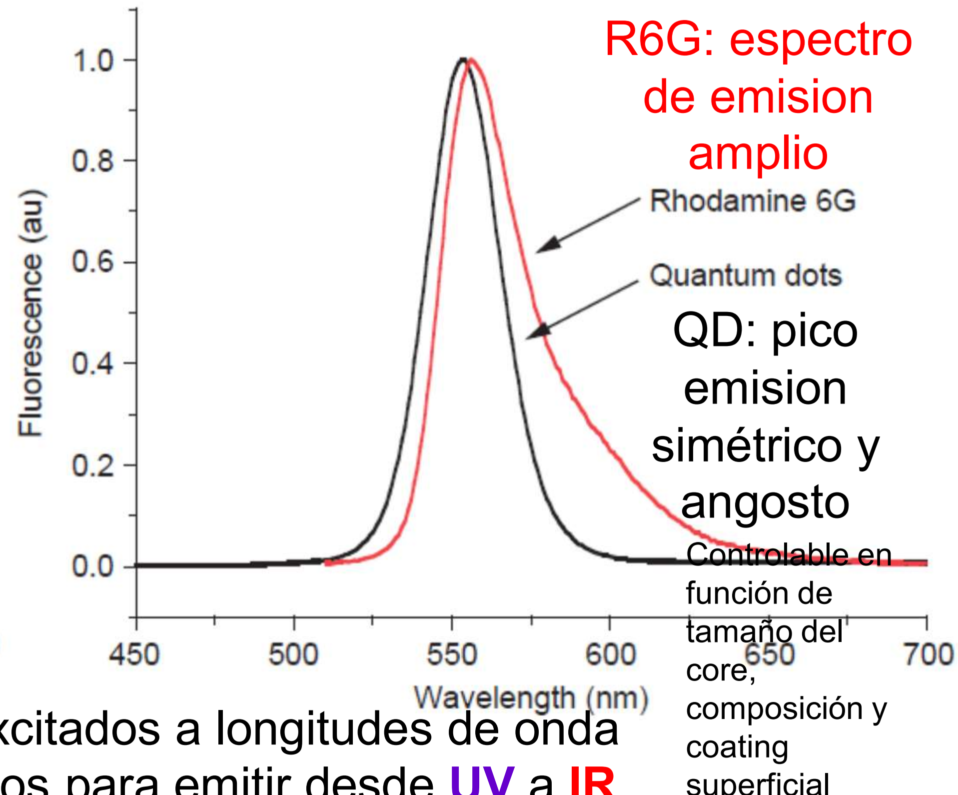
A key property for in vivo imaging is the unusual QD Stokes shift, which can be as large as 300–400 nm, depending on the wavelength of the excitation light

Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales**

Excitation (a) and emission (b) profiles of rhodamine 6G and CdSe QDs.. By contrast, the organic dye rhodamine 6G has a narrow excitation profile and broad emission spectrum.

a





QDs pueden ser eficientemente excitados a longitudes de onda menores a 530 nm, e ingenierizados para emitir desde **UV** a **IR**

Biological applications of quantum dots Timothy Jamiesona , Raheleh Bakhshia , Daniela Petrovaa , Rachael Pococka , Mo Imanib , Alexander M. Seifalian Biomaterials 28 (2007) 4717–4732

Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales**

Fluorophore brightness

The brightness of a given fluorophore is determined by the molar extinction coefficient [absorbance of light by fluorophores follows the Lambert-Beer-Bouguer law] and quantum yield, both of which are specific for each fluor. The **molar extinction coefficient (ε)** is defined as the quantity of light that can be absorbed by a fluor at a given wavelength and is measured in M^{-1} cm^{-1}. The **quantum yield (Φ)** [fluorescence quantum efficiency (*Φf*)] is calculated as the number of photons that are emitted by the fluor divided by the number of photons that are absorbed. This calculation provides the efficiency of a fluorophore and has a maximum of 1.

$$\phi_f = \frac{N_{em}(\lambda_{ex})}{N_{abs}(\lambda_{ex})}.$$

The brightness of a fluorophore is then calculated as the product of ε and Φ.

QDs have molar extinction coefficients that are 10–50 times **larger** than that of organic dyes, which make them much brighter in photon-limited *in vivo* conditions. The long lifetime in the order of 10–40 ns increases the probability of absorption at shorter wavelengths, and produces a broad absorption spectrum.

Clase 2. Introducción a la Nanotecnología. Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales

Photostability

Unlike organic fluorophores which bleach after only a few minutes on exposure to light, QDs are extremely stable and can undergo repeated cycles of excitation and fluorescence for hours with a high level of brightness and photobleaching threshold. QDs have been shown to be more photostable than a number of organic dyes, including Alexa488, reported to be the most stable organic dye. Dihydrolipoic acid (DHLA)-capped cadmium selenide-zinc sulfide (CdSe-ZnS) QDs showed no loss in intensity after 14 h, and were nearly 100 times as stable as, and also 20 times as bright as, rhodamine 6G.

This may be exploited in situations where long-term monitoring of labelled substances is required, and is an area in which QDs may find particular use

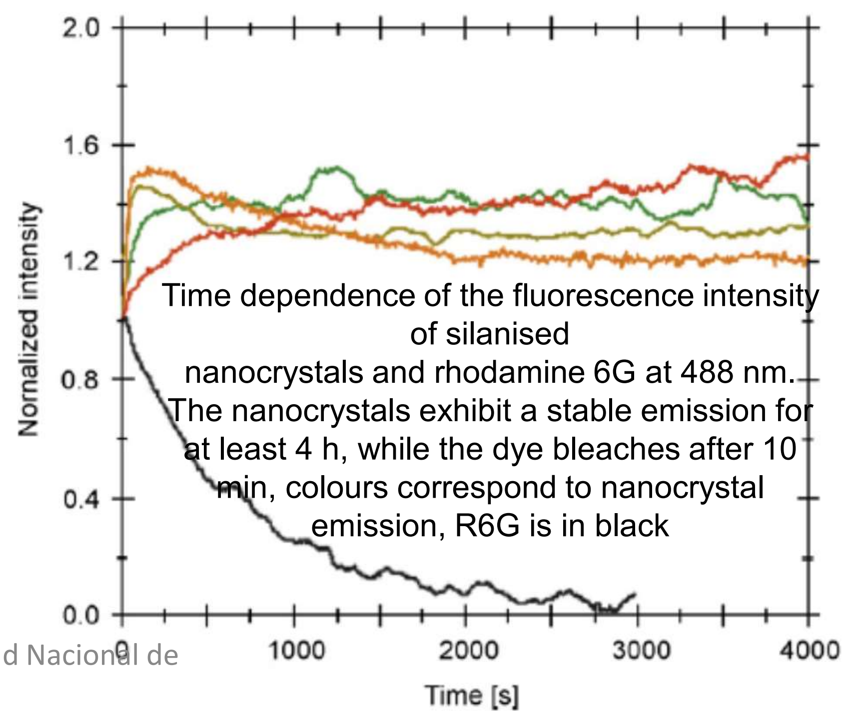
Biological applications of quantum dots Timothy Jamiesona , Raheleh Bakhshia , Daniela Petrovaa , Rachael Pococka , Mo Imanib , Alexander M. Seifalian Biomaterials 28 (2007) 4717–4732

Clase 2. Introducción a la Nanotecnología. **Fundamentos fluorescencia Q DOTS vs fluoroforos convencionales**

QDs also have a long fluorescent lifetime after excitation, which may be taken advantage of in time-gated imaging. The fast fluorescence emission of organic dyes upon excitation (< 5 ns) coincides closely with short-lived autofluorescence background from many naturally occurring species, reducing the signal-to-noise ratio. sensitivity.

Conversely, QDs emit light with a decay time in the order of a few tens of nanoseconds (30–100 ns) at room temperature, which is slower than the autofluorescence background decay, but fast enough to maintain a high photon turnover rate .

In time-gated analysis, photons hitting in the first few nanoseconds are disregarded to decrease background noise and increase



Time dependence of the fluorescence intensity of silanised nanocrystals and rhodamine 6G at 488 nm. The nanocrystals exhibit a stable emission for at least 4 h, while the dye bleaches after 10 min, colours correspond to nanocrystal emission, R6G is in black

Clase 2. Tipos de QD: **Quantum dots Ag_2S**

Quantum silver points present great biomedical potential, due mainly to their photoluminescence in the near infrared region (NIR) [47–53]. The NIR facilitates certain biomedical applications, such as in vitro imaging (and the formation of deep tissue images), and can therefore be used in diagnostics and photodynamic therapy [53].

However, the family of QDs with the greatest future for biomedical applications (particularly in NIR) is silver chalcogenide QDs (Ag_2X, with X = S, Se, Te) which have low toxicity compared to conventional QDs such as CdSe, CdS, and CdTeS [54]. Additionally, silver chalcogenide QDs present high solubility, which allows them to obtain minimal Ag ions in desired applications [54]. **Silver chalcogenides QDs** present a narrow band gap, which for Ag_2S is of the order of 0.9–1.1 eV, for Ag_2Se is 0.15 eV, and for Ag_2Te is 0.67 eV [55–57].

The biomedical application of **silver chalcogenide QDs, Ag_2X**, is dependent upon the type of dopant used. For example, in the case of Ag_2S and Ag_2Se, their most important properties depend directly upon their band gaps, which present emissions in the infrared region of the near-spectrum (NRI I and NRI II) [53]. The compound Ag2Te mainly functions as a biological marker (fluorophores), but it is rarely used due to the high toxicity of tellurium.

Quantum dots for biomedical applications. Nanobiomaterials. https://doi.org/10.1016/B978-0-08-100716-7.00016-7

Clase 2. Tipos de QD: **Quantum dots Ag_2S**

silver chalcogenide Ag2X (X = S, Se, Te) QDs. present two very interesting applications. First is the potential to obtain high-resolution cellular images, and second is the capacity for *in vivo* observation of the cell passage to a specific tumor.

Clase 2. Tipos de QD: **Quantum dots Au**

Gold nanoparticles (GNPs) are inert, nontoxic, biocompatible, and exhibit controlled dispersity, high surface area to volume ratio, ease of functionalization, they are ideal for biomedical nanotechnologies. Useful for imaging and diagnoses, delivery of therapeutic agents, sensitizing cells and tissues to treatment regimens, monitoring and guidance of surgical procedures, and administration of electromagnetic radiation [89–99]. **Gold quantum dots (GQDs) have the same properties as GNPs, but unlike other QDs, they do not fluoresce.** Instead they have colorimetric properties induced by surface plasmon resonance (SPR) depending on particle size, shape, solvent and ligand, dielectric properties, surface functionalization, surrounding medium, and agglomeration which make them useful in biological systems detection applications, such as hybridization assays, DNA sequencing, genetic disorders, immunoblotting, flow cytometry, etc. [100–105]. Also, they do not undergo any photodecomposition, are apparently nontoxic and reasonably stable, they

Quantum dots semiconductores

Semiconductor QDs, also known as semiconductor nanocrystals, are generally formed of II–VI semiconductors (composed from elements of groups II and VI) or III–V semiconductors (elements from groups III and V). These inorganic, small size nanocrystals ranging from 1 to 10 nm exhibit size-dependent optical and electronic properties caused by electronic quantum confinement [127], which takes place when the semiconductor nanocrystal dimensions are of the order of the exciton Bohr radius [128]. QDs have attracted considerable attention in the last two decades due to these extraordinary quantum properties. For example, as compared to common organic fluorescent dyes and proteins, QDs have many unique photophysical properties such as high fluorescent QY, strong signal intensity, stable luminescence, excellent photostability, and narrow and symmetrical emission peaks [129], which have gained attention in many research fields.

Choice of shell and coating are gaining particular importance, as the shell stabilises the nanocrystal and to some extent alters the photophysical properties, whilst the coating confers properties to the QD which allow its incorporation into a desired application.

Capping core nanocrystals with ZnS has been shown to increase stability and performance, producing QDs with improved luminescence, higher photochemical stability and higher quantum yields at room temperature . However, ZnS capping alone is not sufficient to stabilize the core, particularly in biological solutions, but a serendipitous byproduct of modification to render QDs biologically compatible, particularly with polyethylene glycol (PEG), is an increase in stability and a reduction in non-specific adsorption.

Bare core nanocrystals have proven impractical for two reasons.
Firstly, the crystalline structure of the nanoparticle lends itself to imperfections, which results in emission irregularities, particularly blinking, in which single QDs switch between fluorescent and non-fluorescent states despite continuous illumination. Secondly, the cores are highly reactive due to their large surface area:volume ratio, resulting in a very unstable structure which is particularly prone to photochemical degradation.

Clase 2. Introducción a la Nanotecnología. **Propiedades de la materia en la nano-escala. Capping de Quantum dots**

organic capping prevents uncontrolled growth and agglomeration of the nanoparticles

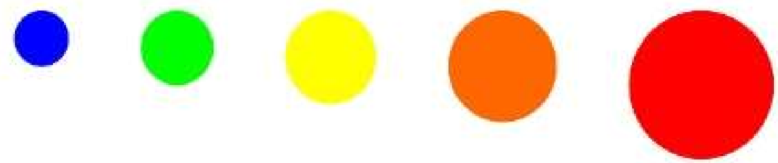
Although significant progress has been made in simplifying synthesis pathways, improving QYs, controlling the size and shape of nanostructures, and elucidating the mechanisms of QD
formation, chemical synthesis usually requires very high reaction conditions, aggressive agents, and toxic organic solvents to produce fluorescent products.

Biosynthetic methods, on the other hand, not only perform under mild conditions, but also exhibit greater biocompatibility and biostability because their formation (by the addition of biomolecules to their structure) occurs without resorting to additional stages of functionalization and encapsulation, thus offering a green synthesis pathway for preparing biocompatible QDs

In recent years, a large number of nanomaterials have been synthesized through biological systems [40,41] These synthesis methods have three characteristics: (i) direct generation of the reduced and functionalized metal from its origin (with amino acids, proteins and chelating peptides, etc.), (ii) modulation of synthesis precursors through genetic engineering, for expression of specific biomolecules regulating growth, size distribution, and fluorescence emission of QDs, and (iii) mild reaction conditions without the use of high temperatures, inert atmospheres, or toxic solvents.

stops the reaction. As a result, NQDs of a particular size form. (b) The colloidal NQDs obtained by the method illustrated in (a) consist of an inorganic CdSe core capped with a layer of TOPO/TOP molecules. (c) Solutions of CdSe NQDs of different radii, under ultraviolet illumination, emit different colors because of the quantum size effect. A 2.4-nm-radius dot has an energy gap of about 2 eV and emits in the orange, whereas a dot of radius 0.9 nm has a gap of about 2.7 eV and emits a blue color.

Quantum Confinement



Size Dependence of Optical Properties

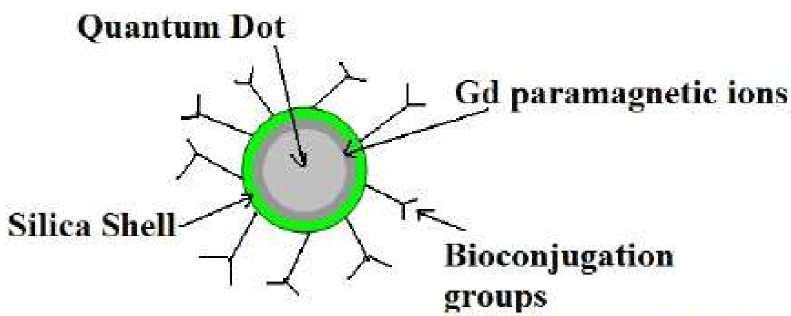
In general, confinement produces a blue shift of the band-gap. Location of discrete energy levels depends on the size and nature of confinement.

Increase of Oscillator Strengths

This implies increase of optical transition probability. This happens anytime the energy levels are squeezed into a narrow range, resulting in an increase of energy density. The oscillator strengths increase as the confinement increases from Bulk to Quantum Well to Quantum Wire to Quantum Dot.

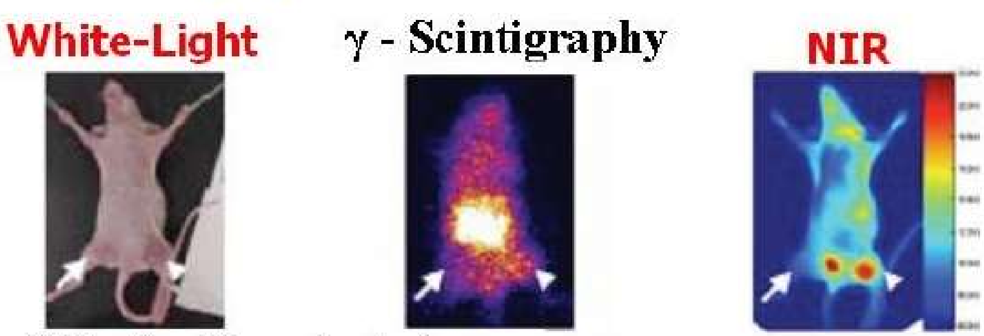
Nanophotonic Bioimaging

Nanoparticles are also used for bioimaging by non-optical techniques like Magnetic Resonance Imaging (MRI), Radioactive Nanoparticles as tracers to detect drug pathways or imaging by Positron Emission Tomography (PET), and Ultrasonic Imaging. For MRI, the magnetic nanoparticles could be made of



oxide particles which are coated with some biocompatible polymer.
Newer Nanoparticle Heterostructures have been investigated which offer the possibility of imaging by several techniques simultaneously. An example is Magnetic Quantum Dot.

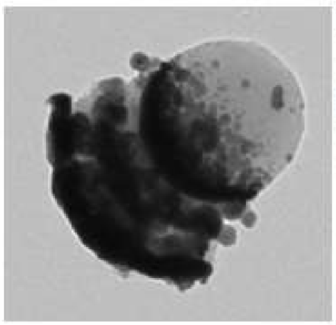
Imaging with Dual-Labeled Probes



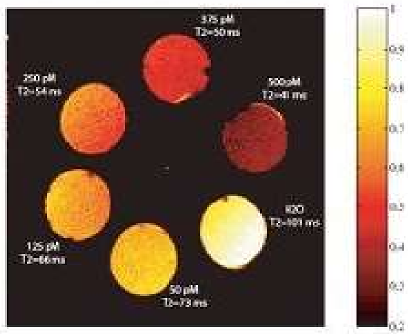
Multifunctional Nanoprobes-Louie: EAD289-Topics in Biophotonics, UC Davis

Nanophotonic Bioimaging

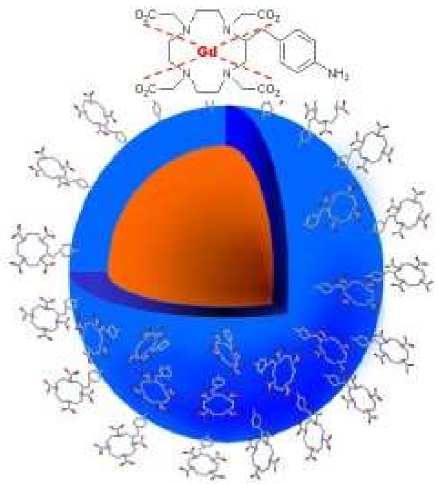
Dual-Functional Nanoprobes for Dual-Modality Animal Imaging



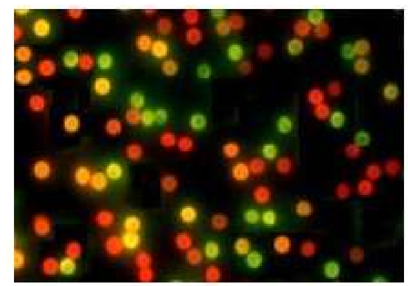
Photoacoustic

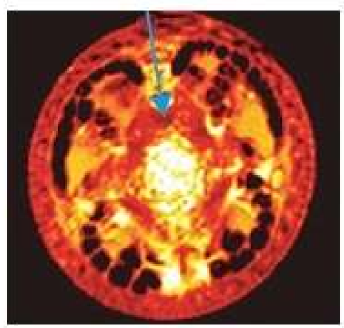


T2 MRI

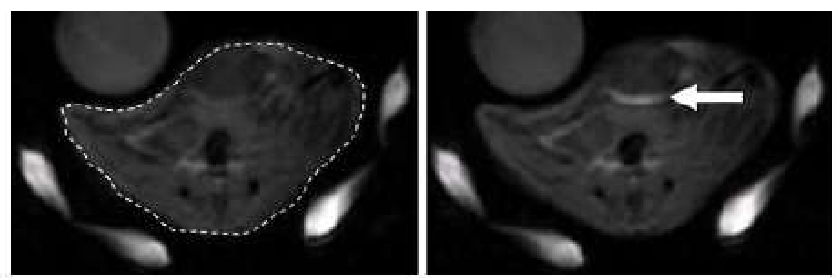


Fluorescence



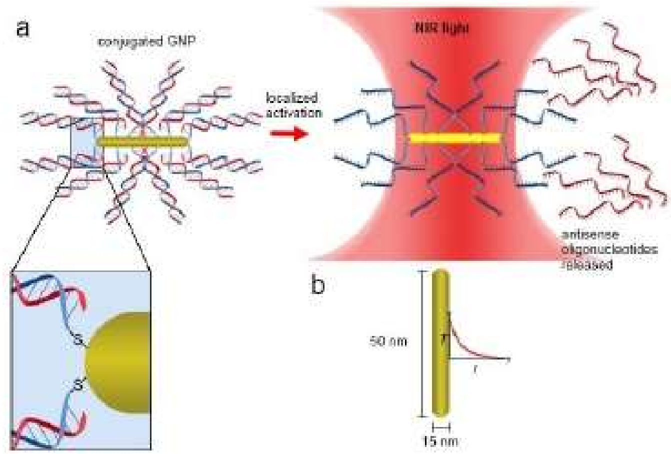


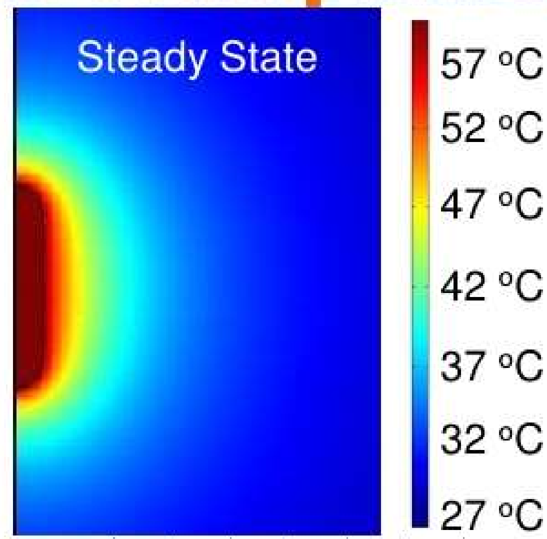
T1 MRI

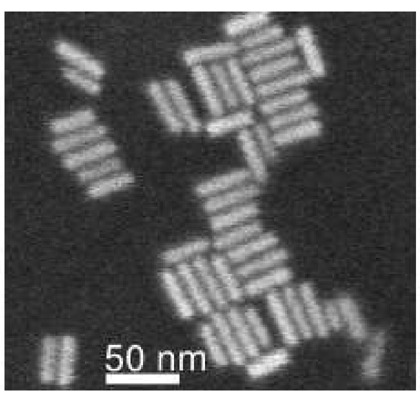


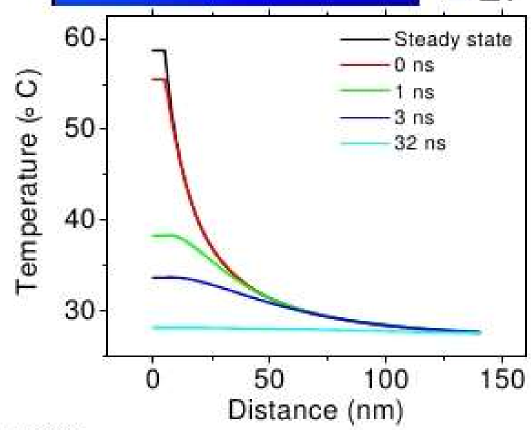
Bouchard and Liu et al, PNAS 2009

Nanophotonic Molecular Manipulation



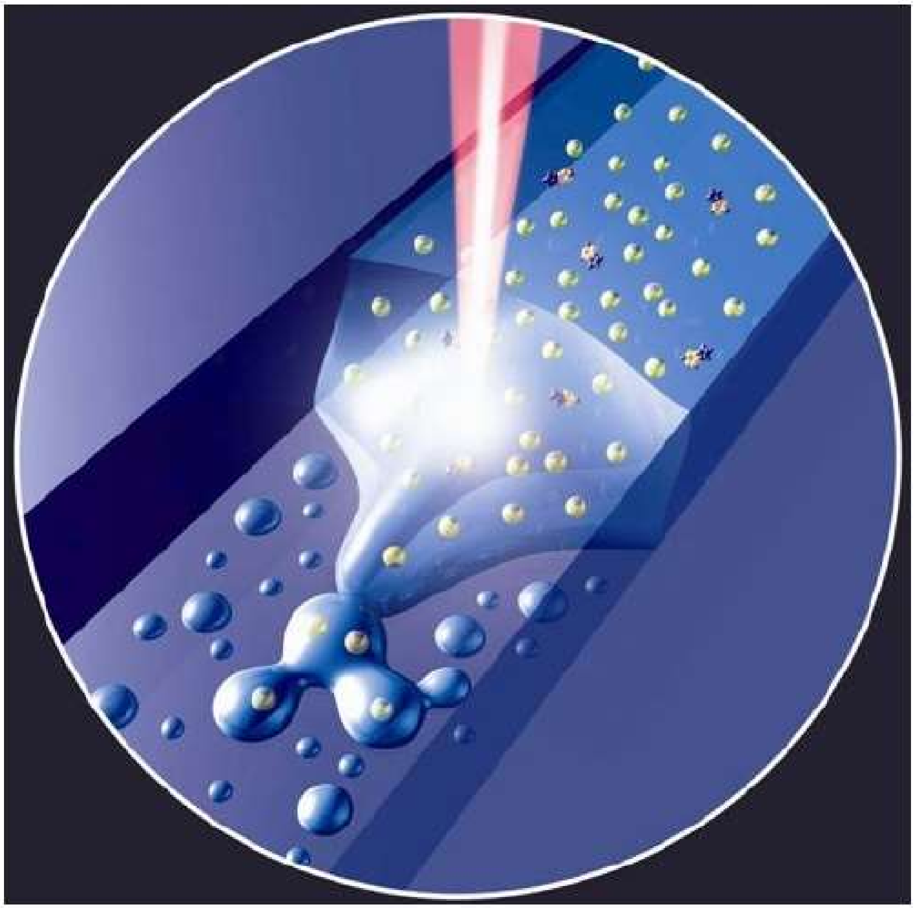


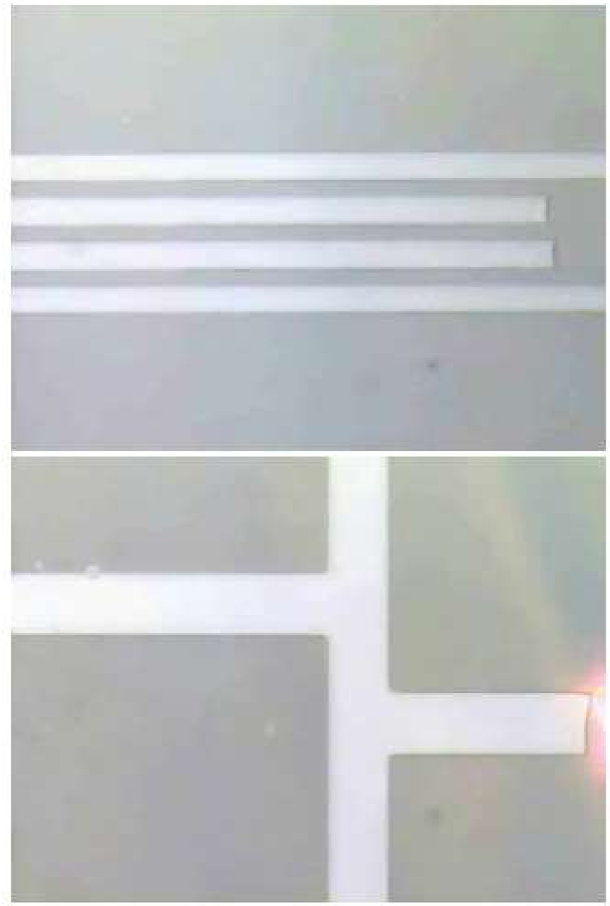




Lee et al, Nano Letter (2009)

Nanophotonic Fluidic Manipulation





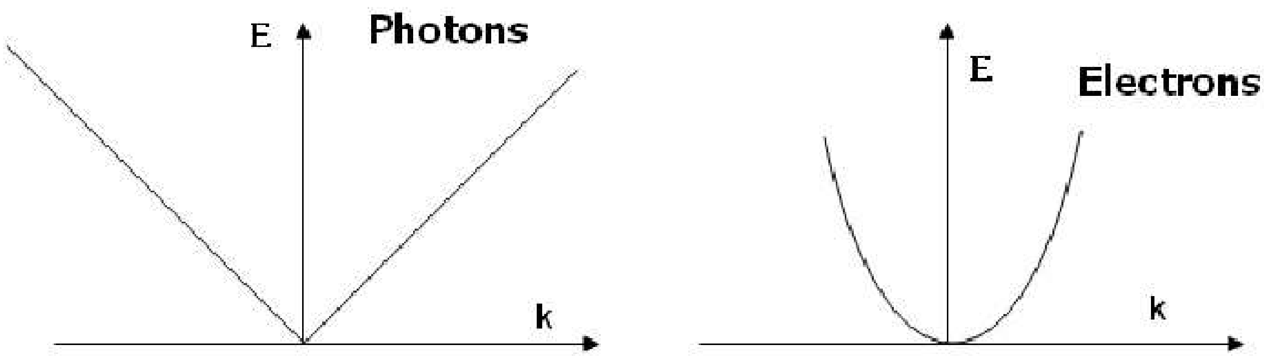
Liu *et al*, ***Nature Materials*** (2006)

Confinamiento cuántico de la luz y de electrones

Foundation of Nanophotonics

- Free space propagation of both electrons and photons can be described by Plane Waves.
- Momentum for both electrons and photons, $\mathbf{p} = (h/2\pi)\mathbf{k}$
- For Photons, $k = (2\pi/\lambda)$ while for Electrons, $k = (2\pi/h)mv$
- For Photons, Energy $E = pc = (h/2\pi)kc$ while for Electrons,

$$E = p^2/2m = (h/2\pi)^2 k^2/2m$$



Free Space Dispersion for Photons and Electrons