Introduction to Nanotechnology and Nanoscience – Class#23

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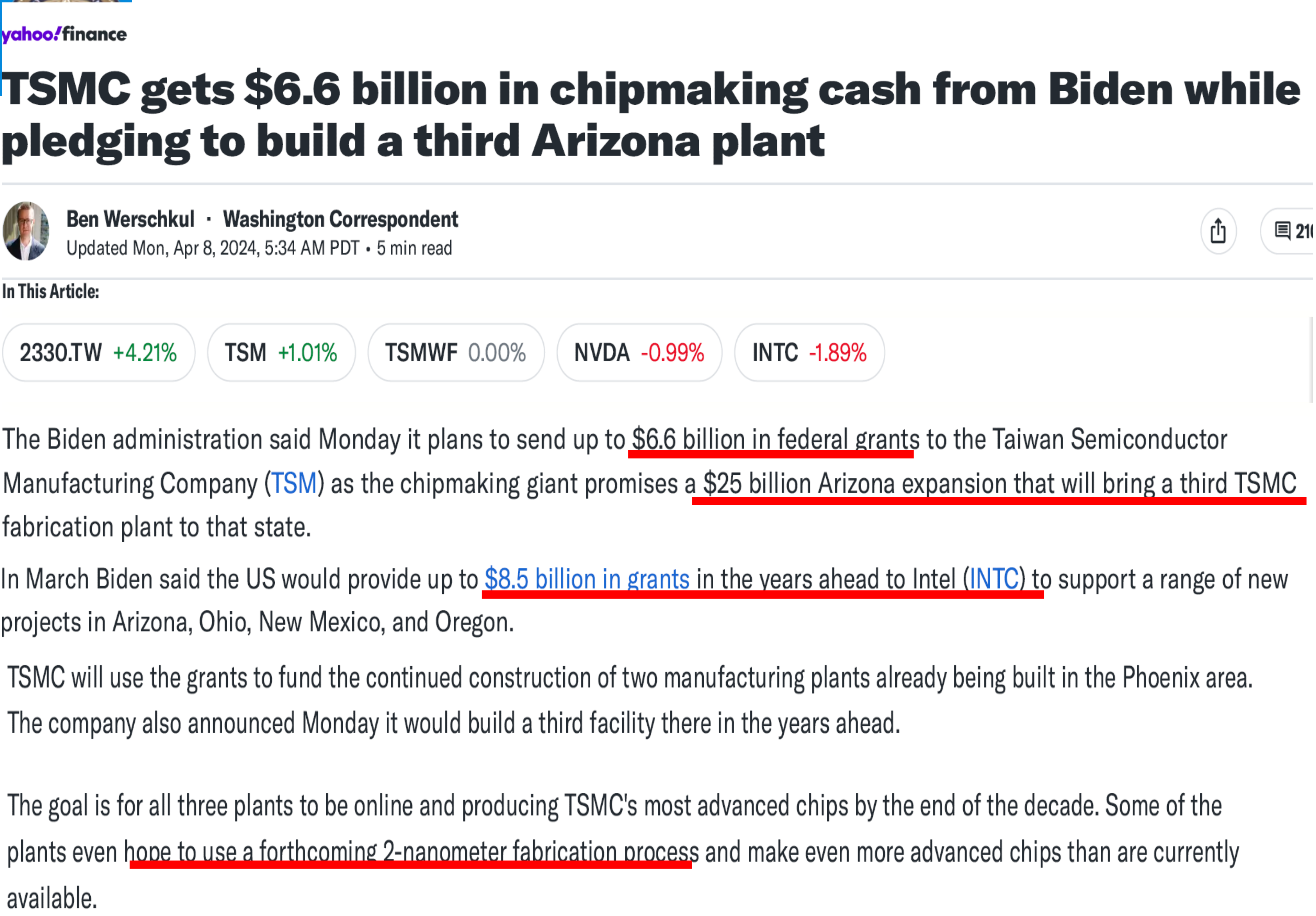
Outline

- ☐ Several Small Project Presentation
- ☐ QDs & Video
- ☐ Paper 10
- ☐ Paper 10-1
- ☐ QD Application Example



yahoo!finance

TSMC gets $6.6 billion in chipmaking cash from Biden while pledging to build a third Arizona plant

Ben Werschkul · **Washington Correspondent**
Updated Mon, Apr 8, 2024, 5:34 AM PDT • 5 min read

In This Article:

2330.TW	+4.21%
TSM	+1.01%
TSMWF	0.00%
NVDA	-0.99%
INTC	-1.89%

The Biden administration said Monday it plans to send up to $6.6 billion in federal grants to the Taiwan Semiconductor Manufacturing Company (TSM) as the chipmaking giant promises a $25 billion Arizona expansion that will bring a third TSMC fabrication plant to that state.

In March Biden said the US would provide up to $8.5 billion in grants in the years ahead to Intel (INTC) to support a range of new projects in Arizona, Ohio, New Mexico, and Oregon.

TSMC will use the grants to fund the continued construction of two manufacturing plants already being built in the Phoenix area. The company also announced Monday it would build a third facility there in the years ahead.

The goal is for all three plants to be online and producing TSMC's most advanced chips by the end of the decade. Some of the plants even hope to use a forthcoming 2-nanometer fabrication process and make even more advanced chips than are currently available.

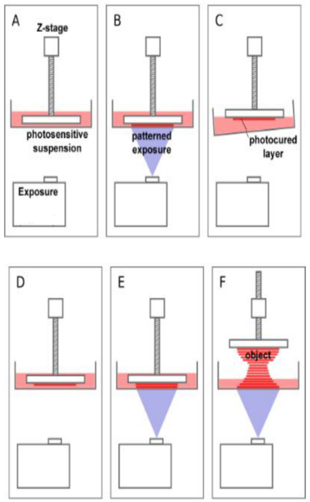
Simulating CNT Alignment in Curing Resin

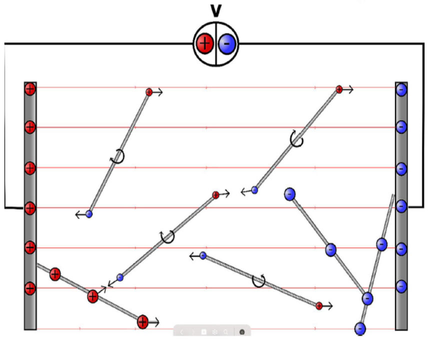
Based on the theoretical process for enhanced SLA 3D printing with CNTs in resin:

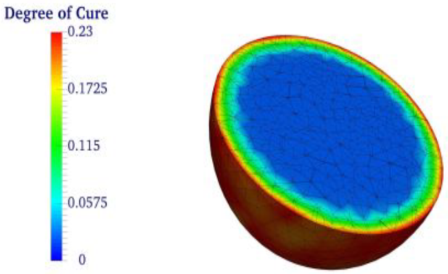
- Given a part structure, define the CNT alignment for each layer
- Apply an electric field between bottom of the resin reservoir and build plate to align CNTs within next layer
- Run through steps A-F of the SLA print process, aligning CNTs each layer

We are looking to simulate the process of CNT alignment within curing resin.

Prior research has been done on cnt alignment within curing resin: On the effect of electric field application during the curing process on the electrical conductivity of single-walled carbon nanotubes–epoxy composites where researchers were able to align CNTs within epoxy and cure the epoxy. Additionally, the resin curing process can be simulated following Numerical Simulation of HTPB Resin Curing Process Using OpenFOAM and Study the Effect of Different Conditions on its Curing Time. Where researchers were able to create a model for the resin curing process.





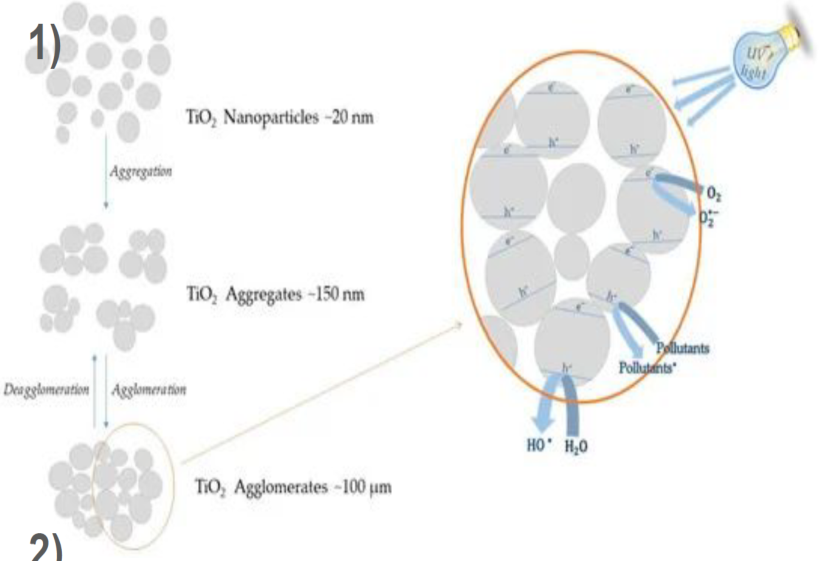


Integrating photocatolinic nanoparticles into CNTs/LDH Composite for increased water purification efficiency

Ali Orouji

- Existing research: filter membrane of CNT/LDH composite leads to improved performance and retention
  - More mass transfer channels (36% increase over LDH)
- Incorporating photocatalytic nanoparticles, like TiO2, into the CNT/LDH composite
  - allow membrane to not only filter out pollutants but also degrade organic contaminants when exposed to UVs
  - Utilize TiO2 nanoparticles to eliminate organic pollutants and microorganisms
- Integrate TiO2 layers into vacuum assembly method
  - Can be prepared in thinner layers
  - Explore into TiO2 post processing
- Long term stability testing and fouling resistance would asses long term operational viability

1)



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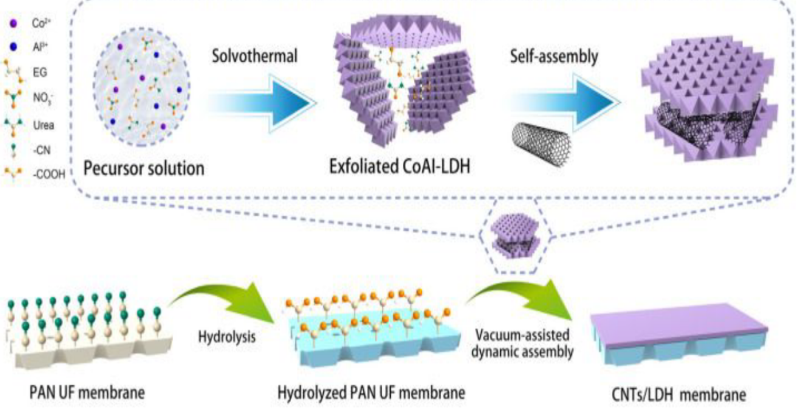


Figure 1. Illustration of TiO2 leading to increased photocatalytic activity through energy transfer

Figure 2, Process flow diagram of creating CNT/LDH composite membrane

1. Li, Q., Song, P., Yang, Y., Li, Y., Wang, N., & An, Q. (2022). CNTs Intercalated LDH Composite Membrane for Water Purification with High Permeance. *Nanomaterials, 12*(1), 59.
2. Armaković, S. J., Savanović, M. M., & Armaković, S. (2023). Titanium Dioxide as the Most Used Photocatalyst for Water Purification: An Overview. *Catalysts, 13*(1), 26
3. Wang, N., Li, Q., (2020). Vacuum-assisted assembly of iron cage intercalated layered double hydroxide composite membrane for water purification. Journal of Membrane Science

Thermoelectric Application of silicon nanowires – combines with thermal insulation pad

3039643206 Johnson Chang

- Motivation:

Combines with my patent: thermal insulation pad (Fig1), which using Bi_2Te_3 as the thermoelectric material. Now change to use silicon wires as thermoelectric source.

- Function:

The thermal insulation pad would equip with 6 thermoelectric modules, this time I will using silicon nanowire modules. And to research about the effectiveness and related economic benefit.

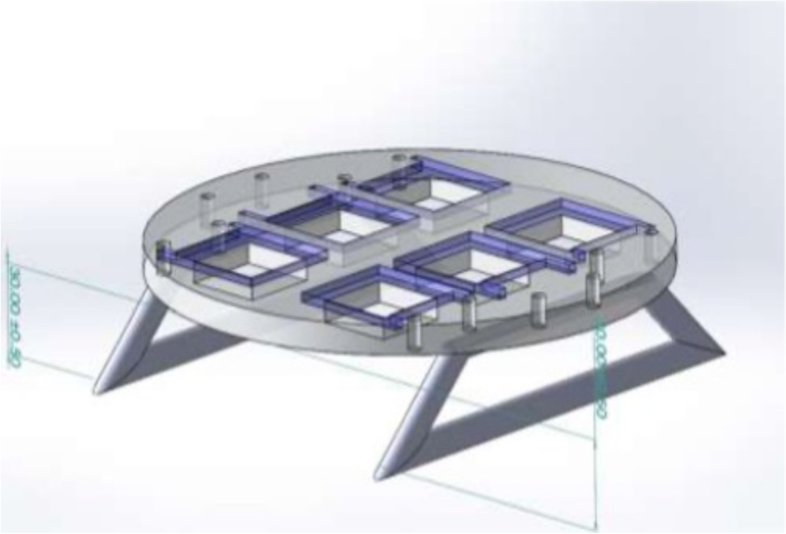
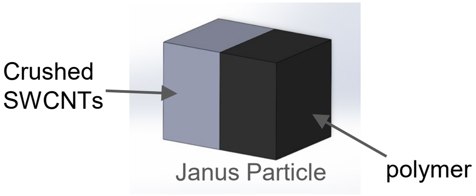
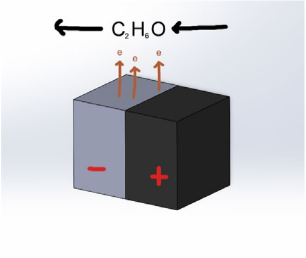
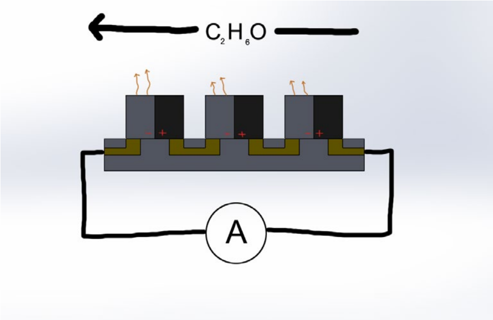


Fig1. Thermal Insulation Pad

SWCNT-Based Breathalyzer







SWCNTs are crushed into a powder and pressed into a sheet. A polymer layer is applied on one surface only and the composite sheet is then cut into smaller pieces, aka “Janus Particles”

In this configuration, SWCNTs are electron donors and can generate an electric potential when exposed to molecules with specific LUMOs levels (Lowest Unoccupied Molecular Orbits) that are also small enough to dissolve into the SWCNT structures - Ethanol fits these requirements!

The polymer layer acts as a diffusion region between the SWCNTs and the ethanol

Janus particles can be connected in series to strengthen the output signal measured by an ammeter to detect the presence of ethanol in the breath

References:
Liu, A.T., Kunai, Y., Cottrill, A.L. *et al.* Solvent-induced electrochemistry at an electrically asymmetric carbon Janus particle. *Nat Commun* 12, 3415 (2021). https://doi.org/10.1038/s41467-021-23038-7

Carbon Nanotubes for 3D Printing Filaments

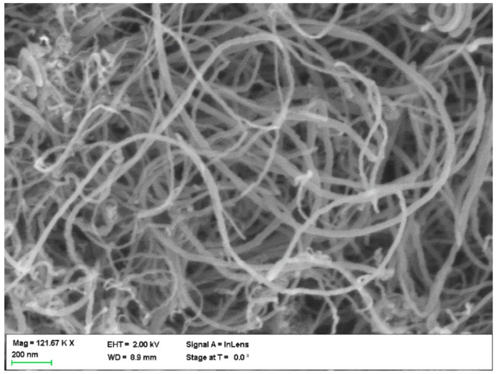
Jason Wang, Rushil Ganguli

Benefits of Using CNT in 3D printing

- improvement in the tensile strength by 12.6%
- varying electrical resistivity depending on the supplied voltage
- possible applications for structural electronics, intelligent structures, and embedded sensors

Future Investigation

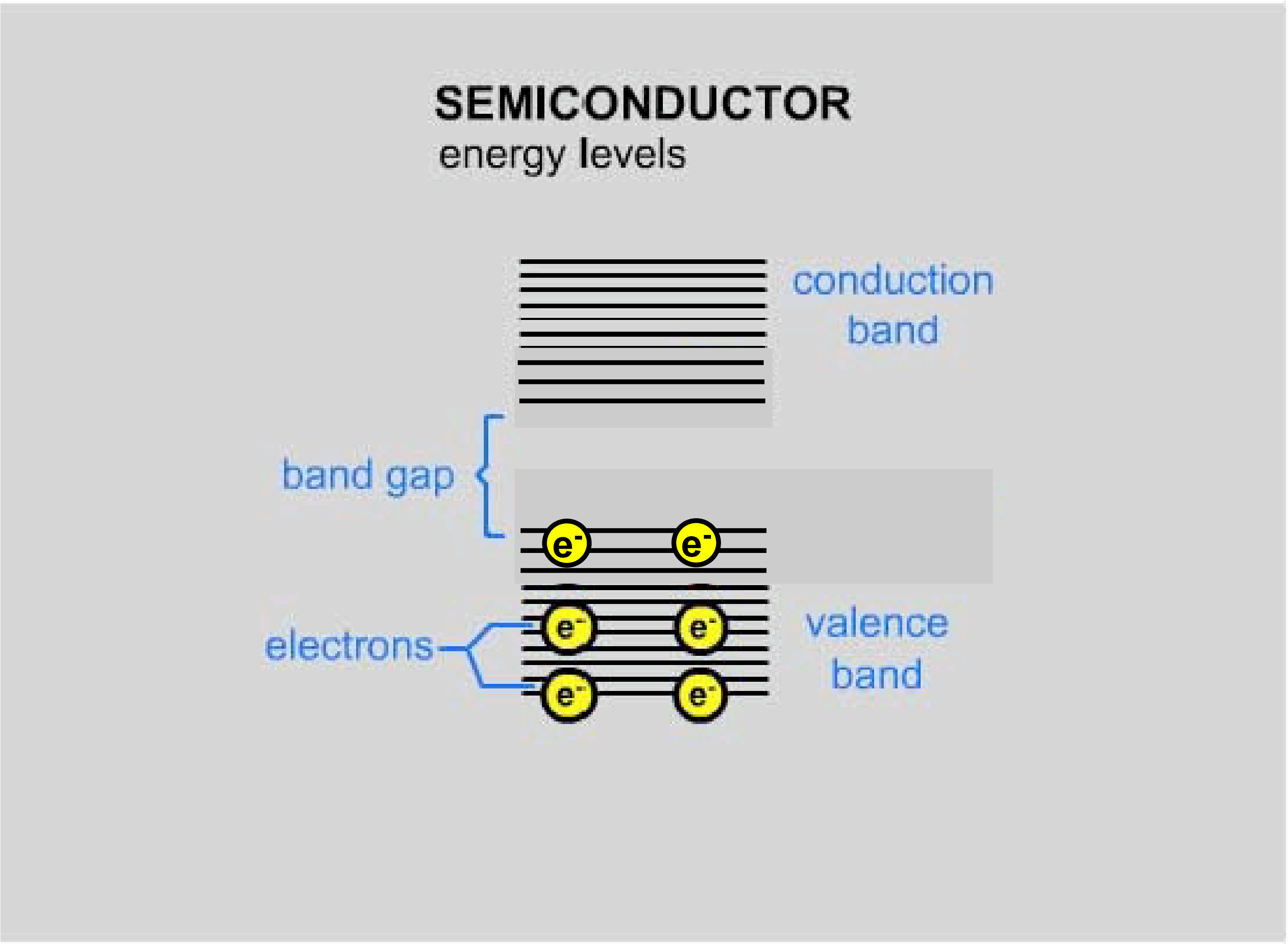
- amount of CNT needed to add to ABS for optimal mechanical and electrical properties
- printing parameters for optimal print qualities (extrusion/print speed, head temperature, porosity)



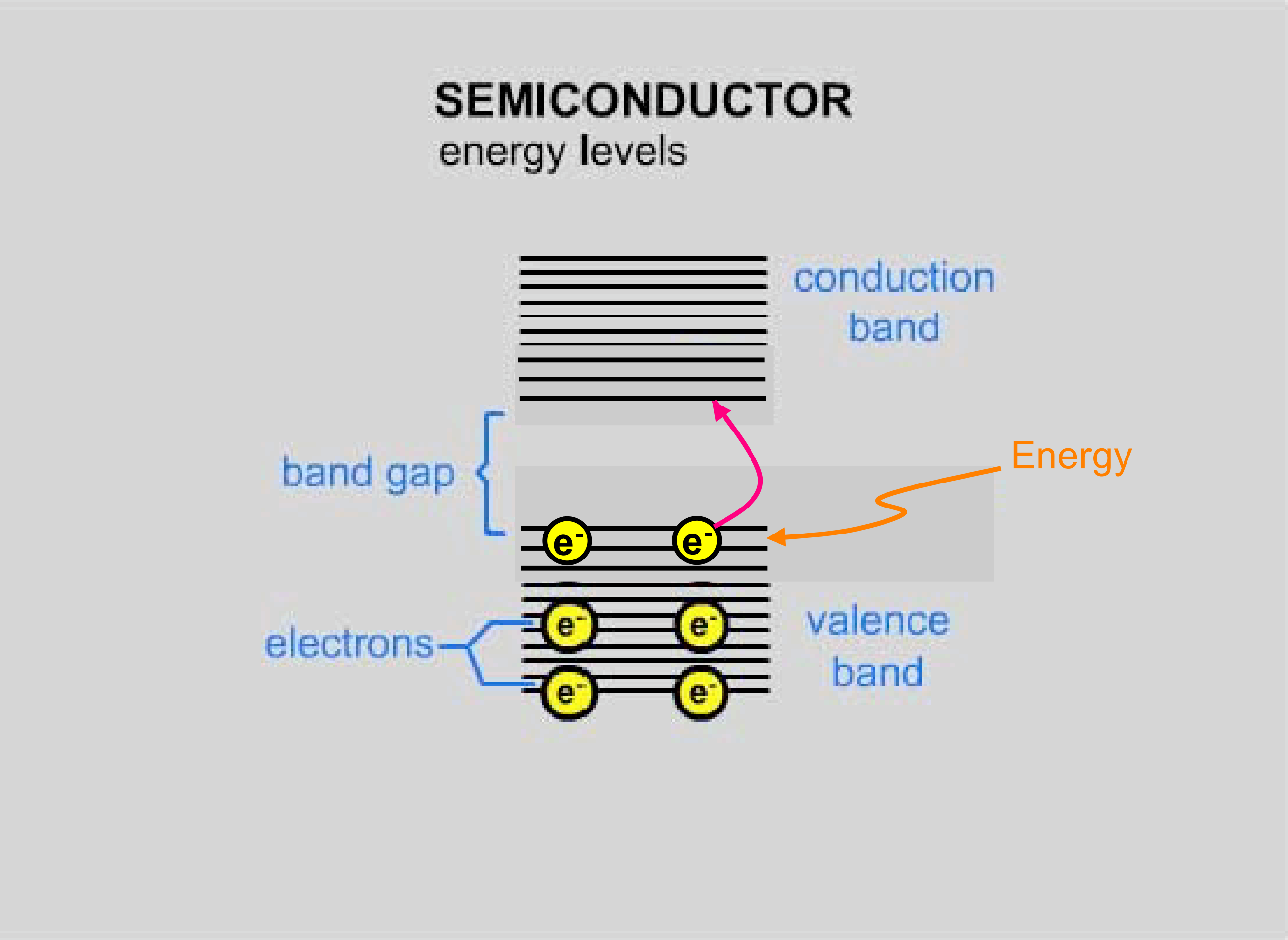
Carbon Nanotube-Based Composite Filaments for 3D Printing of Structural and Conductive Elements, Podsiadły, et al.

Podsiadły, B.; Matuszewski, P.; Skalski, A.; Słoma, M. Carbon Nanotube-Based Composite Filaments for 3D Printing of Structural and Conductive Elements. Appl. Sci. 2021, 11, 1272. https:// doi.org/10.3390/app11031272

QD -> Semiconductors

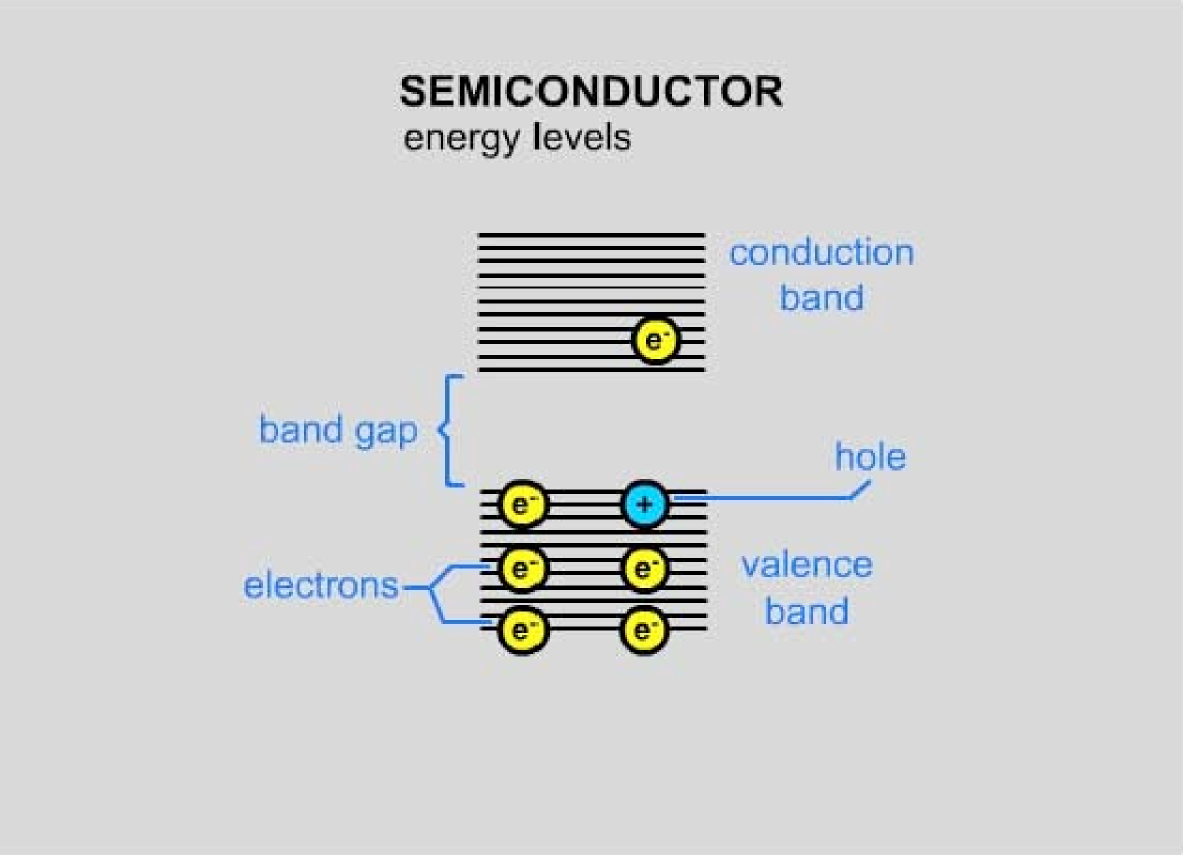


Absorb Energy Higher Than Band Gap

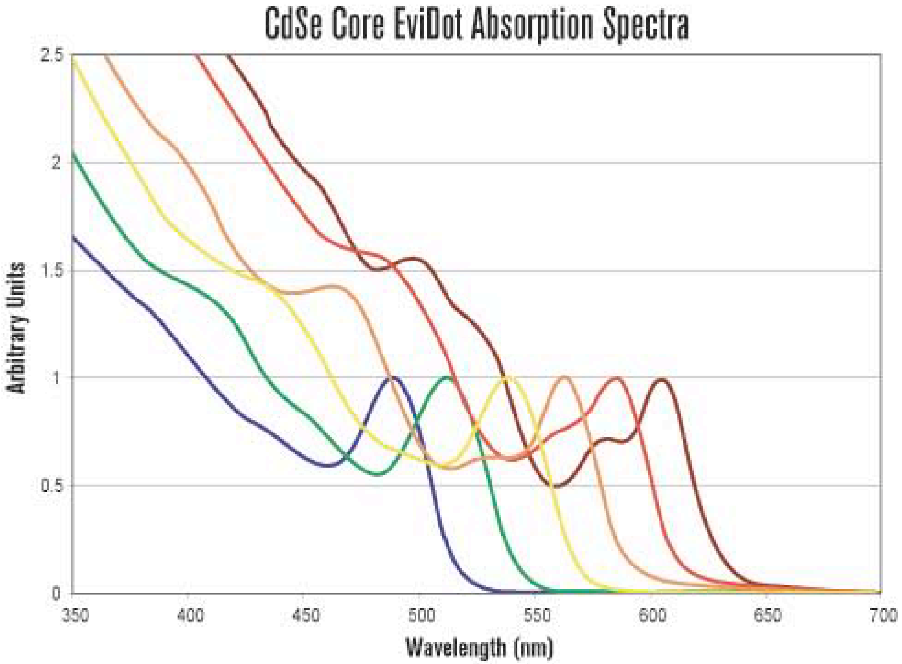


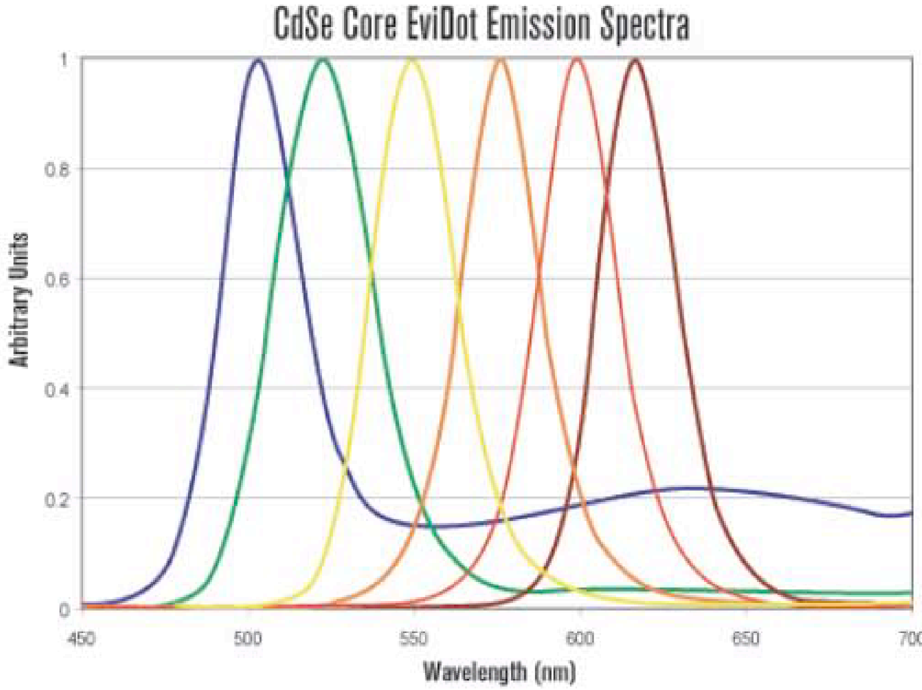
Electron in Conduction Band

Electron in conduction band come down to the edge
→ Jump down to the valence band
→ Release fixed energy of the band gap in the from of light



Absorption & Emission Spectra of CdSe Qdots





Broad absorption

Narrow Emission

http://www.evidenttech.com/products/evidots/quantum-dot-emission-absorption.php

Paper 10 - Semiconductor Nanocrystals as Fluorescent Biological Labels

Marcel Bruchez Jr., Mario Moronne, Peter Gin, Shimon Weiss,* A. Paul Alivisatos*

Presented by - Lakshya Saraf and Shira Shabtian

Cytometry is the measurement of number and characteristics of cells.
Cytogenetics involves testing of tissue, blood or bone samples.
Karyotyping is the process of pairing and ordering all the chromosomes of an organism

Objective – Use of semiconductor nanocrystals as fluorescent probes in biological staining and diagnostics.

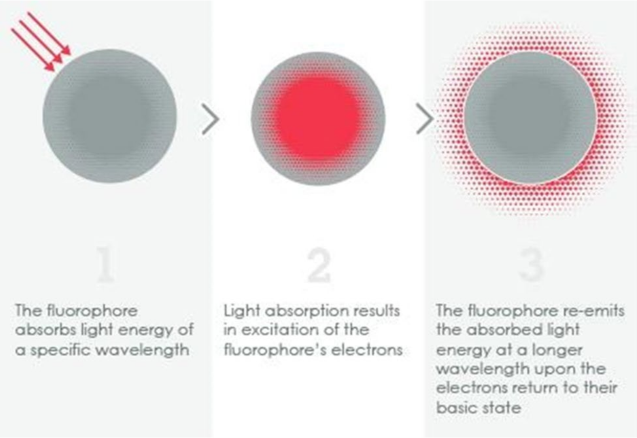
Limitations- Conventional dye molecules impose stringent requirements on the optical systems due to narrow excitation spectrum and broad emission spectrum. There is also photobleaching.

Benefits – Nanocrystals are better than conventional fluorophores as they have a narrow, tunable, symmetric emission spectrum and are photochemically stable.

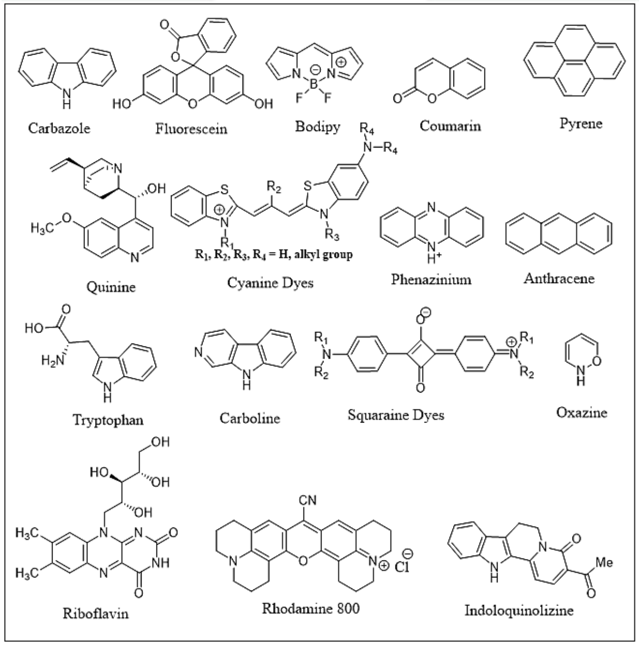
Ideal Probe - Should **emit at spectrally resolvable energies** and have a **narrow, symmetric emission spectrum,** and the whole group of probes should be **excitable at a single wavelength.**

How are fluorescent probes used?

8 color, 3 laser system used to measure **10 parameters** on cellular antigens and cytogenetics and they used combinatorial labelling to generate 24 falsely colored probes for spectral karyotyping (very inefficient).

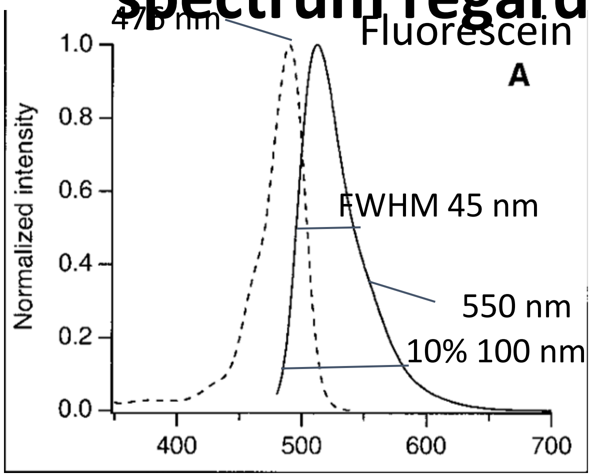


1. The fluorophore absorbs light energy of a specific wavelength
2. Light absorption results in excitation of the fluorophore's electrons
3. The fluorophore re-emits the absorbed light energy at a longer wavelength upon the electrons return to their basic state



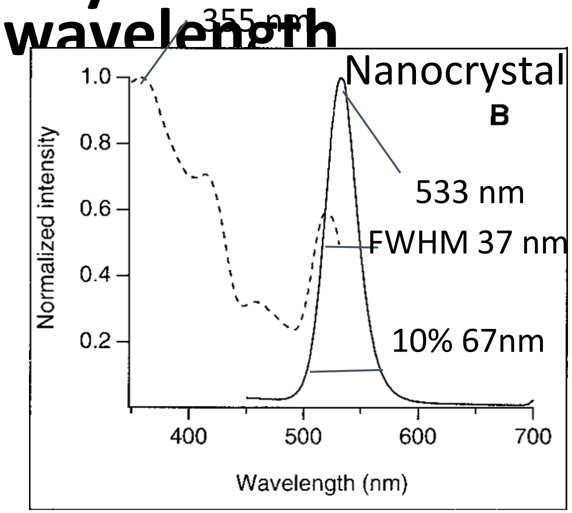
How are semiconductor based nanocrystals made tunable?

- In semiconductor nanocrystals, the **absorbance onset and emission maximum shift to higher energy with decreasing size.**
- **Excitation tracks absorbance**, resulting in a tunable fluorophore that can be **excited efficiently at any wavelength shorter than the emission peak**.
- It however, **still emits the same narrow symmetric spectrum regardless of the excitation wavelength**



The nanocrystals have a much narrower emission, no red tail, and a broad, continuous excitation spectrum.

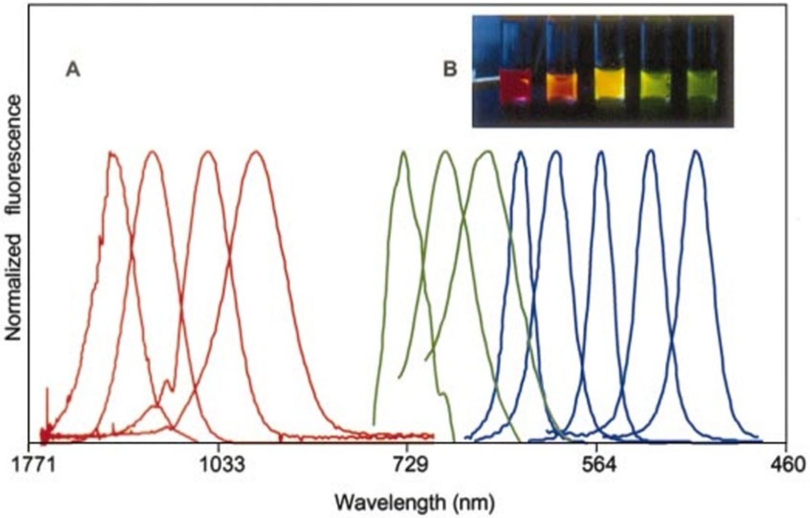
Excitation spectra (dashed)
Fluorescence spectra (solid)



How can we control spectral range?

Variation of the material used for the nanocrystal and variation of the size of the nanocrystal afford a spectral range of 400 nm to 2 m in the peak emission

Typical emission widths of 20 to 30 nm [full width at half maximum (FWHM)]in the visible region of the spectrum and large extinction coefficients in the visible and ultraviolet range (10^5 M^-1 cm^-1)

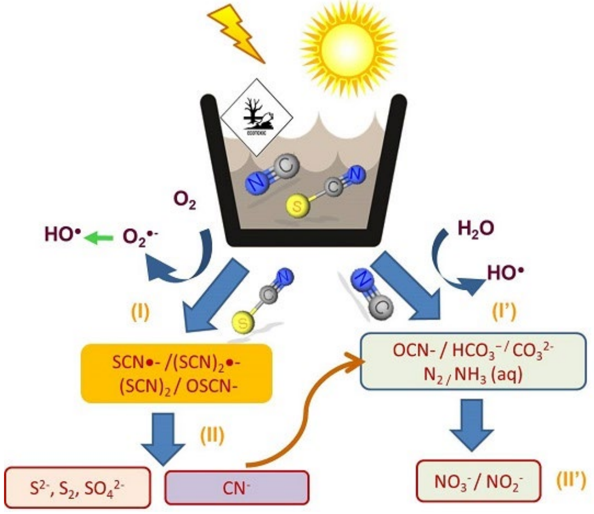


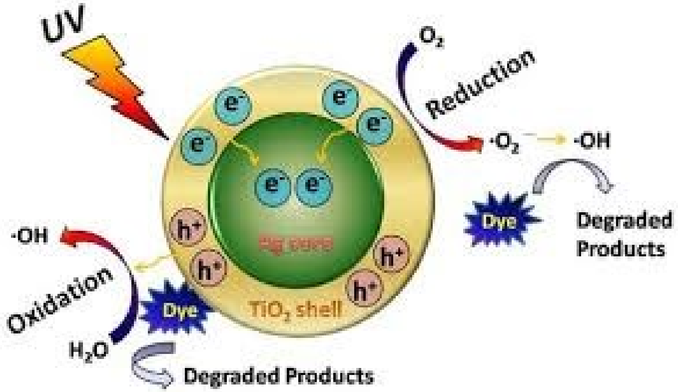
Blue series represents different sizes of CdSe nanocrystals (16) with diameters of 2.1, 2.4, 3.1, 3.6, and 4.6 nm (from right to left). The green series is of InP nanocrystals (26) with diameters of 3.0, 3.5, and 4.6 nm. The red series is of InAs nanocrystals (16) with diameters of 2.8, 3.6, 4.6, and 6.0 nm.

PROBLEM: The high surface area of the nanocrystal might lead to reduced luminescence efficiency and photochemical degradation.

CURRENT PROGRESS: Bandgap engineering concepts have led to the development of core-shell nanocrystal samples with high, room temperature quantum yields (50%) (12±14) and much improved photochemical stability.

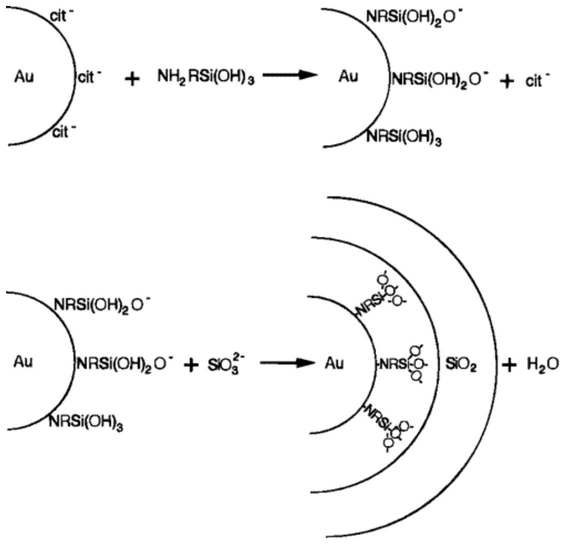
By enclosing a core nanocrystal of one material with a shell of another having a larger bandgap, one can efficiently confine the excitation to the core, eliminating nonradiative relaxation pathways and preventing photochemical degradation.





Biological Applications and Water Solubility

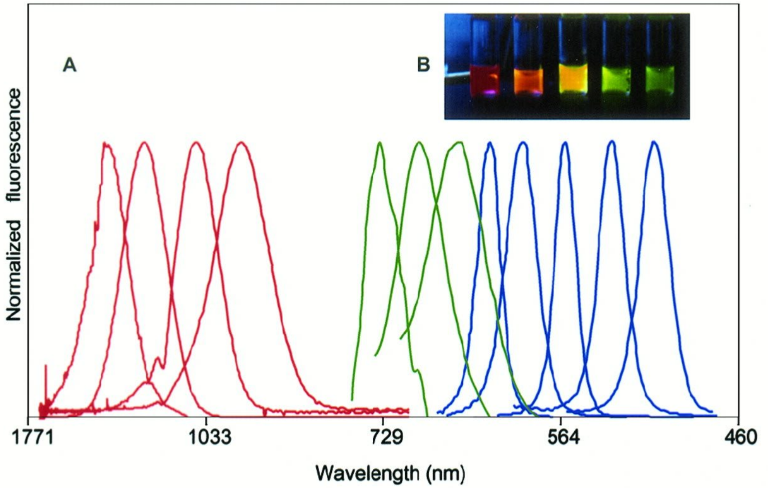
- Addition of silica based third layer creates water solubility
  - Process flow follows that of an addition of a silica shell on citrate-stabilized gold nanoparticles
- Stays water soluble due to multivalency of extensively polymerized polysilane
  - As opposed to strategies that may use single direct bonds to the NC
- Functionalization of this layer through the addition of other groups allow for controlled interactions with biological sample



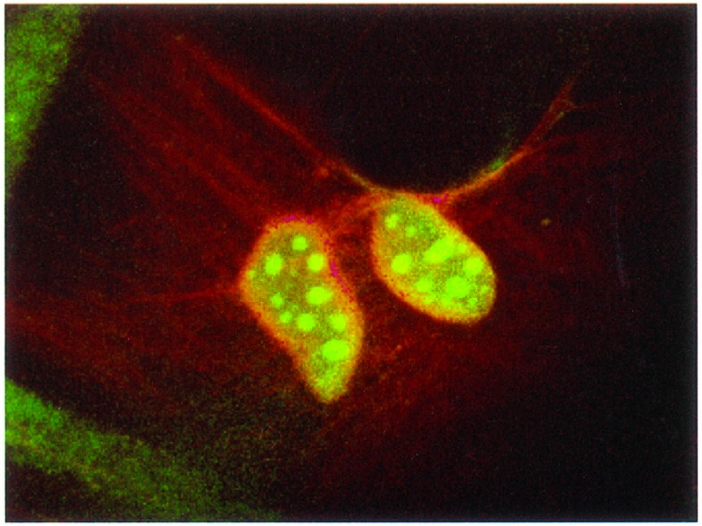
[1] Langmuir 1996, 12, 18, 4329–4335, Publication Date:September 4, 1996, https://doi-org.libproxy.berkeley.edu/10.1021/la9601871

High Yield and Consistent Tuning Chemistry

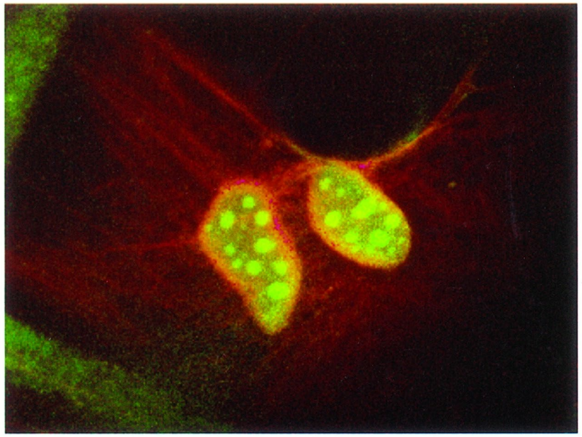
- Core-shell NCs prepared accordingly are soluble and stable in water or buffered solutions
- Figure 2B highlights the large quantum yield expected (up to 21% in comparison to conventional dies that range typical yields between 14 and 71%)
- NCs are a spectrally tuned family where all different core sized NCs follow the same modification chemistry
  - Organic dyes are tuned on a case by case basis due to their specific chemistries

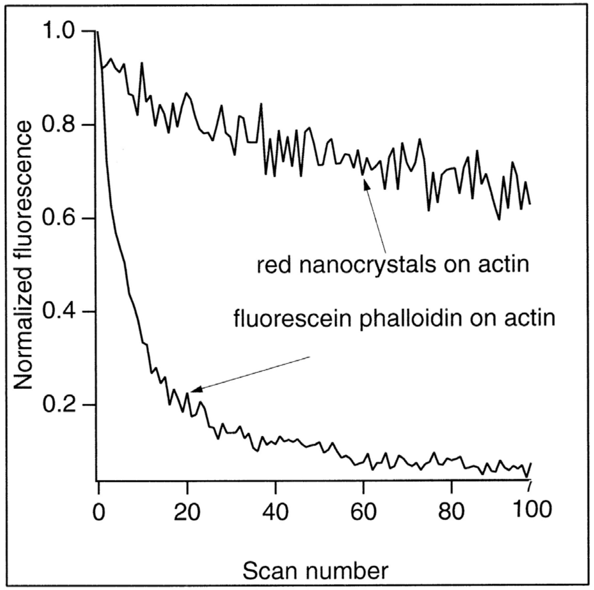


3T3 Mouse Fibroblast Cell Fluoroscopy



- Cells labeled using two different size CdSe-CdS core-shell NCs enclosed in silica shell (2-nm core emitted green fluorescence @ max 550nm, 4-nm core emitted red @max 630 nm)
- Surface of NCs tailored to interact with the biological sample
  - Electrostatic and hydrogen bonding interactions
  - Specific ligand-receptor interactions
- Avidin-biotin based ligand-receptor interaction
  - Used here to specifically label F-actin filaments with red NC probes
- NCs w trimethoxysilylpropyl urea and acetate groups bind with high affinity in cell nucleus
  - This can be suppressed with anionic silane reagent or through incubating with NCs in a 0.2% SDS solution
- Relies on silanized NC surface to control the binding





- Biotin covalently bonded to NC surface to label fibroblasts which were incubated in phalloidin-biotin and streptavidin
    - One round of amplification with streptavidin then with red biotinylated NCs again
- Imaged with both conventional wide field and laser scanning confocal fluorescence microscopes
- Nonspecific labeling of nuclear membrane by both red and green probes resulted in yellow color
- Red actin filaments specifically stained
- Filaments were not visible or only faintly visible in control experiments lacking phalloidin-biotin
- NC labeled experienced very little photobleaching, far less than conventional dye molecules

Future applications of NC based fluoroscopy

- Opens up new possibilities for multicolor experiments and diagnostics
- Tunability allows for their use as direct probes or sensitizers for traditional probes
- Long fluorescence life (hundreds of nanoseconds) allow for time gated detection for autofluorescence suppression
- Direct immunolabeling, in situ hybridization, incorporation into microspheres all will be significant for applications like cytometry and immunoctyobiology identifying tissues, cells, and proteins
- Potential applications in other contrast mechanisms (x-ray, electron microscopy, scintillation proximity imaging)

Nanocrystals in Biodetection

Aryan Sood, Hana Trinh, Anisa Silva, Keval Shah, Brendan Unggul

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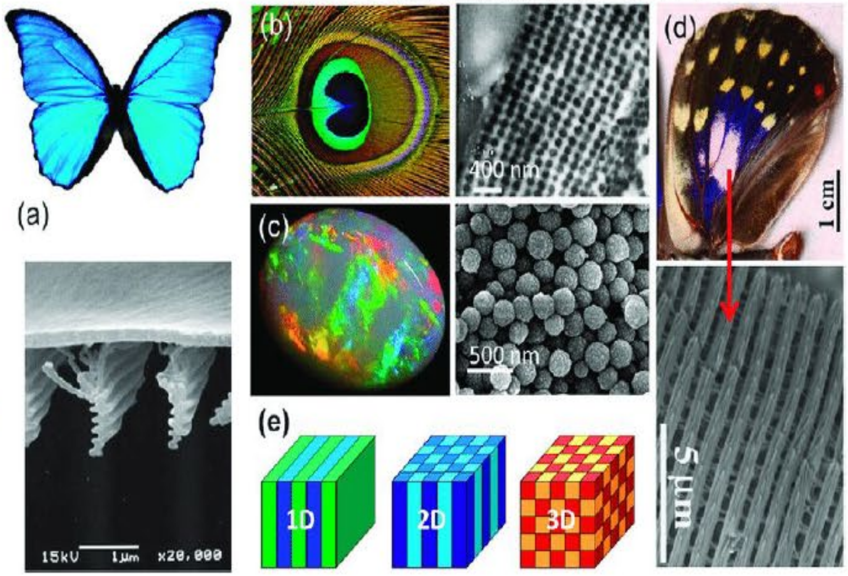
keval

Photonic Crystals

- Eli Yablonovich proposed that it should be possible to control the density of photon states via medium with artificial varying index of refraction
- “Photonic crystals” or semiconductors for light – materials whose dielectric function is periodic in one, two, or three spatial dimensions
- Want to control the patterns of materials to create materials with designed optical characteristics
    - Patterns will have length scale similar to the wavelength of lights in 1D, 2D, 3D
- In nature: opal, butterfly wings, peacock feathers, etc.



Armstrong, Eileen & O'Dwyer, Colm. (2015). Artificial Opal Photonic Crystals and Inverse Opal Structures – Fundamentals and Applications from Optics to Energy Storage. Journal of Materials Chemistry. 3. 6109-6143. 10.1039/C5TC01083G.

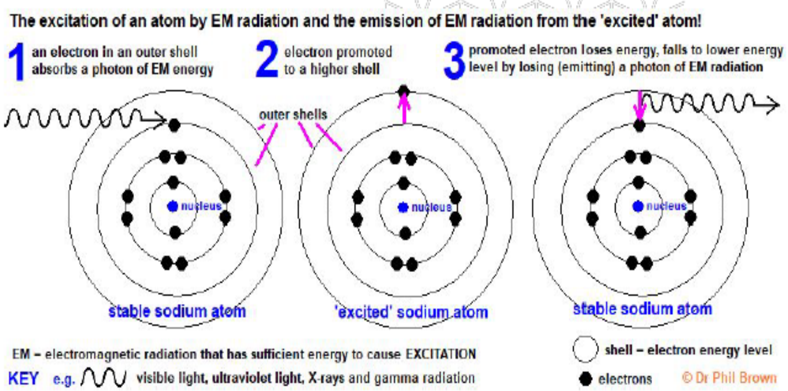
By Rob Lavinsky, iRocks.com – CC-BY-SA-3.0, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=10135016

Anisa

Photonic Crystals

- In order for an electronically excited atom or molecule to radiate, there must be a state for the outgoing photon
- Fermi's golden rule:

quantum mechanical radiative rate of a molecule ∝ **photon density states of the surrounding medium**

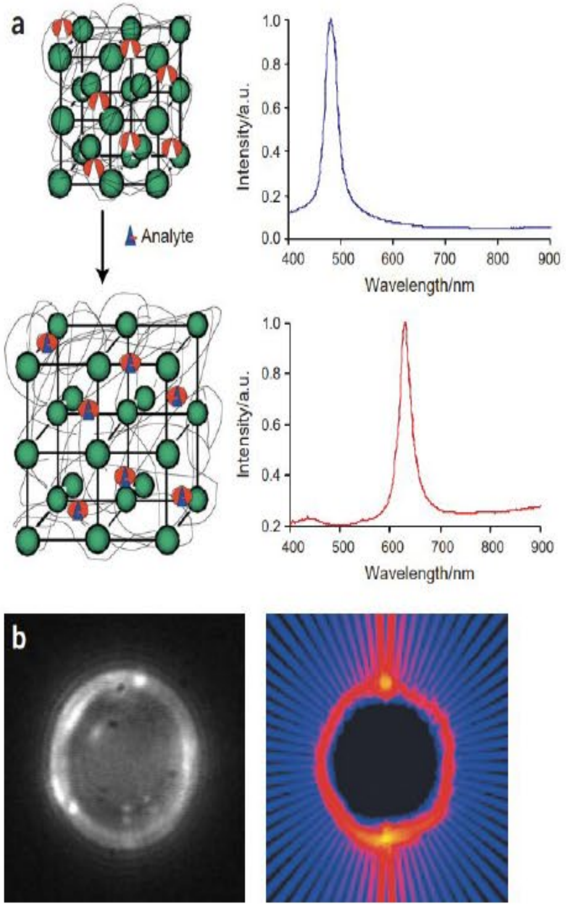


https://www.docbrown.info/ephysics/wavesemr10.htm

- Possible to control rates and directions of light emitted by molecule by embedding in a photonic crystal
- Photonic band-gap materials can be formed, some potentially compatible with incorporation of biological molecules

Photonic Crystals

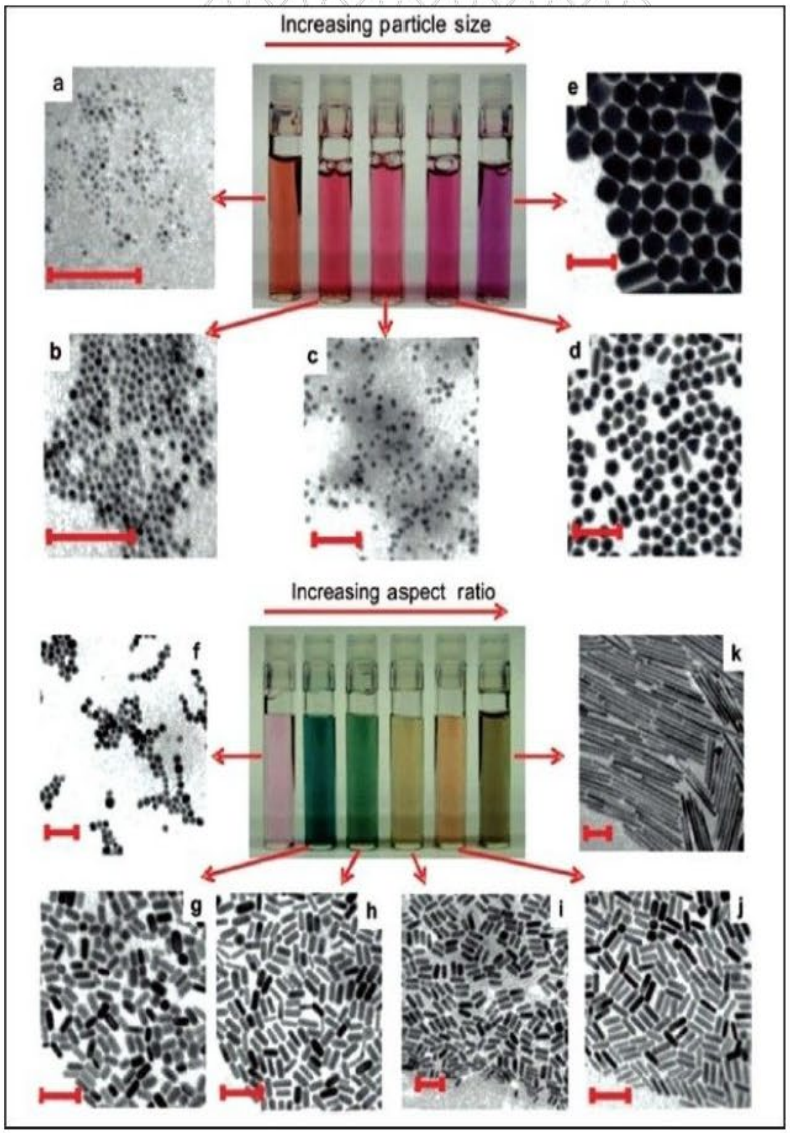
- Photonic crystals with array of silica beads hundred nanometers in size
    - Voids large enough to incorporate a variety of biological macromolecules
    - A binding event within the macromolecules can change spacing in beads or the index of refraction of surrounding medium
- Ex: lead ions and carbohydrates in blood



Anisa

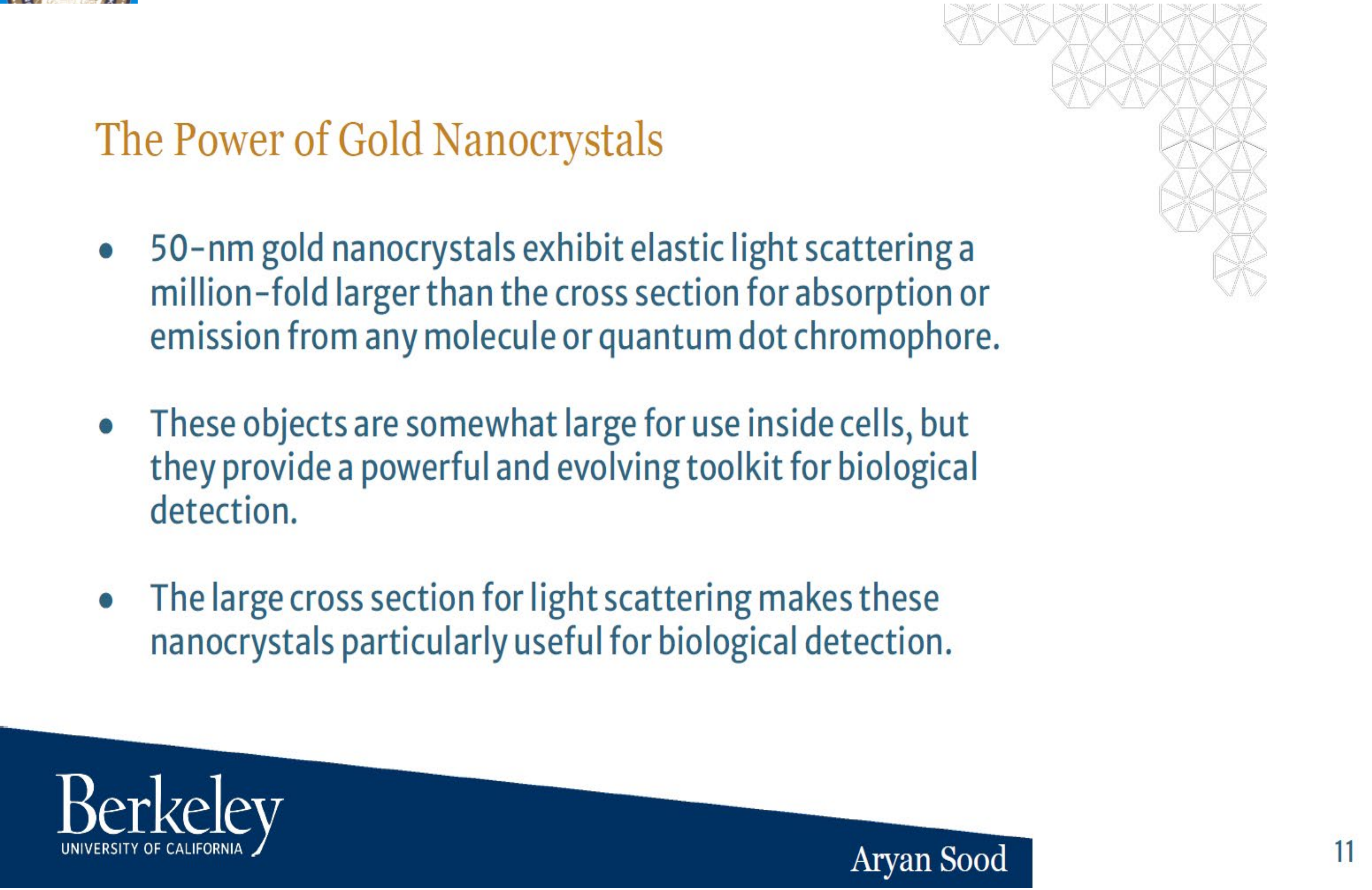
Metallic Nanoparticles

- Most promising avenues for enhance optical detection schemes → through use of noble metal nanocrystals
- Incident light can couple to plasmon excitation of the metal – involves light-induced motion of all valence electrons
- Desirable optical properties, large surface energies, plasmon excitation, and quantum confinement [1]
- Exhibit strong plasma absorption, enhanced Rayleigh scattering, surface-enhanced Raman scattering [1]



[1] M. Thakur, "Modern applications and current status of green nanotechnology in environmental industry," in *Green Functionalized Nanomaterials for Environmental Applications*, Amsterdam, Netherlands ; Cambridge, Ma: Elsevier, 2022.

[2] Mody VV, Siwale R, Singh A, Mody HR. Introduction to metallic nanoparticles. J Pharm Bioallied Sci. 2010 Oct;2(4):282-9. doi: 10.4103/0975-7406.72127.



The Power of Gold Nanocrystals

- 50-nm gold nanocrystals exhibit elastic light scattering a million-fold larger than the cross section for absorption or emission from any molecule or quantum dot chromophore.
- These objects are somewhat large for use inside cells, but they provide a powerful and evolving toolkit for biological detection.
- The large cross section for light scattering makes these nanocrystals particularly useful for biological detection.

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Aryan Sood

11

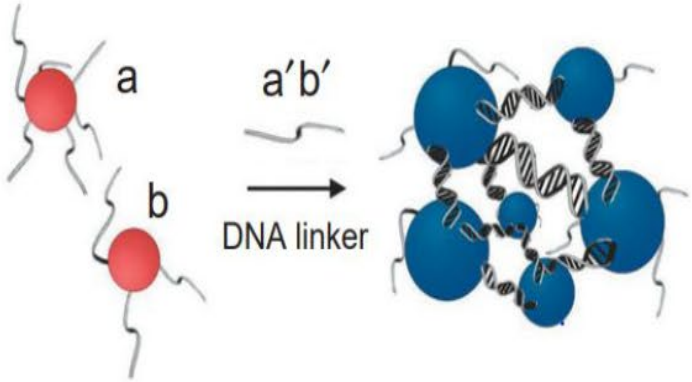
Shape and Size: Influencing Plasmon Resonance

- Plasmon resonance varies with the shape and size of nanoparticles.
- This variation allows the creation of a diverse range of light scatterers detectable at different wavelengths.
- These nanoparticles can be bio-conjugated and are commercially available, making them accessible for various applications.

Aryan Sood

DNA-Induced Aggregation: A Sensitive Probe for Oligonucleotides

- DNA-induced aggregation of gold nanocrystals results in a shift in plasmon resonance.
- This shift has been developed as a sensitive probe for oligonucleotides.
- The ability to detect this shift has led to the development of new methods for detecting nucleic acids.



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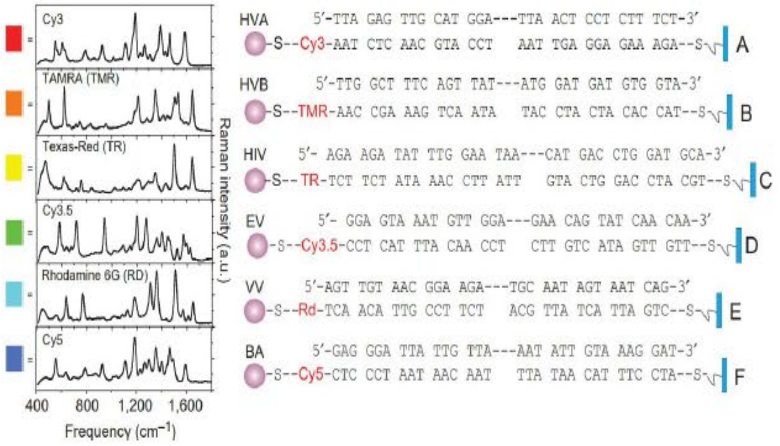
Aryan Sood

Surface Enhanced Raman Scattering (SERS): A New Era of Optical Detection

- The large field enhancement near gold nanocrystals leads to the SERS effect.
- SERS allows the detection of a wide range of biological macromolecules through binding events involving gold nanocrystals coated with specific molecules.
- The SERS effect provides an enhancement of as great as 105 in Raman cross section for molecules on a rough gold surface.



Future Directions: From Biological Sensors to Controlled Plasmon Resonances

- Future developments may include biological sensors consisting of a biological macromolecule with specific affinity, located in the gap between two 50-nm gold nanocrystals.

- It is possible to alternately pattern metal and dielectric materials radially in shells, providing a high degree of control over plasmon resonances and the Raman scattering process.

- These advancements provide an important tool for biological detection and offer a high degree of specificity and sensitivity.

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Aryan Sood

Detection Systems: Optical

- Most widely used for biological imaging and detecting biological events
- Future goals
  - Achieve in vivo despite large background present which could be done with combination of
    - Quantum-confined systems
    - Plasmon excitations in metal nanoparticles
    - Manipulation of local fields in their environment
    - Control over photon density of states

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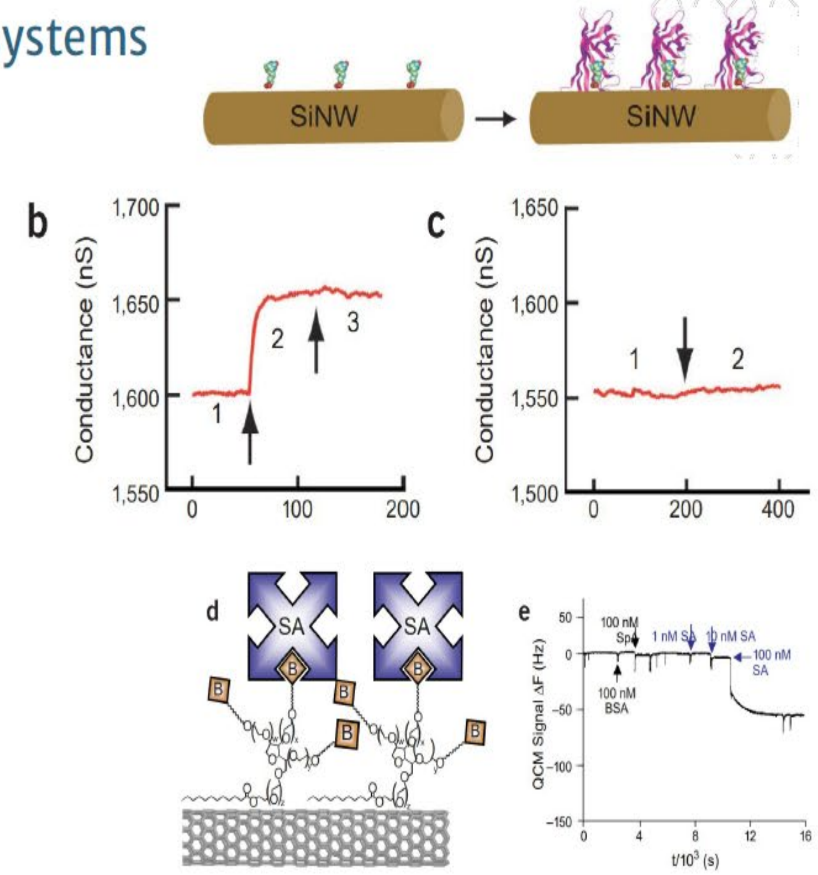
Detection Systems: Electrical

Can be miniaturised and integrated into systems

Pseudo 1D Structures
(CNT, Nanowires)

- Sensitive enough to measure any change in biological macromolecule attached to it

Eg. nanowire that is functionalized with biological macromolecules and can sense binding events by change in conductance over time



Detection Systems: Electrical

Can be miniaturised and integrated into systems

Ion Transportation

(Instead of electrons)

- Transport of ions through protein pores
    - Inverse of nanotubes and nanowires
- Sensitivity and control can be maximised
- Can be selective

Eg. Sense and distinguish base pairs of DNA as they pass through electrodes surrounding a nanopore (alpha hemolysin protein channel)

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Detection Systems: Magnetic

Nanoscale magnetic systems and superconductors
- Much more complex than
    - Single electron behaviour of quantum-confined semiconductor system
    - Metals with collective plasmon excitations
    - Ordinary electrical devices

Magnetic nanocrystals are widely used in
- Artificial biological detection
- Separation systems

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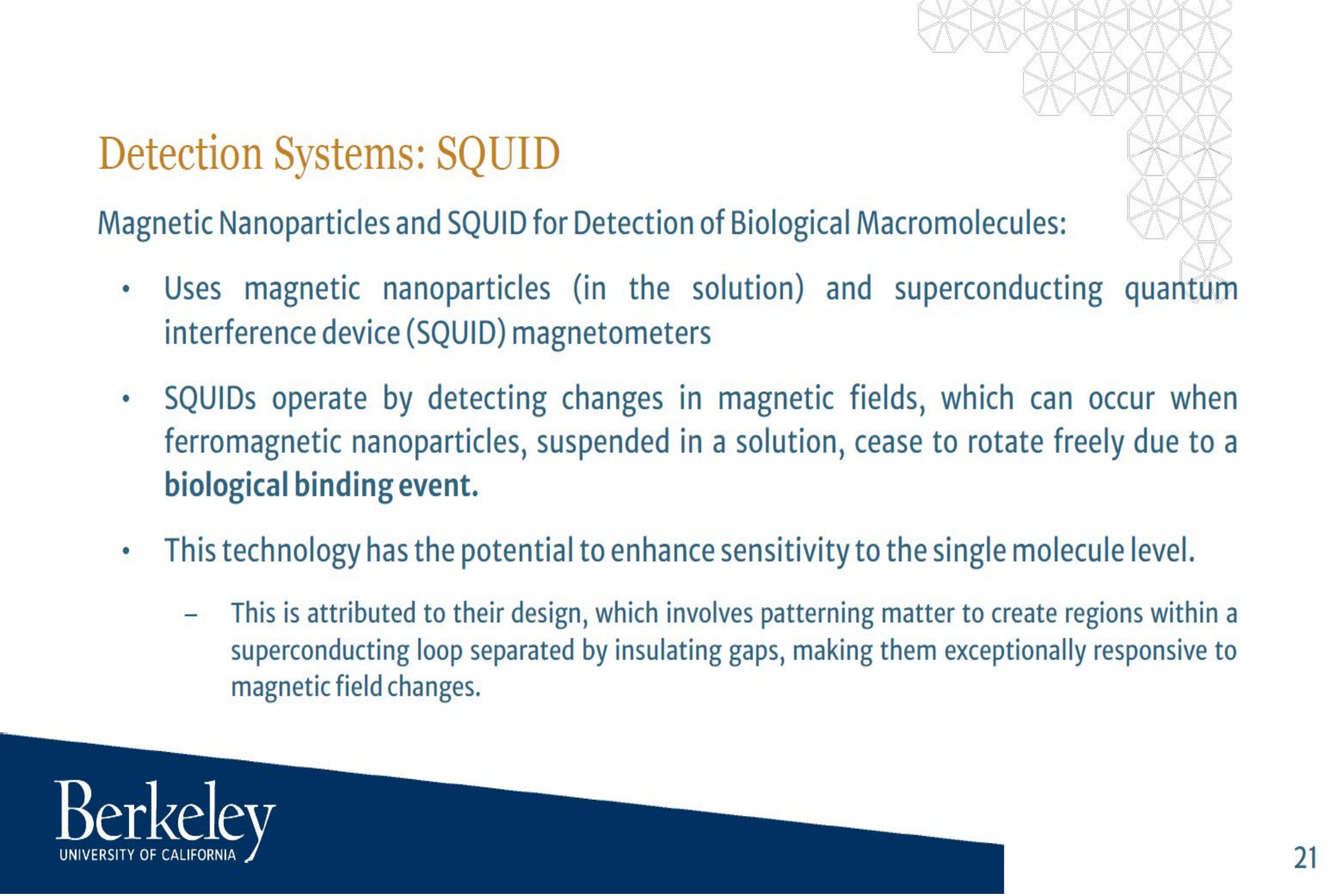
Detection Systems: Magnetic

How does it work?

- Magnetic crystals have single magnetic domain
- All the spins inside the crystal are aligned to create a large magnetic moment
  - Small crystal + high temperature: moment changes randomly (superparamagnetic)
  - Large crystal (above a critical size) + low temperature: moment is fixed (ferromagnetic)

Critical sizes

- Iron oxide: 25 nm
- Cobalt: 11nm



Detection Systems: SQUID

Magnetic Nanoparticles and SQUID for Detection of Biological Macromolecules:

- Uses magnetic nanoparticles (in the solution) and superconducting quantum interference device (SQUID) magnetometers
- SQUIDs operate by detecting changes in magnetic fields, which can occur when ferromagnetic nanoparticles, suspended in a solution, cease to rotate freely due to a **biological binding event.**
- This technology has the potential to enhance sensitivity to the single molecule level.
  - This is attributed to their design, which involves patterning matter to create regions within a superconducting loop separated by insulating gaps, making them exceptionally responsive to magnetic field changes.

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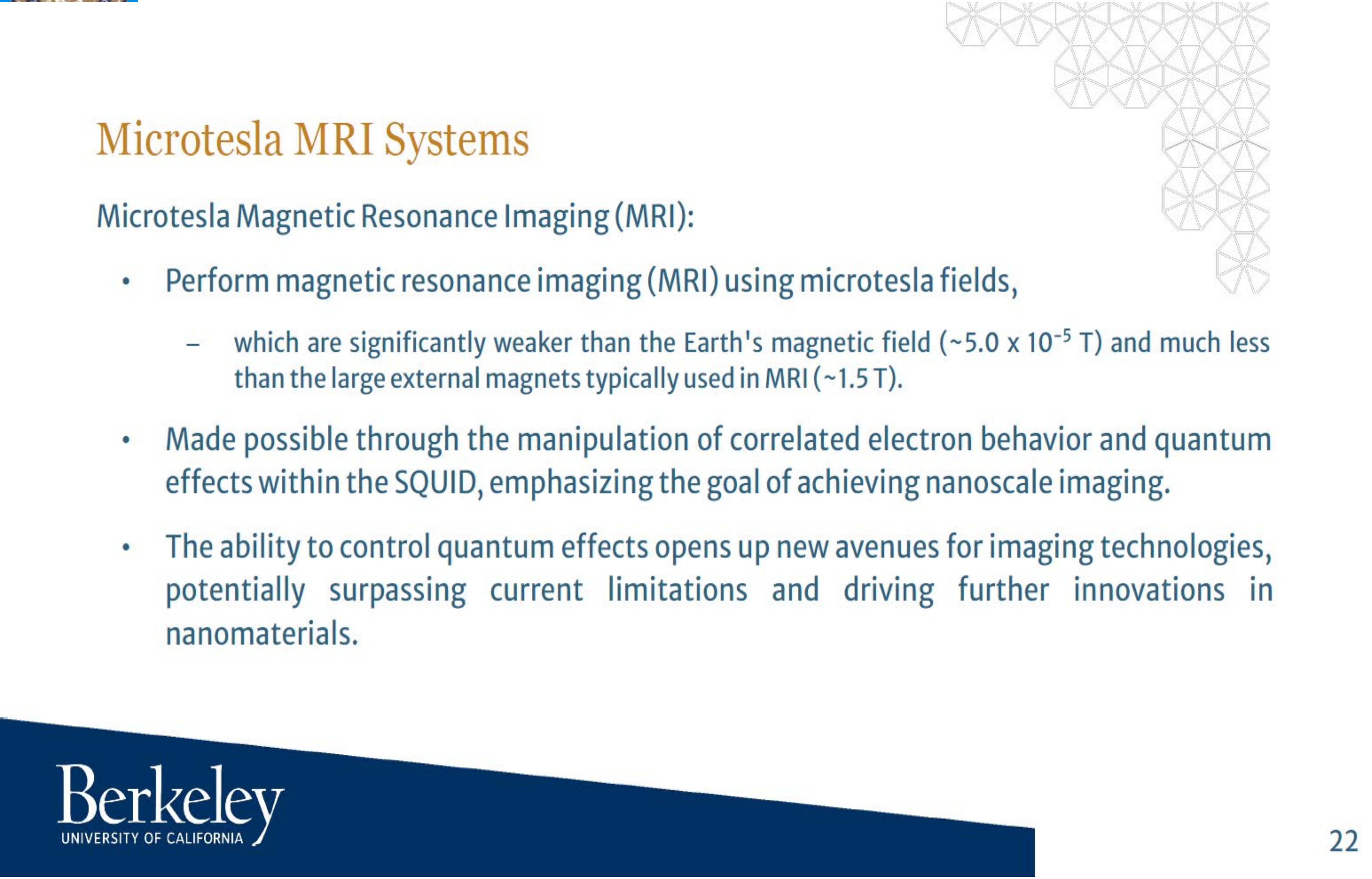

Microtesla MRI Systems

Microtesla Magnetic Resonance Imaging (MRI):

- Perform magnetic resonance imaging (MRI) using microtesla fields,
  - which are significantly weaker than the Earth's magnetic field (~5.0×10^{-5} T) and much less than the large external magnets typically used in MRI (~1.5 T).
- Made possible through the manipulation of correlated electron behavior and quantum effects within the SQUID, emphasizing the goal of achieving nanoscale imaging.
- The ability to control quantum effects opens up new avenues for imaging technologies, potentially surpassing current limitations and driving further innovations in nanomaterials.

Perspectives

Blinking Issue with Colloidal Quantum Dots:

- Colloidal quantum dots tend to "blink" or emit light intermittently when excited with high intensity.
    - This is attributed to multiple-charge nonradiative inelastic scattering and the difficulty of growing a thick shell of high band-gap material to fully confine the photo-generated charges.
- In contrast, embedded dots grown by molecular beam epitaxy do not exhibit this.
- However, it is most likely possible to make them not blink (further research required, potentially through colloidal quantum rods due to their larger volume)

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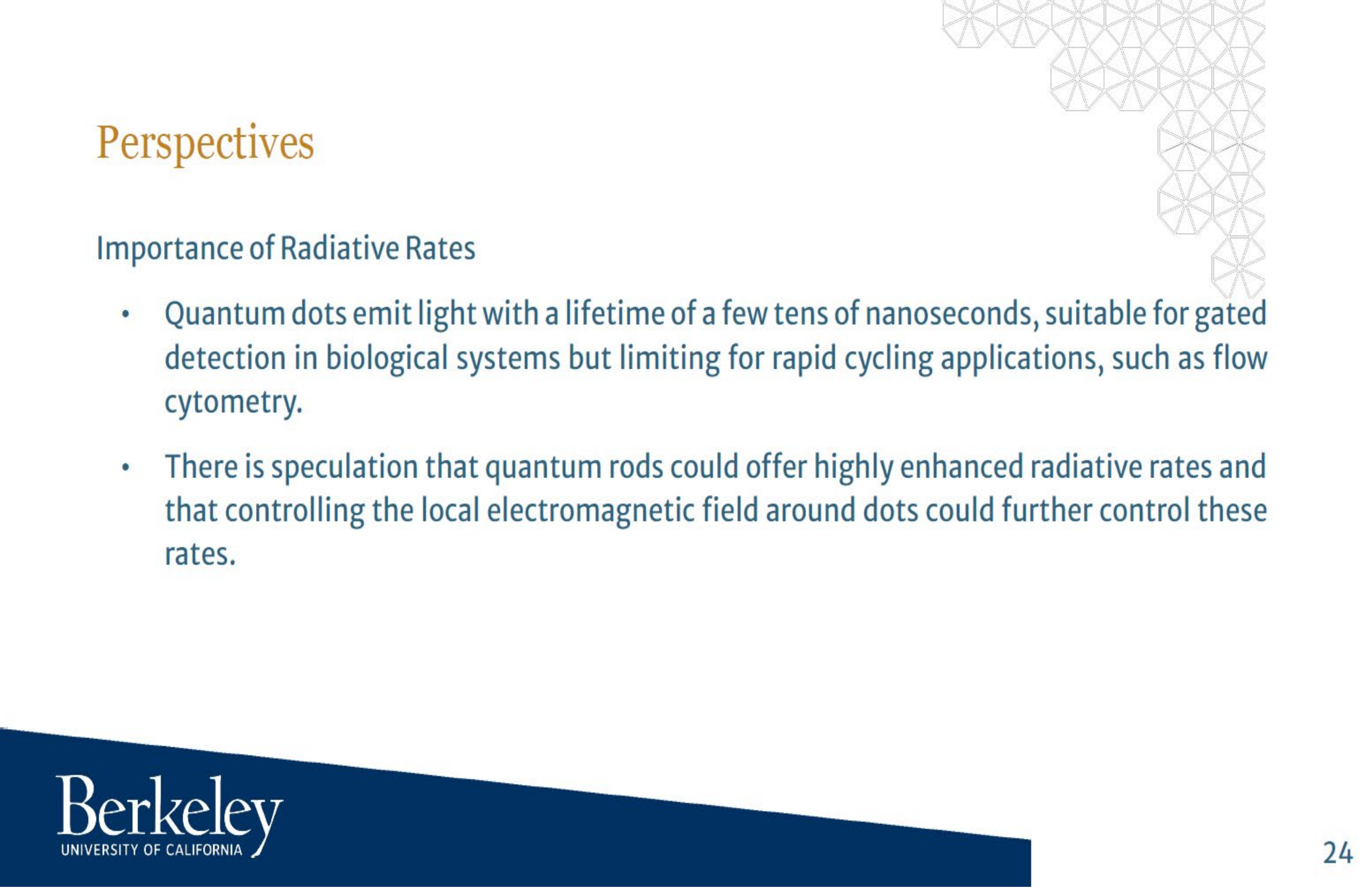
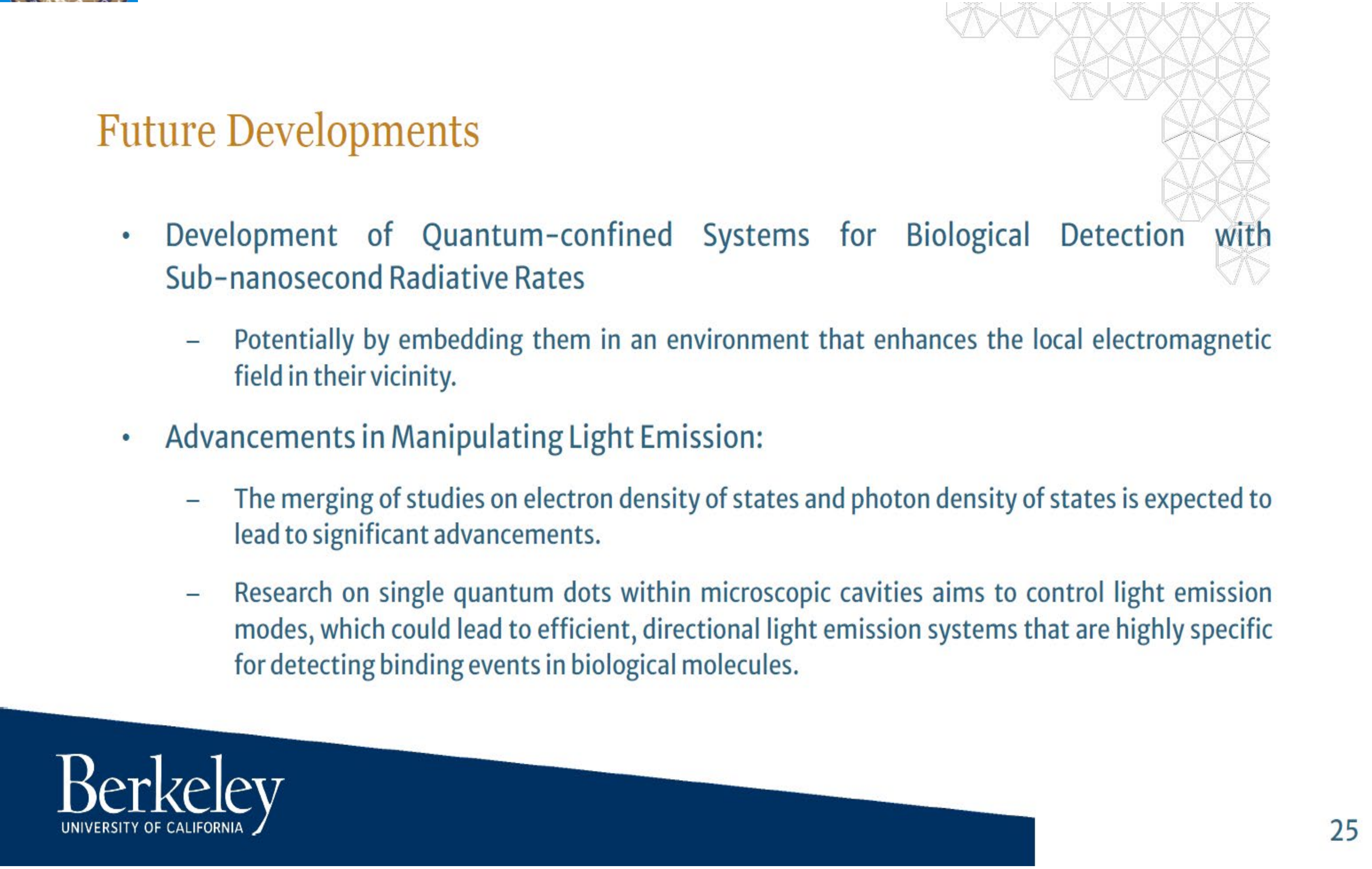


Perspectives

Importance of Radiative Rates

- Quantum dots emit light with a lifetime of a few tens of nanoseconds, suitable for gated detection in biological systems but limiting for rapid cycling applications, such as flow cytometry.
- There is speculation that quantum rods could offer highly enhanced radiative rates and that controlling the local electromagnetic field around dots could further control these rates.



Future Developments

- Development of Quantum-confined Systems for Biological Detection with Sub-nanosecond Radiative Rates
  - Potentially by embedding them in an environment that enhances the local electromagnetic field in their vicinity.
- Advancements in Manipulating Light Emission:
  - The merging of studies on electron density of states and photon density of states is expected to lead to significant advancements.
  - Research on single quantum dots within microscopic cavities aims to control light emission modes, which could lead to efficient, directional light emission systems that are highly specific for detecting binding events in biological molecules.

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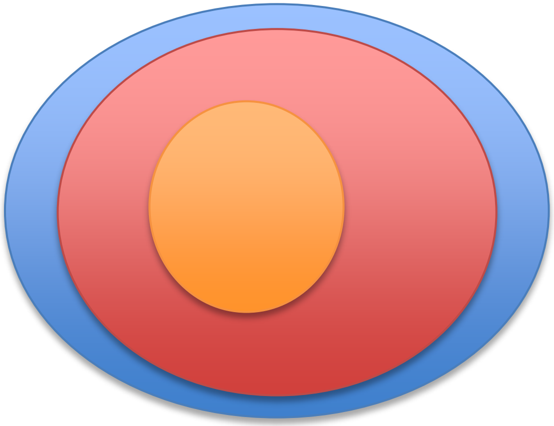
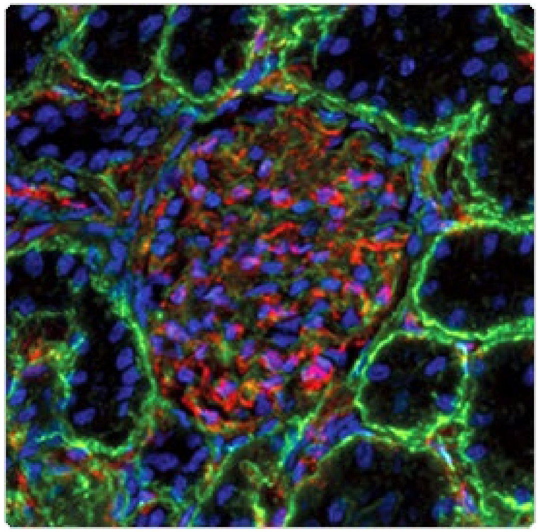
- The use of semiconductor nanocrystals: problematic；
- The high surface area of the nanocrystal might lead to reduced luminescence efficiency and photochemical degradation;
- Solution: By enclosing a core nanocrystal of one material with a shell of another having a larger bandgap
- BUT, soluble only in nonpolar solvents
- By adding a third layer of silica that makes the core-shell water soluble



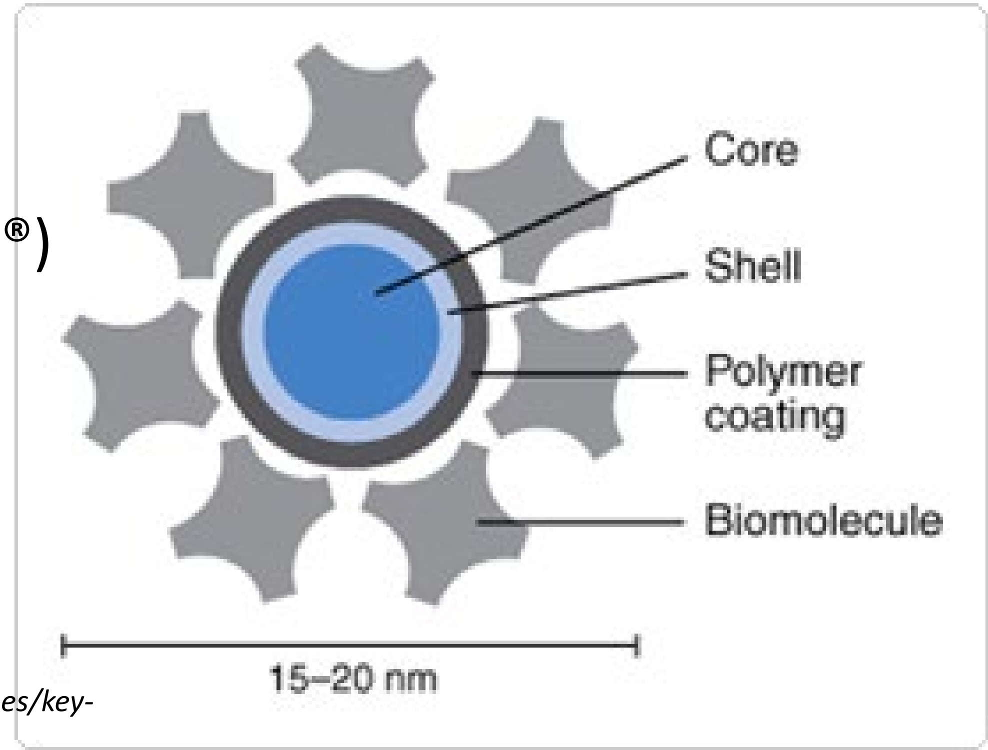
Orange: Fluorescent nanocrystals
Red: material with a larger bandgap
Blue: silica

Applications

- As predicted by this 1998 paper:
  - Multicolor biological experiments and diagnostics
  - Cytometry and immunocytobiology
  - X-ray fluorescence, x-ray absorption, electron microscopy, scintillation proximity imaging
  - Infrared dyes



  - Commercially available (Qdot®)
  - Multispectral flow cytometry
  - Cell tracking
  - Cell/tissue staining
  - *In vivo* imaging

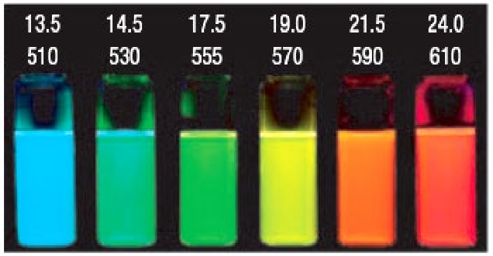


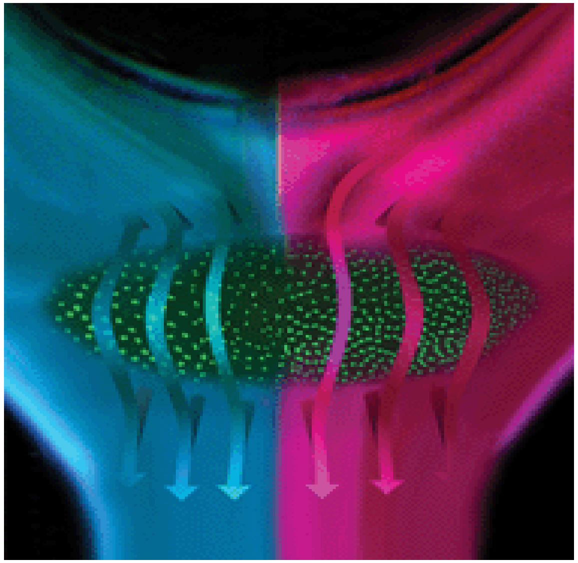
Bruchez, M. *et al*. *Science* **1998**, 281, 2013-2015.
https://www.thermofisher.com/us/en/home/brands/molecular-probes/key-molecular-probes-products/qdot.html

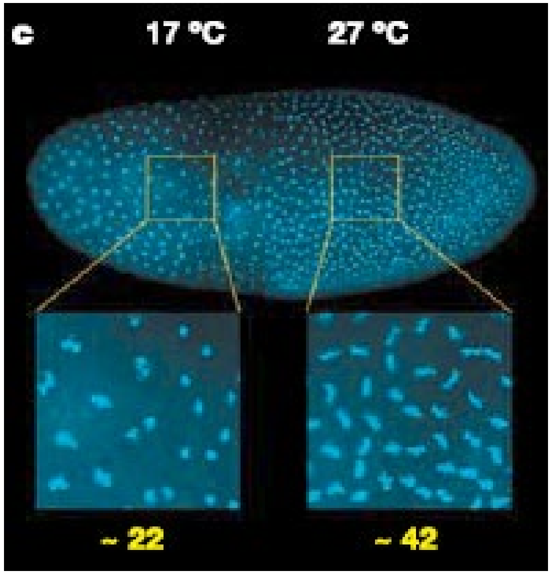
Introduction – QD as Thermometers

Temperature response to the environmental variations and/or cells response to environmental temperatures

ex: cold exposure, heat shock, thermogenesis…







E. M. Lucchetta, M. S. Munson, R. F. Ismagilov, *Nature* 434, 1134 (Apr, 2005)

- **Pros**
  - Photostability
  - Broad absorption, narrow emission
  - Long fluorescence lifetime
  - Tunable spectra
- **Cons**
  - Blinking