

Good Evening!!!
Welcome to Session 8

A little bit more on surfaces (and colors)

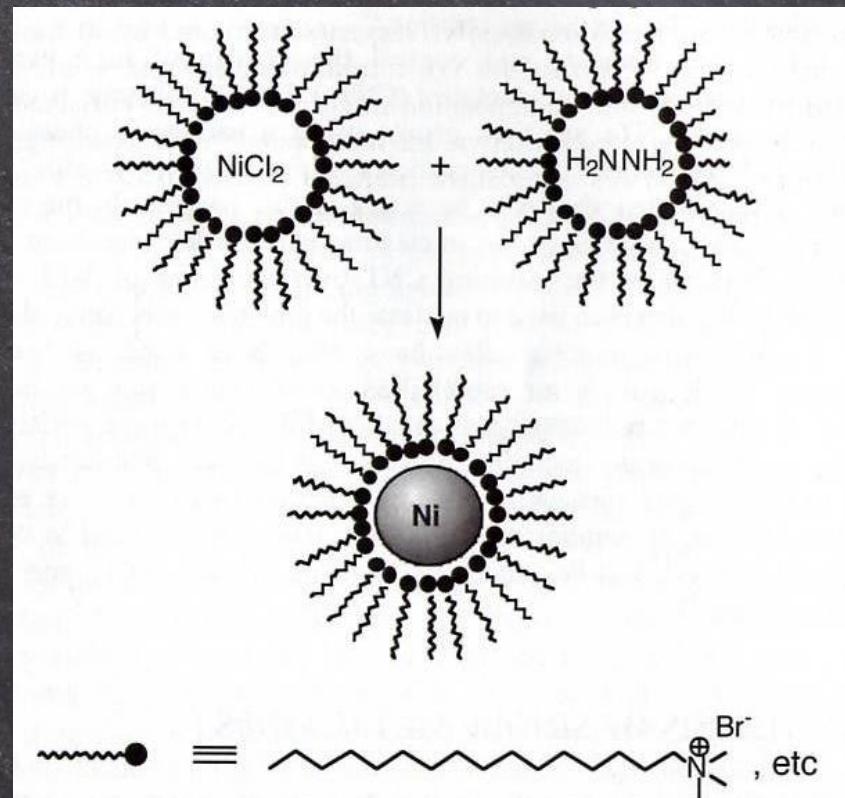
Chunlei Guo: Using femtosecond lasers to create new material properties

https://www.youtube.com/watch?v=FLnKgXWlO_Y&t=10s

Production of Metal Nanoparticles

Method I: The Reduction of Metal Salts

- Size control: conducting the reaction in a confined reactor
- Nano confined reactor such as water-in-oil or oil-in-water micro-emulsion system
- Size of confined space can be defined by varying amount of both surfactant and solvent
- Successful examples included Fe, Ni and Co particles

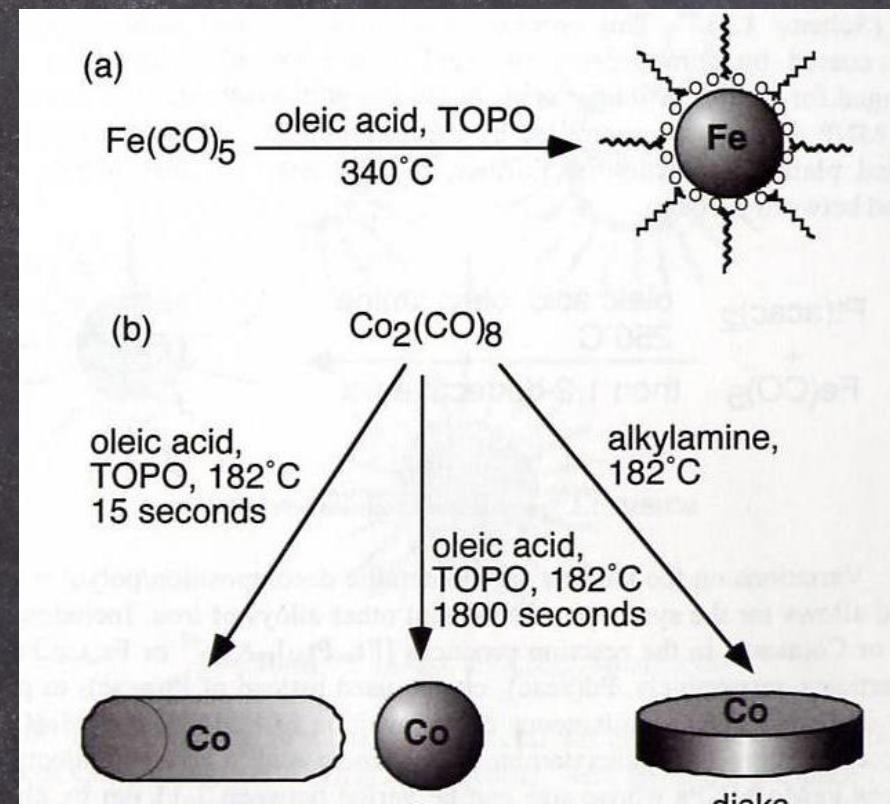


Courtesy from Vincent Rotello, Nanoparticles

Synthesis of Single Metal MNP

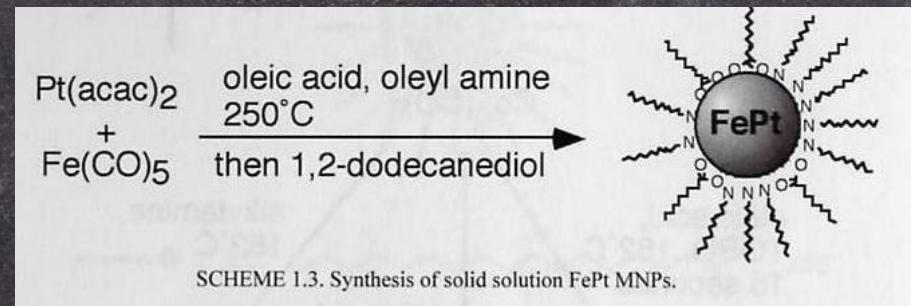
-- Method II: Thermal Decomposition

- Thermal Decomposition of organo-metallic complexes can produce highly mono-disperse nano particles.
- Size and dispersity control is attained through high reaction temperature.
- Capping ligands (e.g. Oleic Acid) can also mediate the particle growth by forming a monolayer of nano particles
- Most common precursors: Metal Carbonyl complexes.
- Morphology can also be controlled through various capping ligands



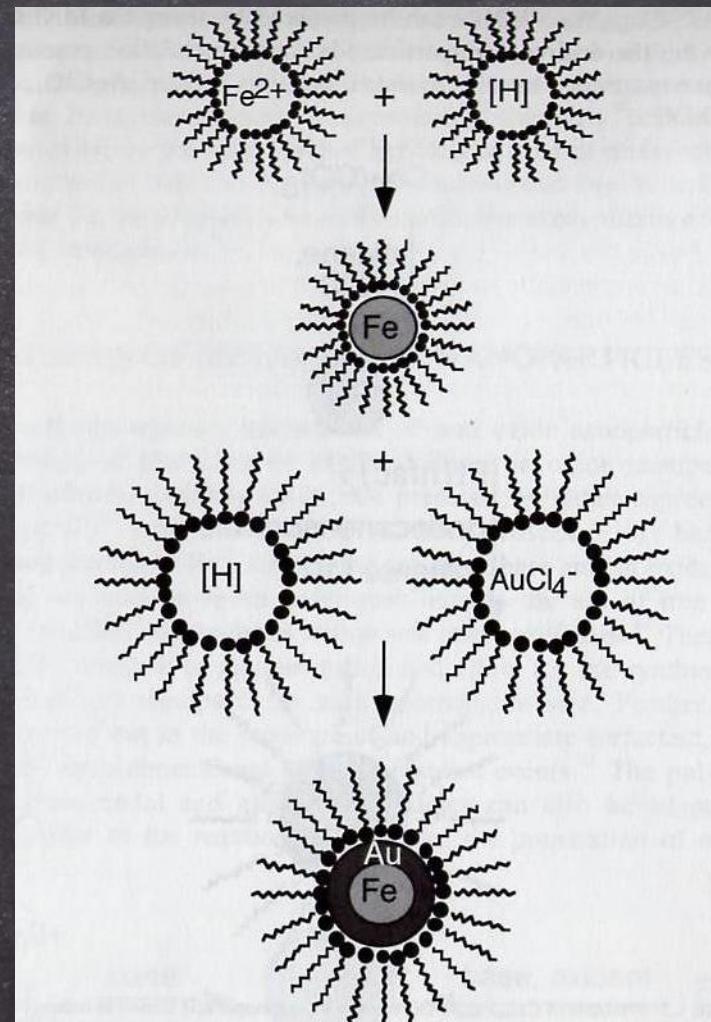
Courtesy from Vincent Rotello, Nanoparticles
TOPO: Trioctylphosphine Oxide

Alloyed Metal Nano Particles



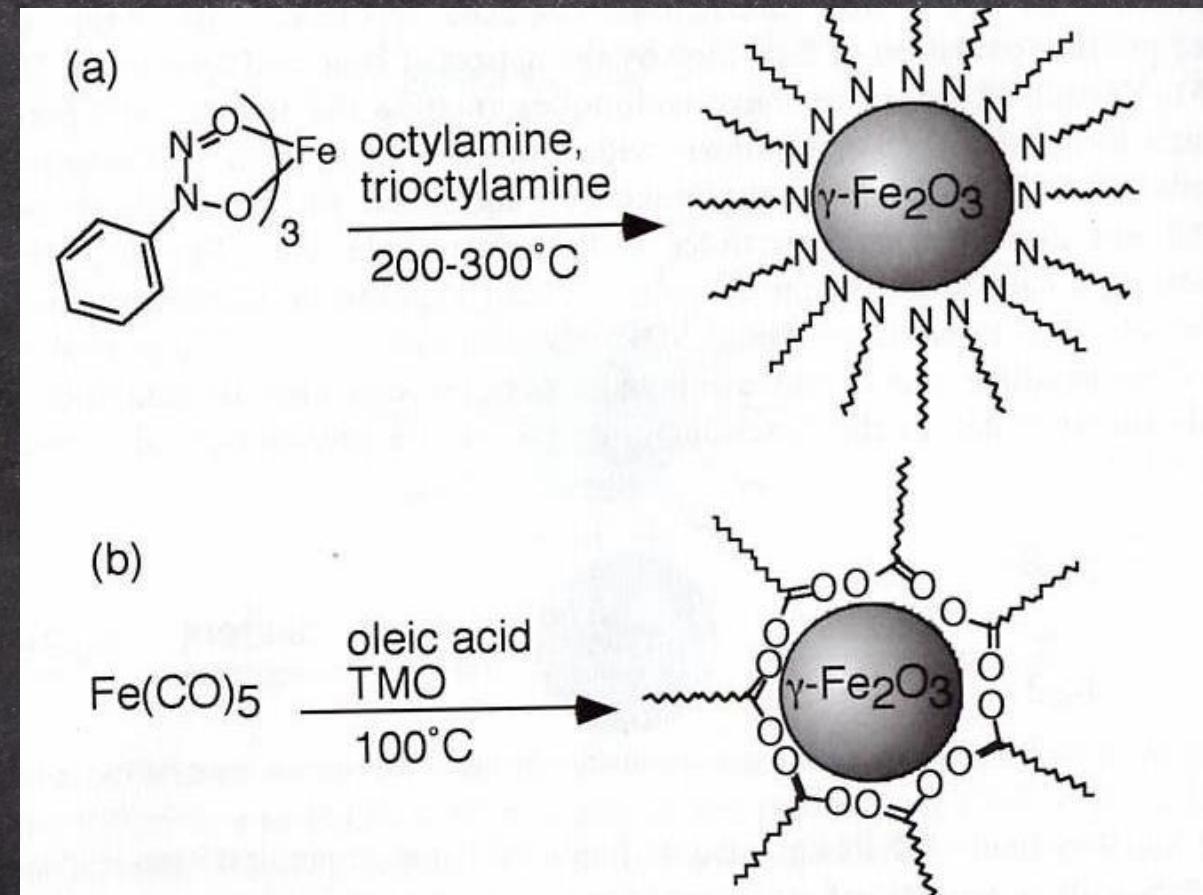
Solid-solution alloyed metallic nano particles can be attained through simultaneous thermal decomposition

Core-shell alloyed nano particles are produced by a stepwise reduction process where each successive step uses larger diameter water droplet to yield the alloyed core-shell particles



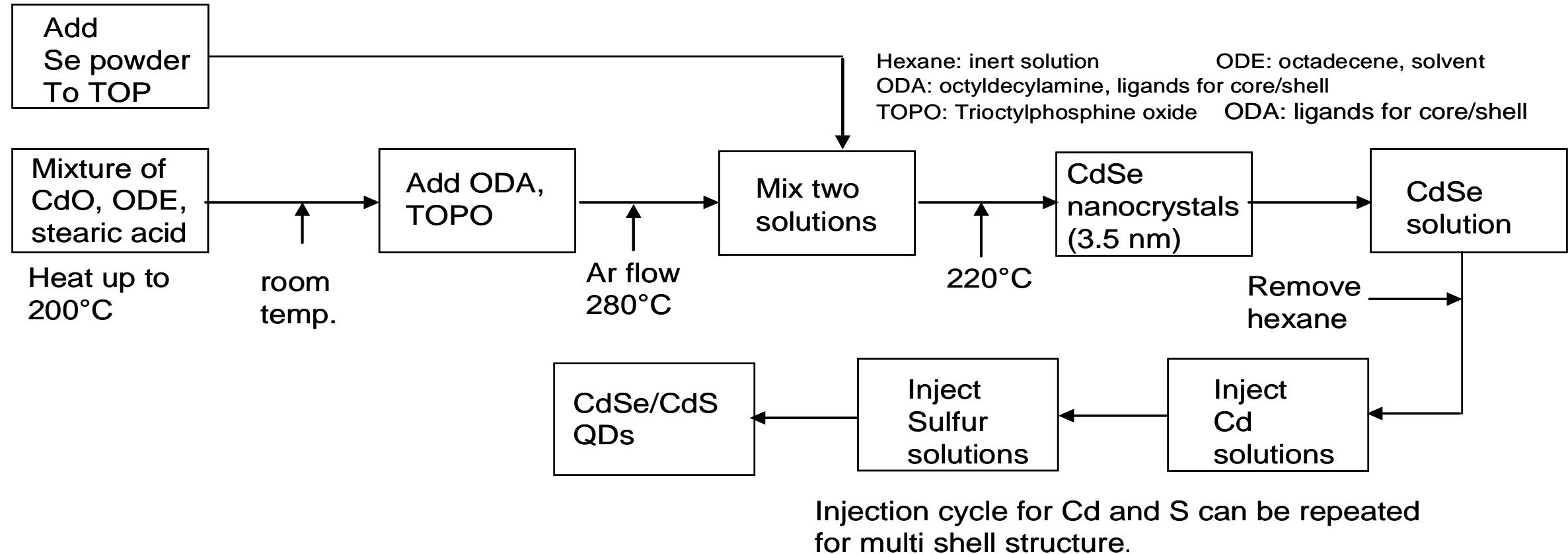
Courtesy from Vincent Rotello, Nanoparticles

Metal Oxide Nano Particles



- Thermal decomposition of metal organic precursors on a hot surface.
- The size of the nano particles can be controlled by reaction temperature and / or the ratios of precursor verse capping ligands

Process flow for synthesis of CdSe/CdS core shell structure



Au nanoparticles: Is it New?



Lycurgus Cup that was manufactured in the **5th to 4th century B.C.**
It is ruby red in transmitted light and green in reflected light, due to the presence of gold colloids.

Au nanoparticles: Is it New?



“Labors of the
Months” (Norwich,
England, ca. 1480
(The ruby color is
probably due to
gold nanoparticles.

How can we produce Au-Nanoparticles

Synthesis of Au & Ag

Synthesis of Nanoparticles

Au nanoparticles: How to prepare?

1. Turkevich Method (1951)

Turkevich, J.; Stevenson, P. C.; Hillier, J. Nucleation and Growth Process in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc.* **1951**, 11, 55-75.

Reduction of Gold ion by citrate ions

2. Brust Method (1994)

Synthesis of Thiol-Derivatized Gold Nanoparticles in a Two phase Liquid-Liquid System. *J. Chem. Soc., Chem. Commun.* **1994**, 801-802.

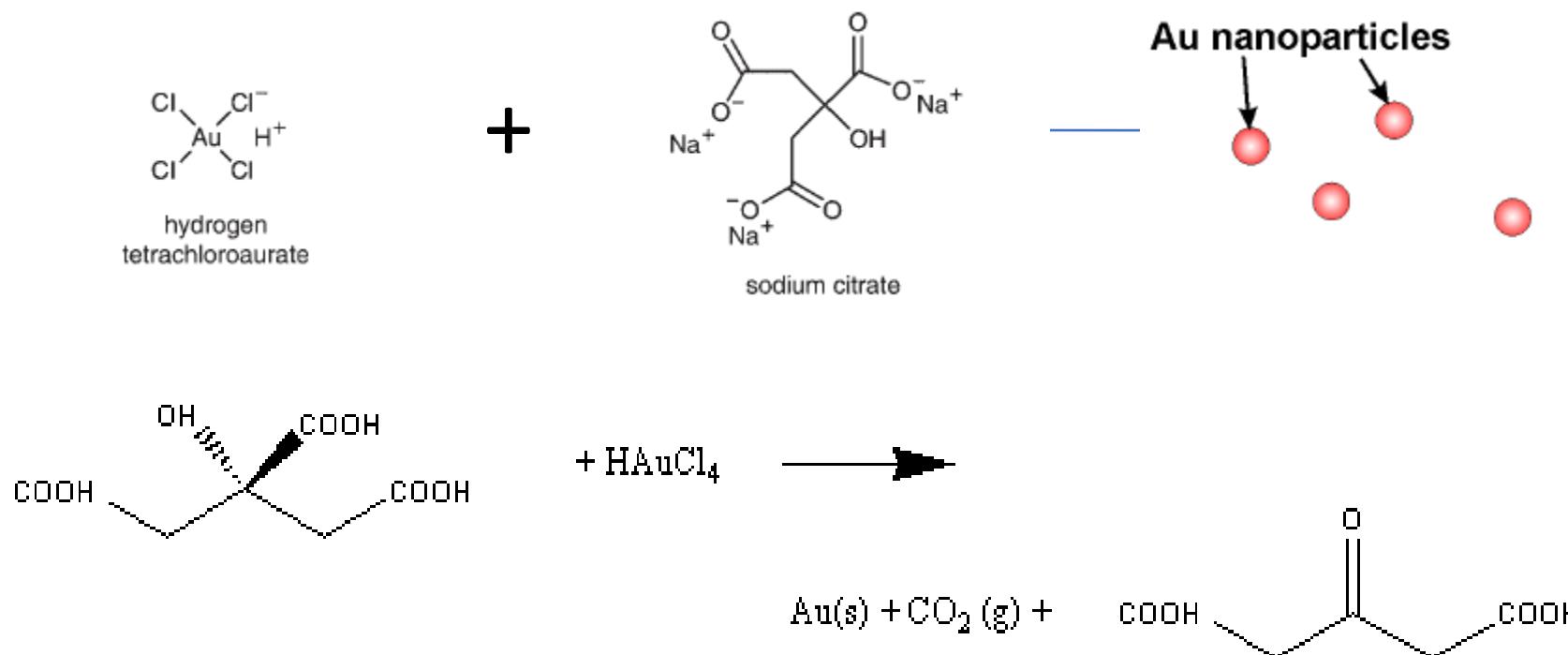
Reduction of Au colloid by NaBH_4 in presence of phase transfer agent.



Au nanoparticles: How to prepare?

1. Turkevich Method (Reduction of Gold ion by citrate ions)

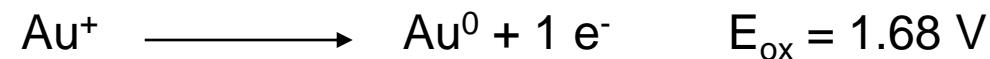
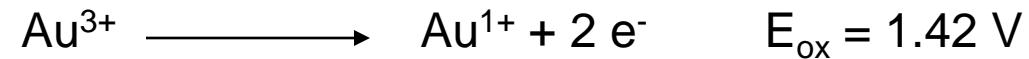
(Adapted from *Color My Nanoworld* by Adam D. McFarland, Christy L. Haynes, Chad A. Mirkin, Richard P. Van Duyne, and Hilary A. Godwin*, *J. Chem. Educ.* **2004**, *81*, 544 A.



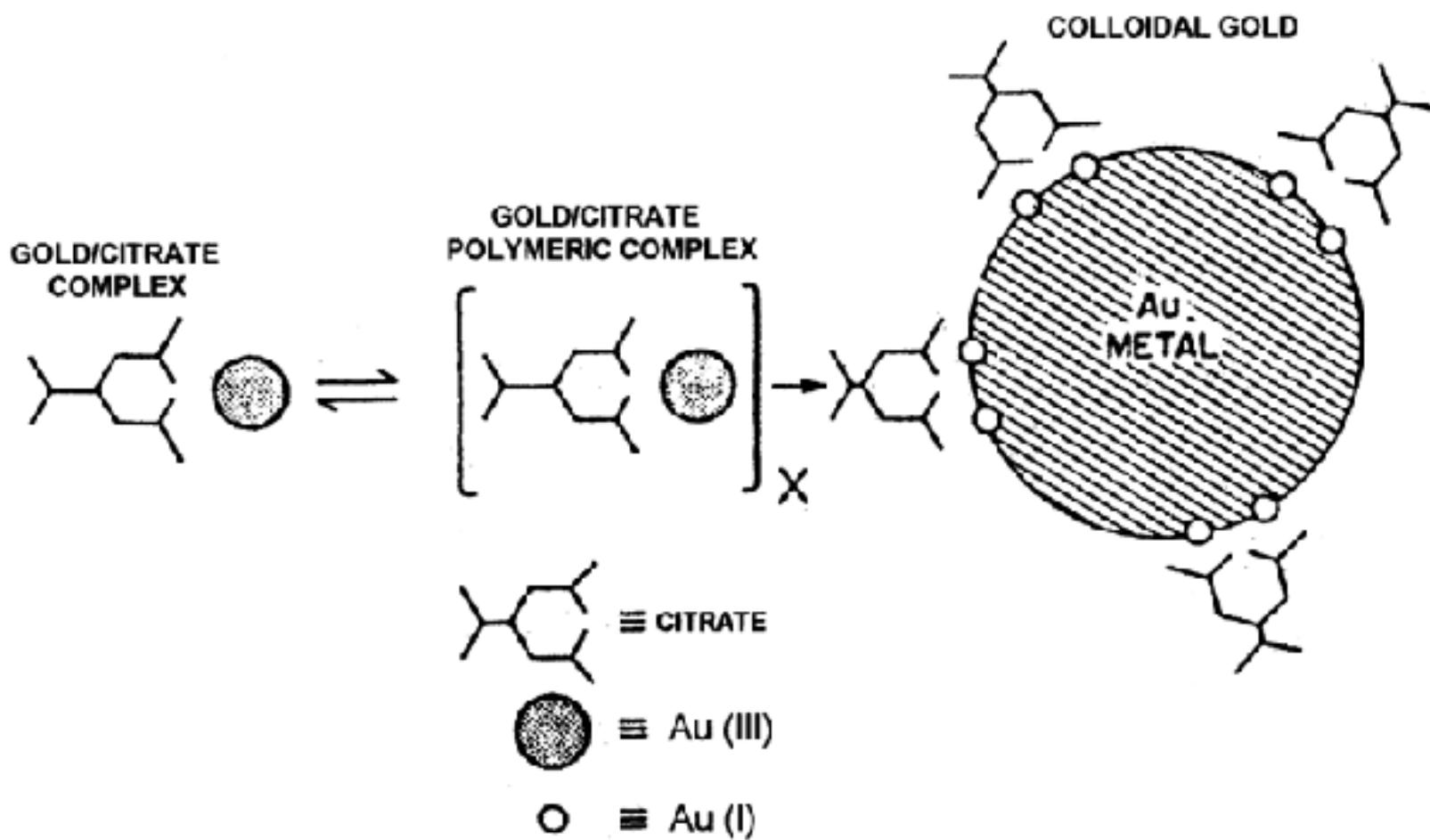
Gold Reduction

The primary reaction is the reduction of a gold salt (HAuCl_4) into a gold metal.

Gold can exist in three oxidation states: Au^{3+} , Au^+ and Au^0



Mechanism of reaction

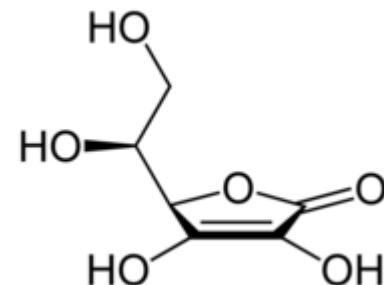
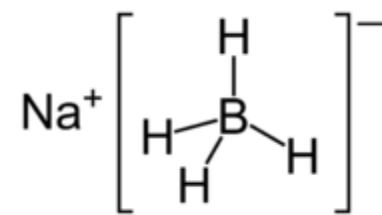
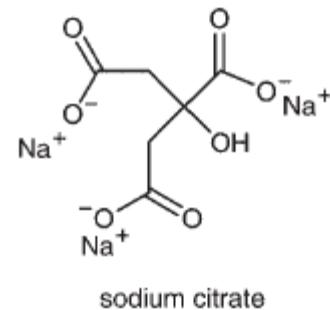


Au nanoparticles: Preparation

You will need:

1. HAuCl_4
2. $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (sodium citrate)
3. Table salt (NaCl)
4. Table sugar (sucrose)
5. Deionized water
6. Sodium borohydride (NaBH_4)
7. Ascorbic acid

6. 100-mL beaker(s)
7. Test tubes
8. Graduated cylinder
9. Dropper/Pasteur pipette
10. Stir/hot plate
11. Balance
12. Pipette



Au Nanoparticles Synthesis

Turkevich Method (Reduction of Gold ion by citrate ions)

(Adapted from *Color My Nanoworld* by Adam D. McFarland, Christy L. Haynes, Chad A. Mirkin, Richard P. Van Duyne, and Hilary A. Godwin, *J. Chem. Educ.* 2004, 81, 544 A.)

Preparation of stock solutions

1. Prepare 1.0 mM HAuCl₄ by dissolving 0.1 g of the solid in 500 mL of distilled water.
2. Prepare a 38.8 mM Na₃C₆H₅O₇ (sodium citrate) by dissolving 1 g of the solid in 100 mL of distilled water.
3. Prepare a second solution of sodium citrate of concentration 19.9 mM.
4. Prepare a third solution of sodium citrate of concentration 10 mM.
5. Prepare a 38.8 mM solution of sodium borohydride by dissolving 0.15 g in 100 mL water.
6. Prepare a second solution of sodium borohydride of concentration 19.9 mM.
7. Prepare a third solution of sodium borohydride of concentration 10 mM.
8. Prepare a 38.8 mM solution of ascorbic acid by dissolving 0.7 g in 100 mL water.
9. Prepare a second solution of ascorbic acid of concentration 19.9 mM.
10. Prepare a third solution of ascorbic acid of concentration 10 mM.

Au nanoparticles: Preparation

A. Preparation of Gold Nanoparticles

1. Pour ~60 mL of deionized water into the 100 mL beaker. Place the solution on a hotplate and heat the solution to boiling.
2. In a test tube (label it as A), add 2 mL of the 1.0 mM solution of gold salt. To this solution add 1 mL of 38.8 mM sodium citrate solution and leave it at room temperature.
3. Observe to see any color change.
4. Now place this test tube in the beaker containing boiling water. Wait for 5-10 minutes and note the change in the color.
5. Take another test tube (label it as B) and add 2 mL of 1.0 mM solution of gold salt. Add 1 mL of 38.8 mM sodium citrate solution. Place this test tube in the beaker containing boiling water. Note the change in the color of the solution and the time taken for the color to develop.
6. Repeat the same set of experiments with 19.9 mM and 10 mM sodium citrate solution (as in step 5) and note the color (if any) and the time taken for the color to develop. Label the test tubes as C, and D.
7. Now repeat the same set of experiments with NaBH_4 and Ascorbic acid as the reducing agents at different concentrations and note the color and the time taken for the color to develop.

Au nanoparticles: Questions

Questions

1. Based on the fact that the citrate anions cover the surface of each nanoparticle, explain what keeps the nanoparticles from sticking together (aggregating) in the original solution.
2. Why does adding the salt solution produce a different result from adding the sugar solution?
3. What would happen if a lower concentration (i.e. ~ 20 mM) of citric acid is used for preparation of Au nanoparticles?
4. Can other reducing agent be used for the preparation? If so, give some examples.
5. How can the aggregation caused by NaCl be used for applications of Au nanoparticles for sensing applications?



Experiments y Observaciones

Nano-sizing Causes Changes In Color

Macroscale vs. Nanoscale Gold

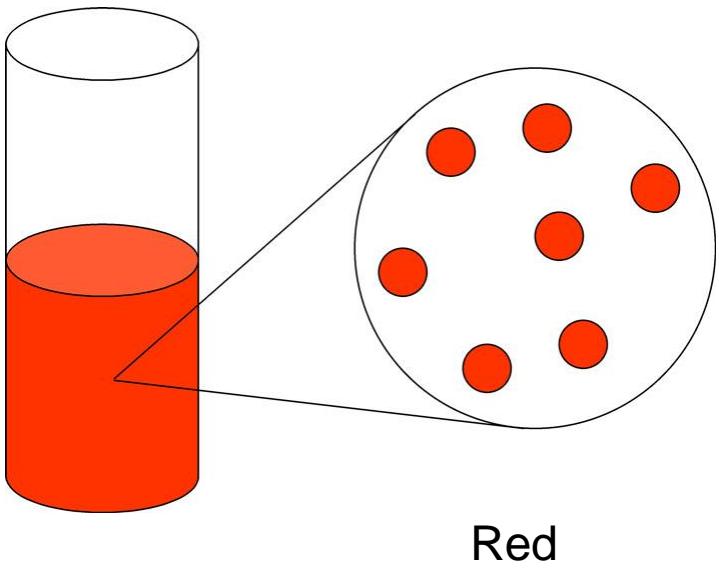


Why ?

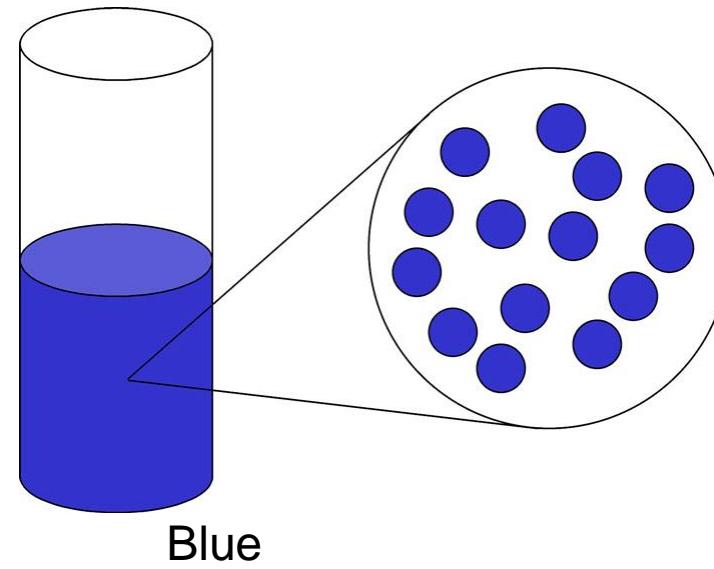
Does something else changes?

Video

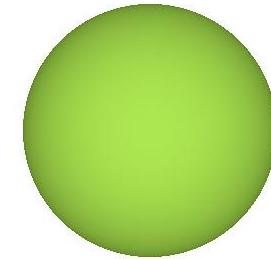
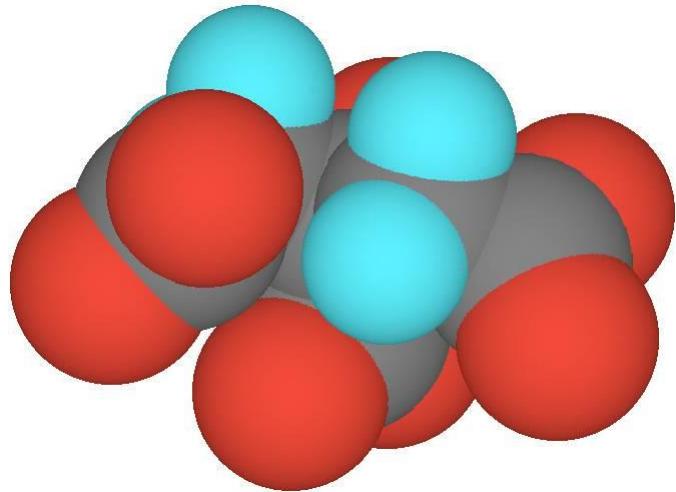
Au nanoparticles: Observations



Red



Blue



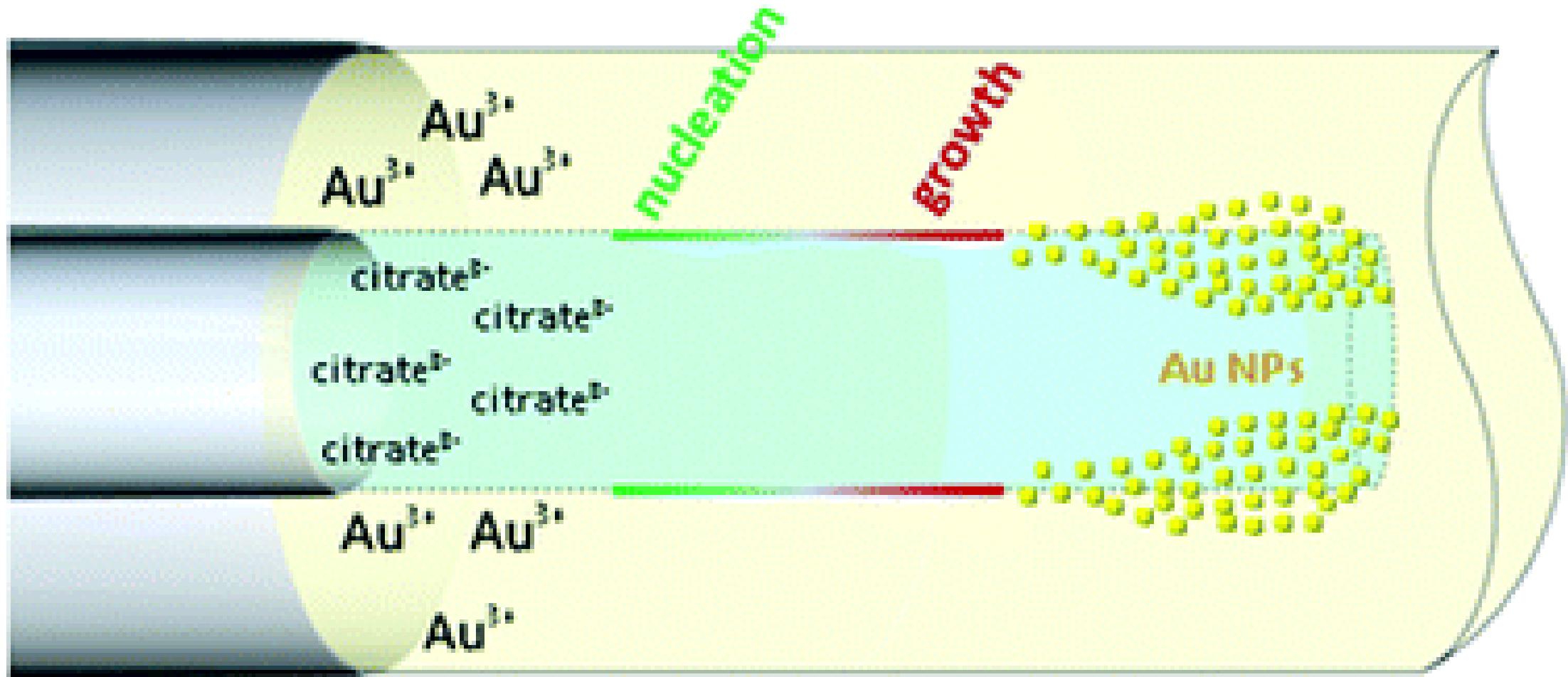
Ag nanoparticles: How to prepare?

A. Preparation of Silver Nanoparticles

1. Pour ~60 mL of deionized water into the 100 mL beaker. Place the solution on a hotplate and heat the solution to boiling.
2. In a test tube (label it as A), add 2 mL of the 1.0 mM solution of silver salt. To this solution add 1 mL of 38.8 mM sodium citrate solution and leave it at room temperature.
3. Observe to see any color change.
4. Now place this test tube in the beaker containing boiling water. Wait for 5-10 minutes and note the change in the color.
5. Take another test tube (label it as B) and add 2 mL of 1.0 mM solution of gold salt. Add 1 mL of 38.8 mM sodium citrate solution. Place this test tube in the beaker containing boiling water. Note the change in the color of the solution and the time taken for the color to develop.
6. Repeat the same set of experiments with 19.9 mM and 10 mM sodium citrate solution (as in step 5) and note the color (if any) and the time taken for the color to develop. Label the test tubes as C, and D.
7. Now repeat the same set of experiments with NaBH_4 and Ascorbic acid as the reducing agents at different concentrations and note the color and the time taken for the color to develop.

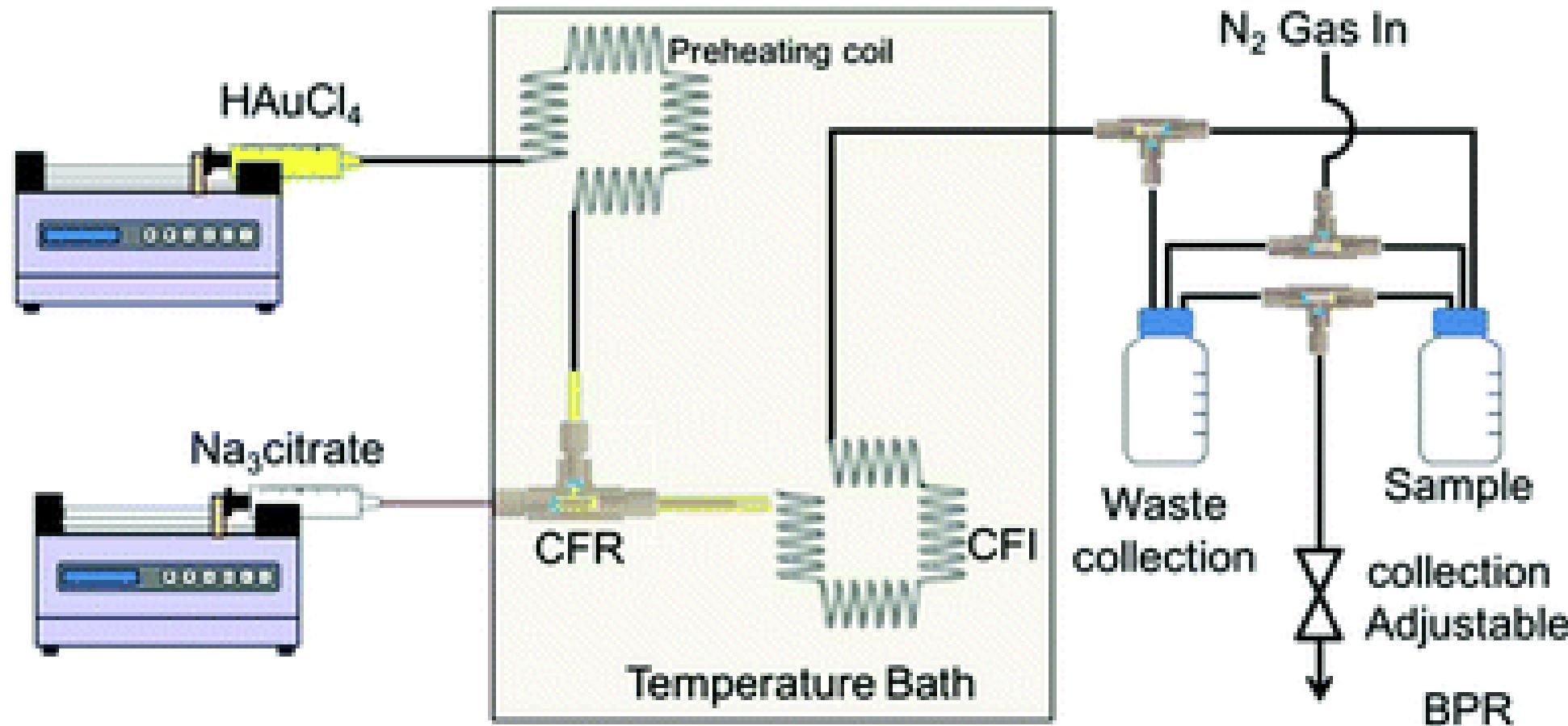
An engineering approach to synthesis of gold and silver nanoparticles by controlling hydrodynamics and mixing based on a coaxial flow reactor.

In this work we present a detailed study of flow technology approaches that could open up new possibilities for nanoparticle synthesis. The synthesis of gold and silver nanoparticles (NPs) in a flow device based on a coaxial flow reactor (CFR) was investigated. The CFR comprised of an outer glass tube of 2 mm inner diameter (I.D.) and an inner glass tube whose I.D. varied between 0.142 and 0.798 mm. A split and recombine (SAR) mixer and coiled flow inverter (CFI) were further employed to alter the mixing conditions after the CFR. The ‘Turkevich’ method was used to synthesize gold NPs, with a CFR followed by a CFI. This assembly allows control over nucleation and growth through variation of residence time. Increasing the total flow rate from 0.25 ml min^{-1} to 3 ml min^{-1} resulted initially in a constant Au NP size, and beyond 1 ml min^{-1} to a size increase of Au NPs from $17.9 \pm 2.1 \text{ nm}$ to $23.9 \pm 4.7 \text{ nm}$. The temperature was varied between $60\text{--}100^\circ\text{C}$ and a minimum Au NP size of $17.9 \pm 2.1 \text{ nm}$ was observed at 80°C . Silver NPs were synthesized in a CFR followed by a SAR mixer, using sodium borohydride to reduce silver nitrate in the presence of trisodium citrate. The SAR mixer provided an enhancement of the well-controlled laminar mixing in the CFR. Increasing silver nitrate concentration resulted in a decrease in Ag NP size from $5.5 \pm 2.4 \text{ nm}$ to $3.4 \pm 1.4 \text{ nm}$. Different hydrodynamic conditions were studied in the CFR operated in isolation for silver NP synthesis. Increasing the Reynolds number from 132 to 530 in the inner tube created a vortex flow resulting in Ag NPs in the size range between $5.9 \pm 1.5 \text{ nm}$ to $7.7 \pm 3.4 \text{ nm}$. Decreasing the inner tube I.D. from 0.798 mm to 0.142 mm resulted in a decrease in Ag NP size from $10.5 \pm 4.0 \text{ nm}$ to $4.7 \pm 1.4 \text{ nm}$. Thus, changing the thickness of the inner stream enabled control over size of the Ag NPs.



An engineering approach to synthesis of gold and silver nanoparticles by controlling hydrodynamics and mixing based on a coaxial flow reactor.

Nanoscale, Issue 37, 2017; [Razwan Baber](#),^a [Luca Mazzei](#),^a [Nguyen Thi Kim Thanh](#)*^{bc} and [Asterios Gavriilidis](#)*^a



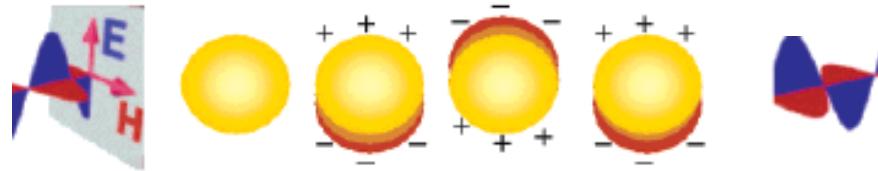
IMPORTANT PROPERTIES:

- 1) Electromagnetic ENHANCEMENT around nanoparticle
- 2) Enhancement has a RESONANT frequency
- 3) Resonance SHIFTS based on environment, shape, size and material

Why different sizes “have” different colors?

Surface Plasmon (SP) Resonance

Surface electromagnetic waves that propagate parallel along a metal interact with the electric field.

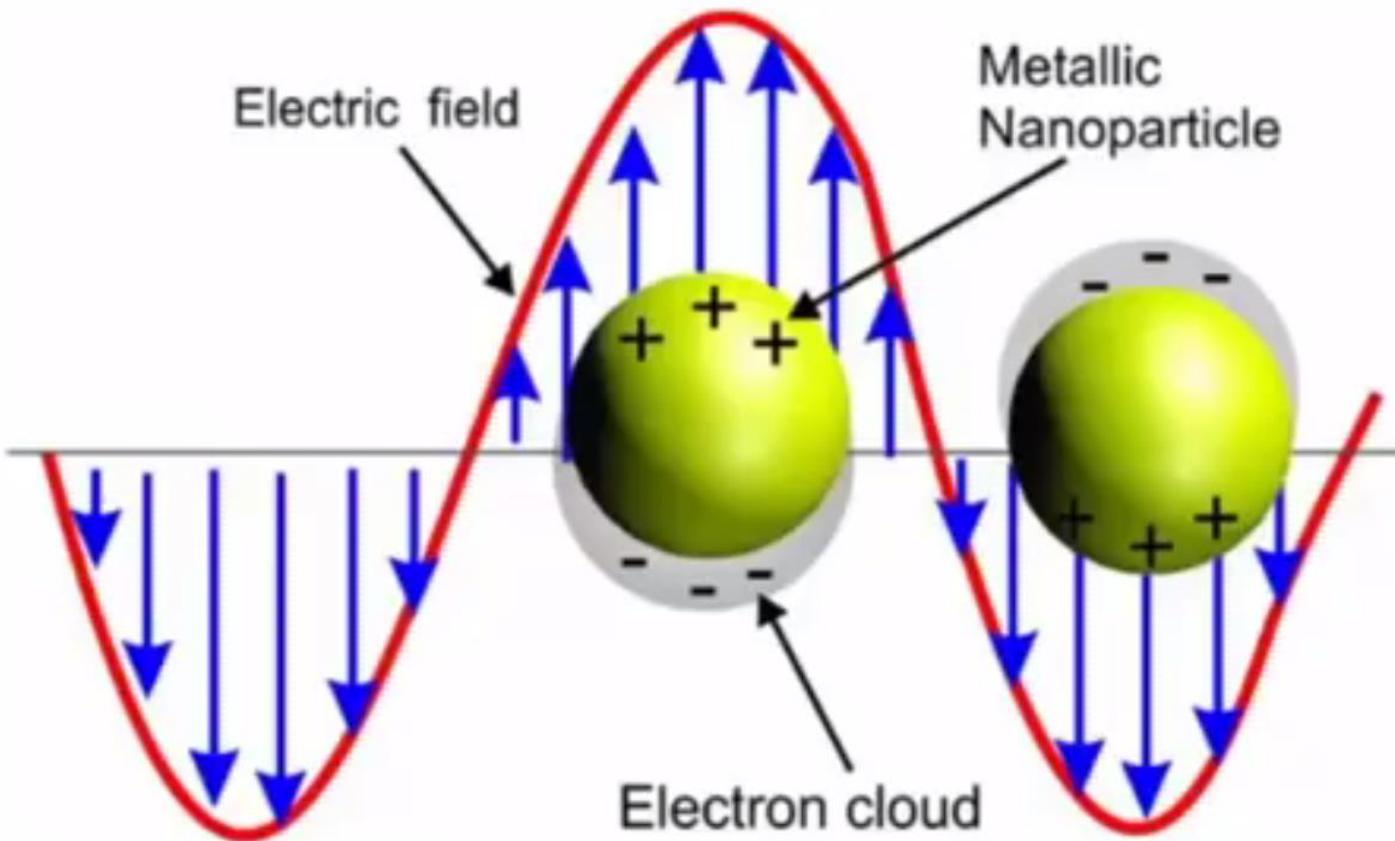


An SP is a natural oscillation of the electron (6s) gas inside a gold particle.

Surface plasmon is excited when a long-wavelength electromagnetic wave is incident on a metallic sphere.

SP frequency depends on the dielectric function of the gold, and the shape of the nanoparticle.

The wavelengths of the light are larger than the size of the particles....



Plasmon energy equation

The plasmon energy is described classically:

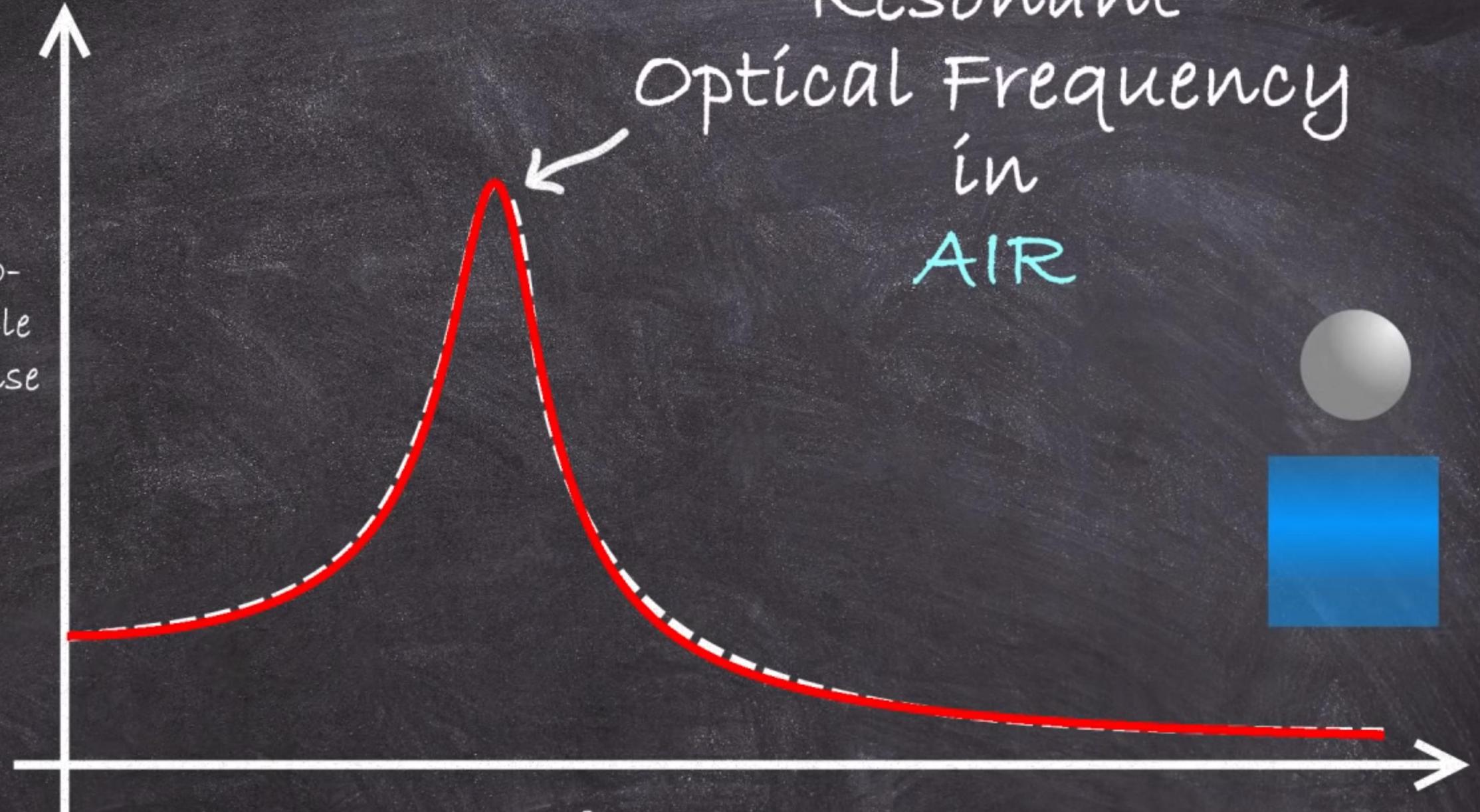
$$\omega_p^2 = \frac{Ne^2}{m\epsilon_0}$$

Here, ω_p is the plasmon resonance frequency, N is the number density of the electrons ($1/m^3$), e is the electron charge, m is the electron mass, and ϵ_0 is the permittivity of free space. So an increased electron density causes an increase in the plasmon resonance frequency (blue-shift). This helps explain why different materials (like Ag vs. Au) have nanoparticles that are different colors, even if they are the same size and shape.

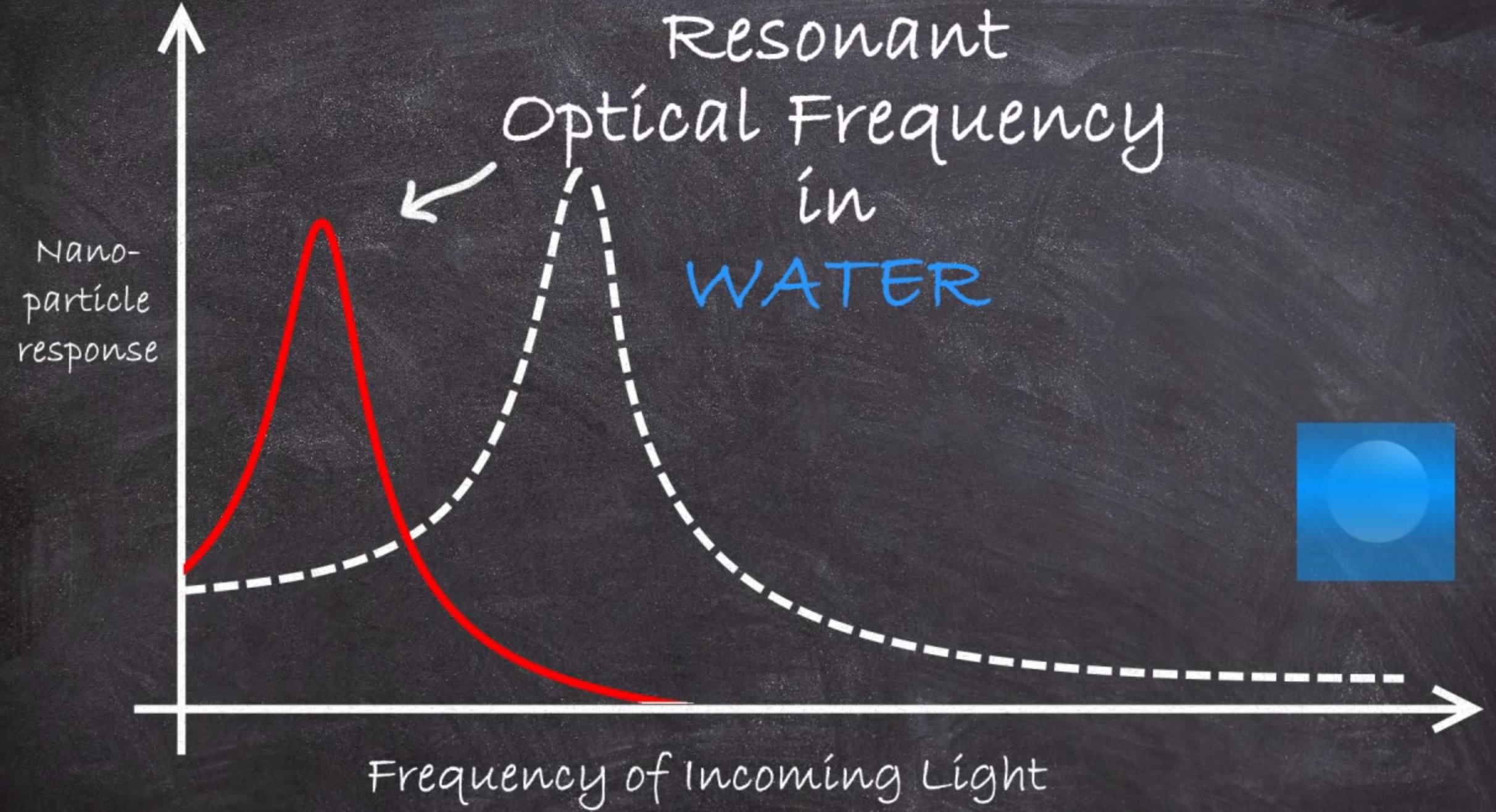
Resonant

Optical Frequency
in
AIR

Nano-
particle
response



Frequency of Incoming Light



Effect of size and surroundings

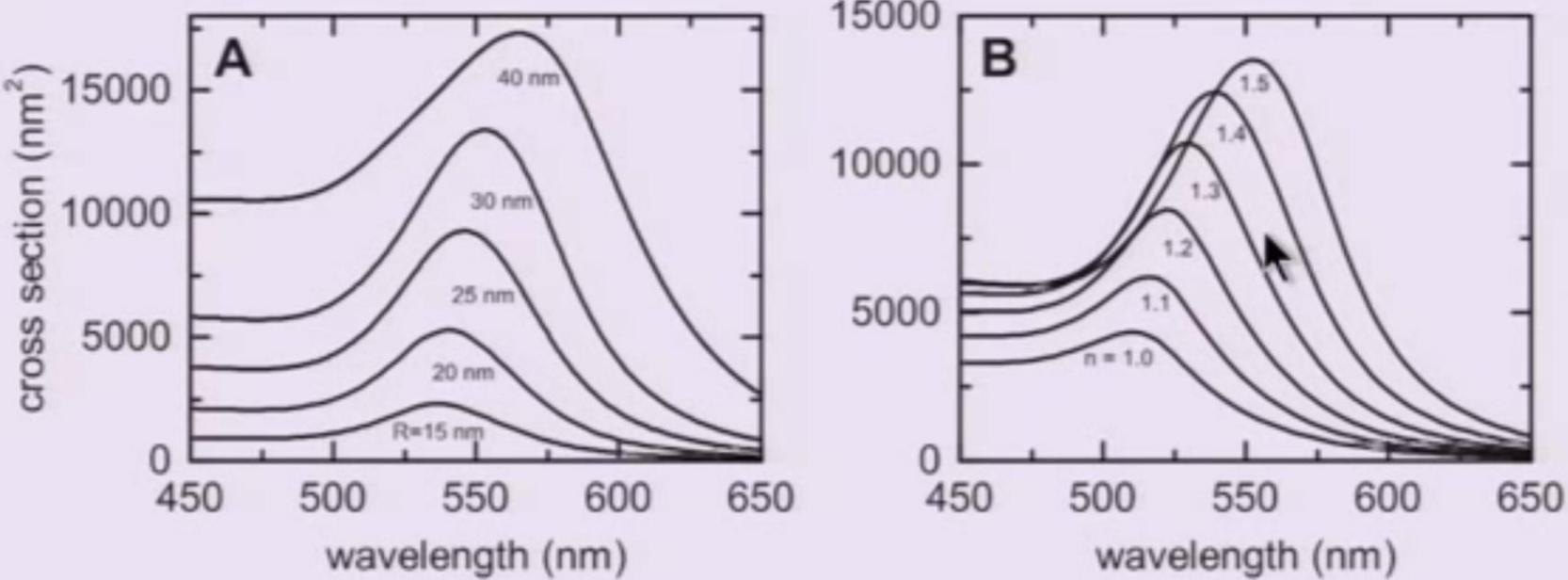
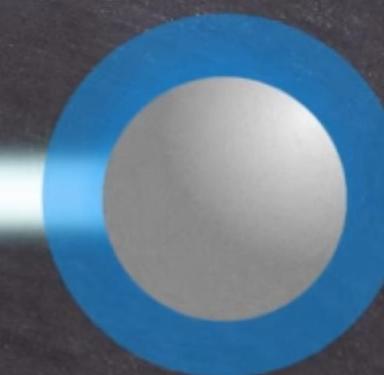
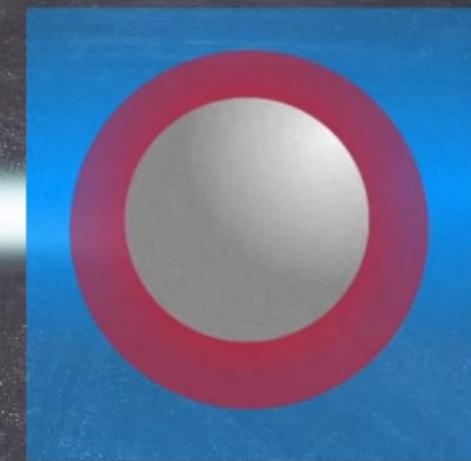
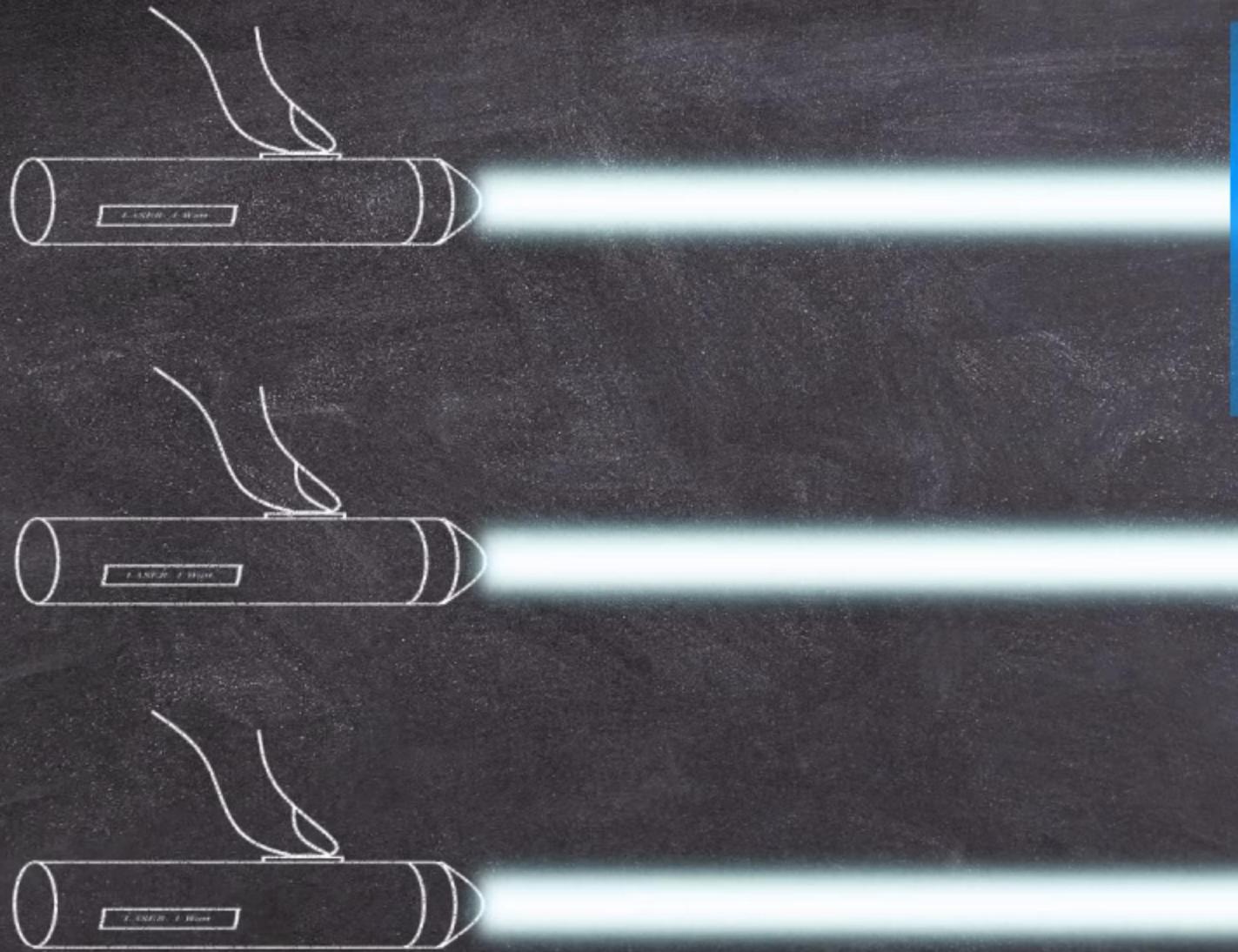
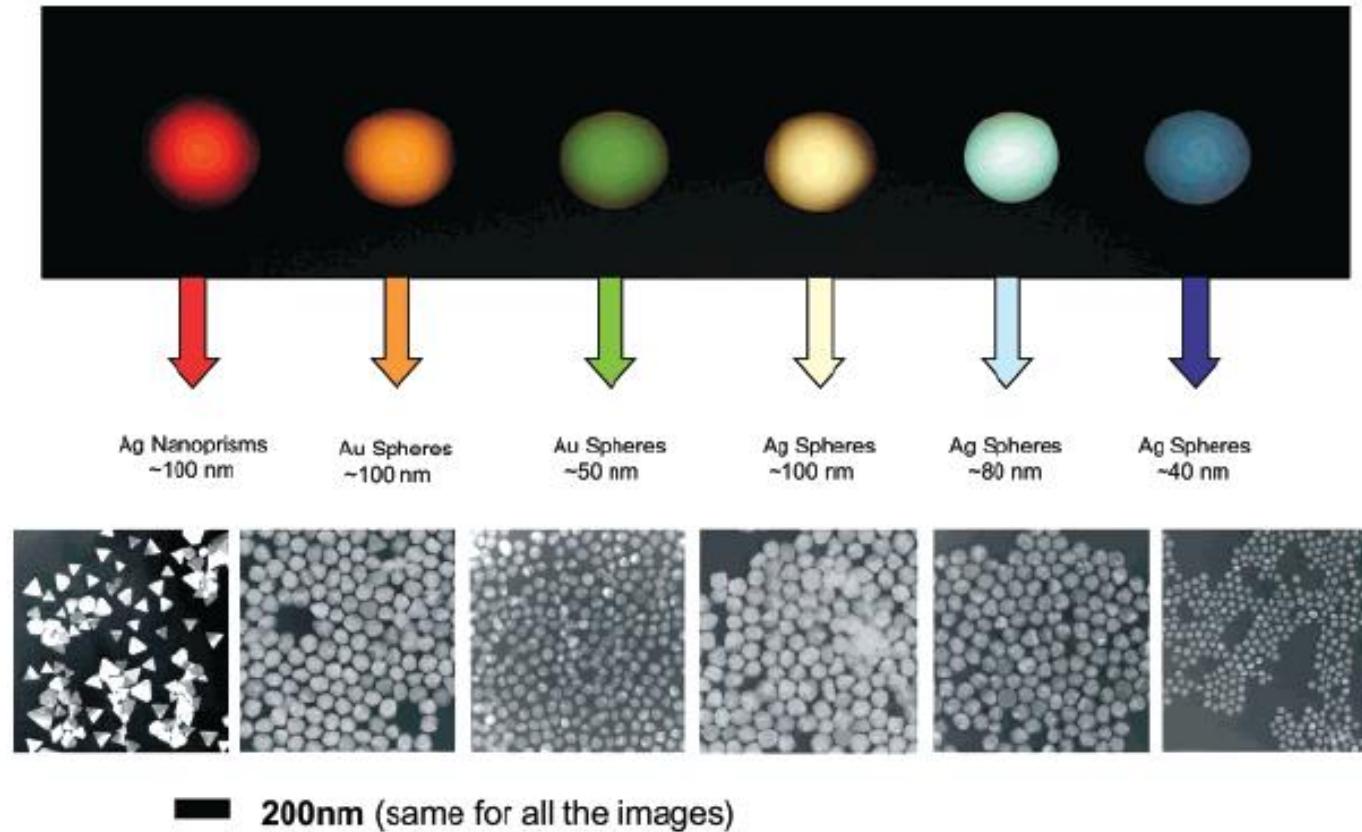


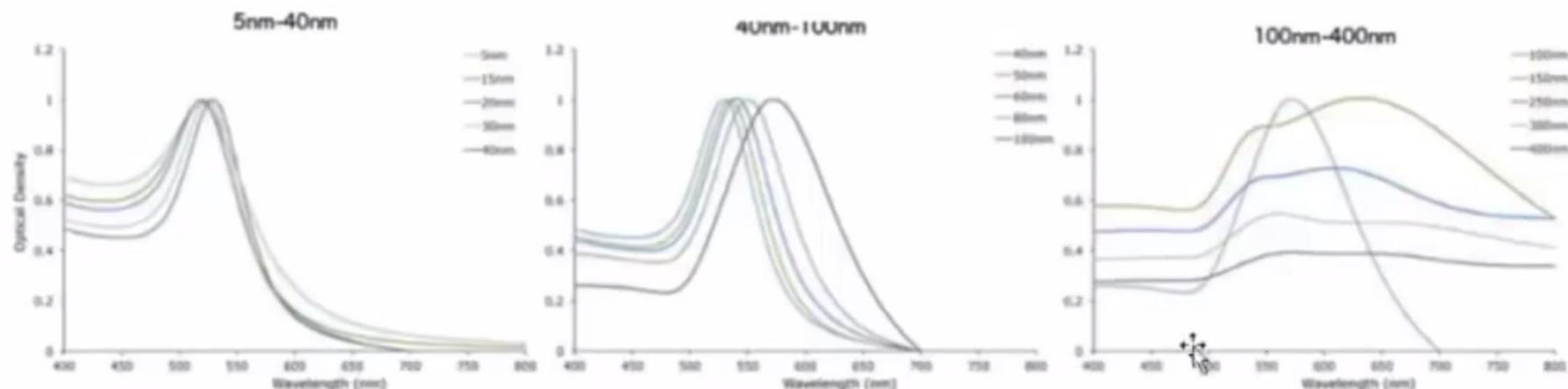
Figure 1.4: Absorption spectra for increasing radius with $n_m = 1.5$ (A), and for increasing refractive index with $R = 30 \text{ nm}$ (B).



Metal Nanoparticles: Color depends on shape and size



UV-Vis Spectra of Au nanoparticles



From Sigmaaldrich.com: The absorbance of incident light changes as you change the size of the nanoparticle. You can see a distinct peak in the nanoparticle's spectrum, that changes wavelength as the particle size changes. As the particle gets larger, you can see the spectrum becomes more and more continuous, similar to bulk gold.

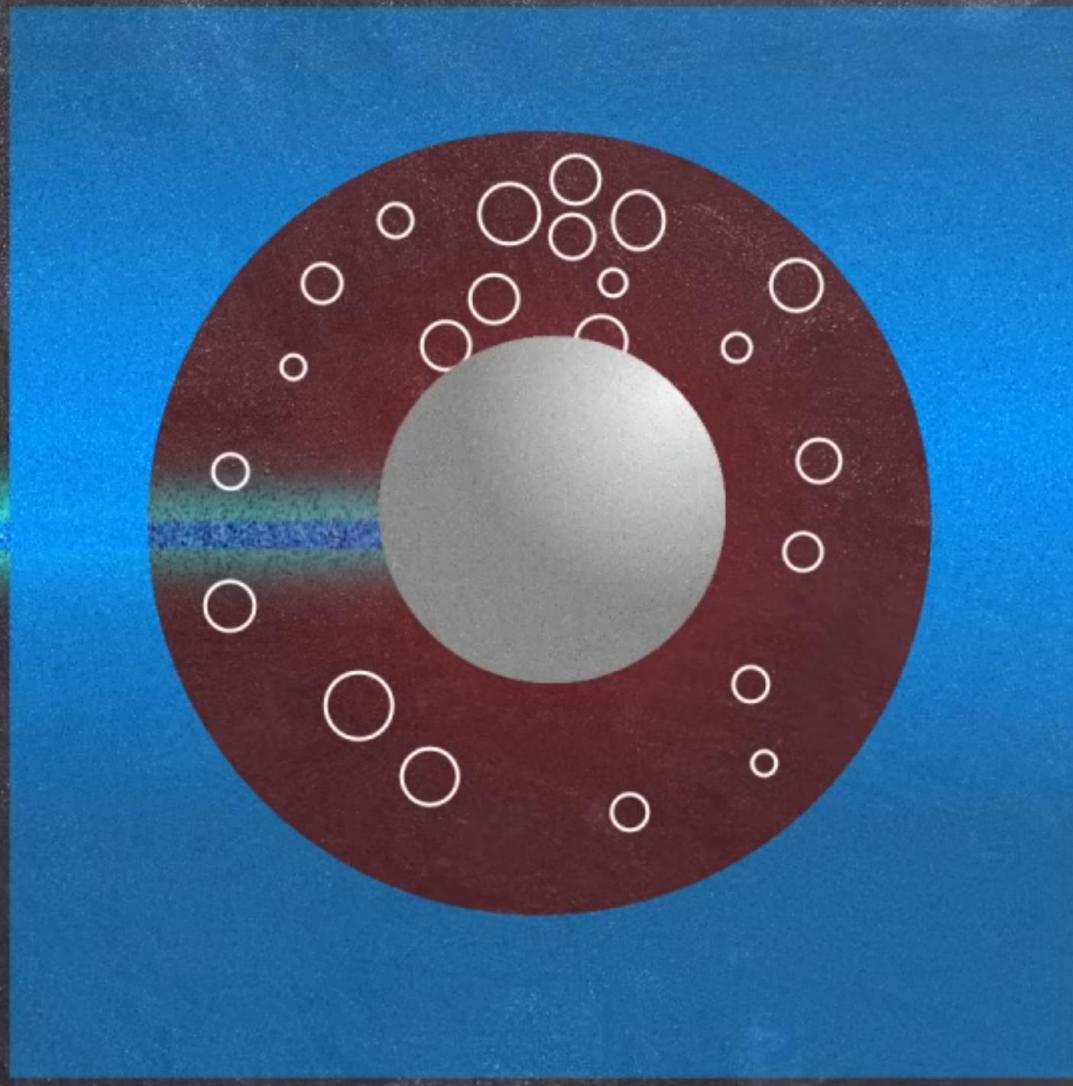


Ok... but what do you
DO with them?

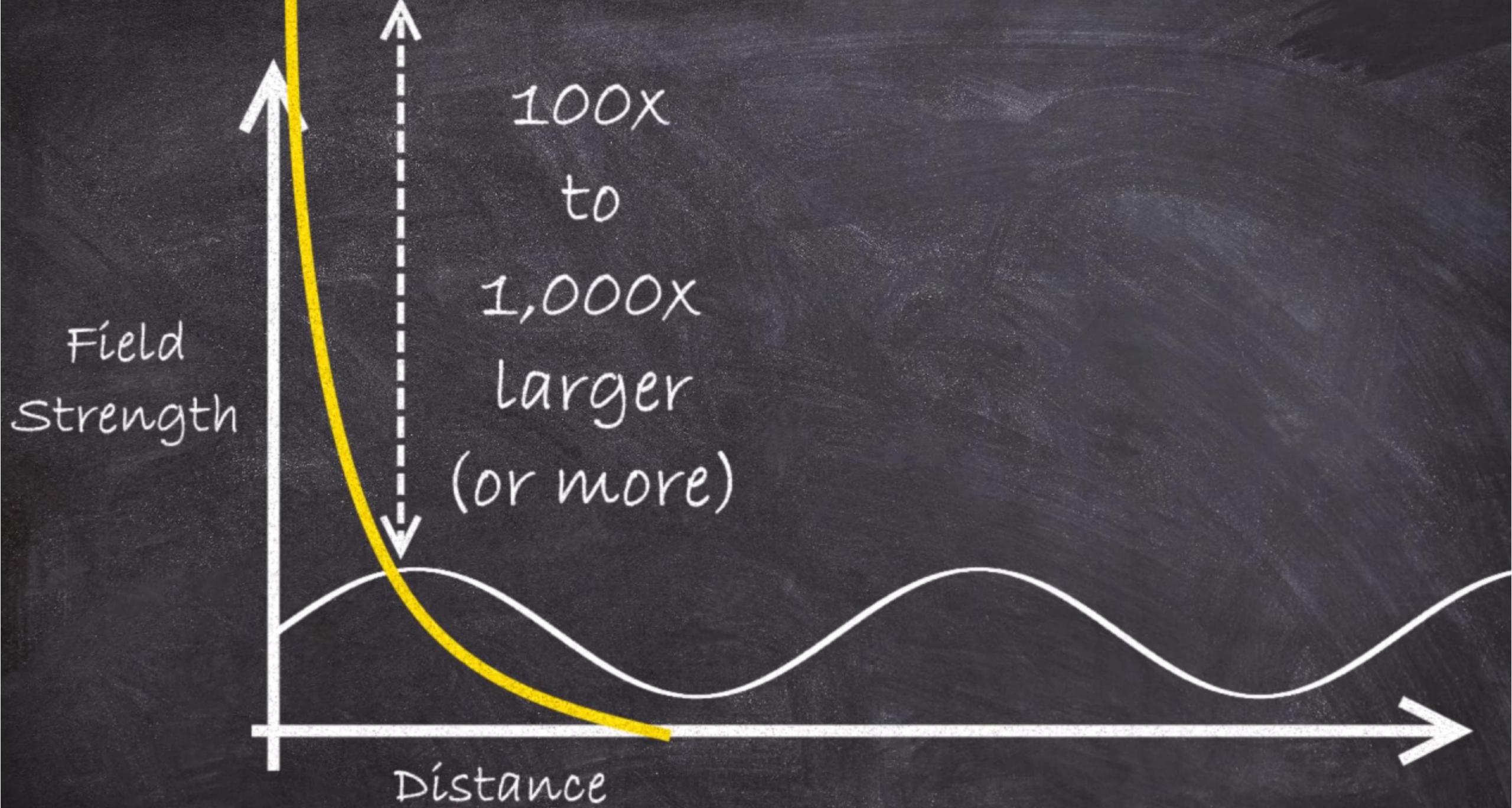
Field Enhancement

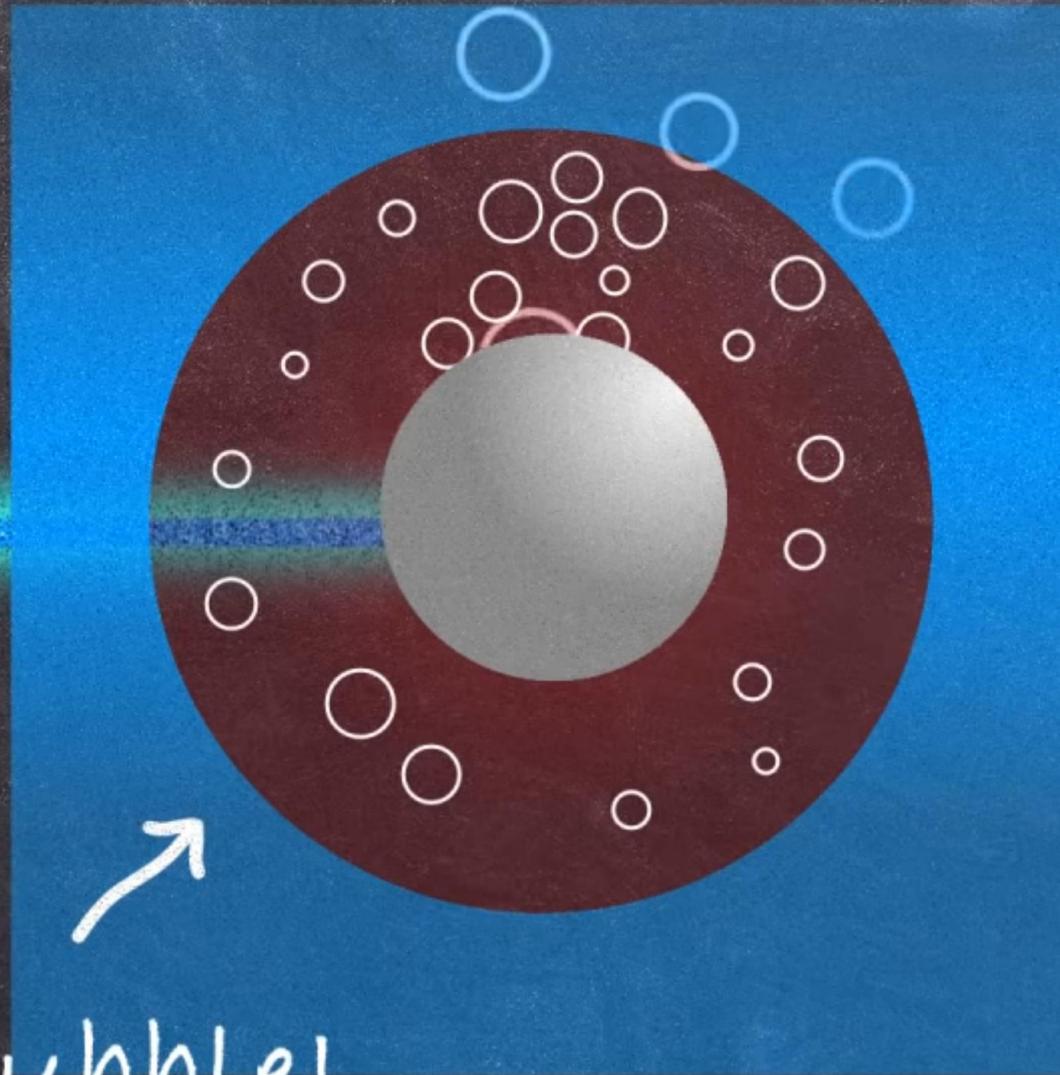
can enhance

LIGHT ABSORPTION

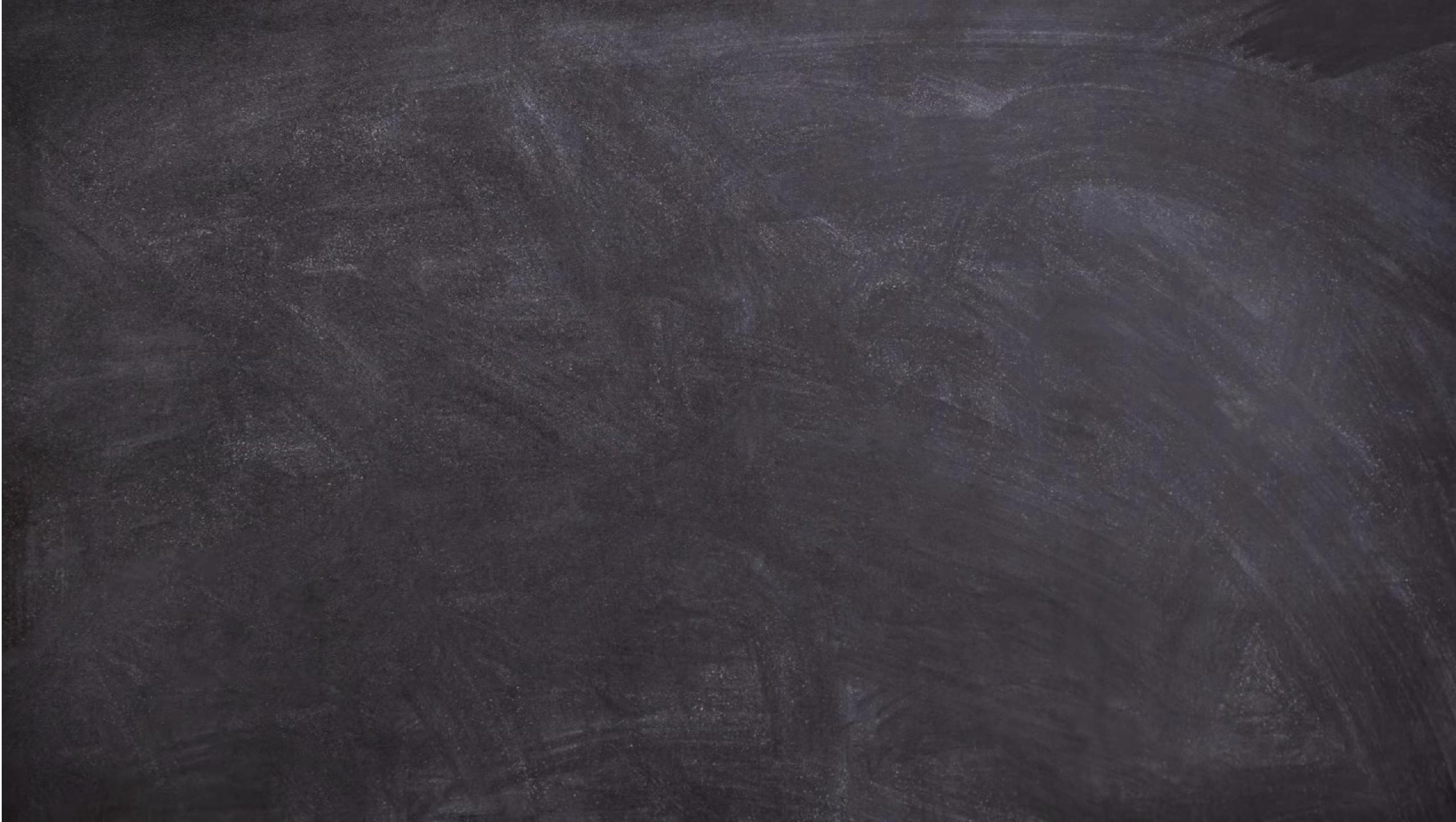


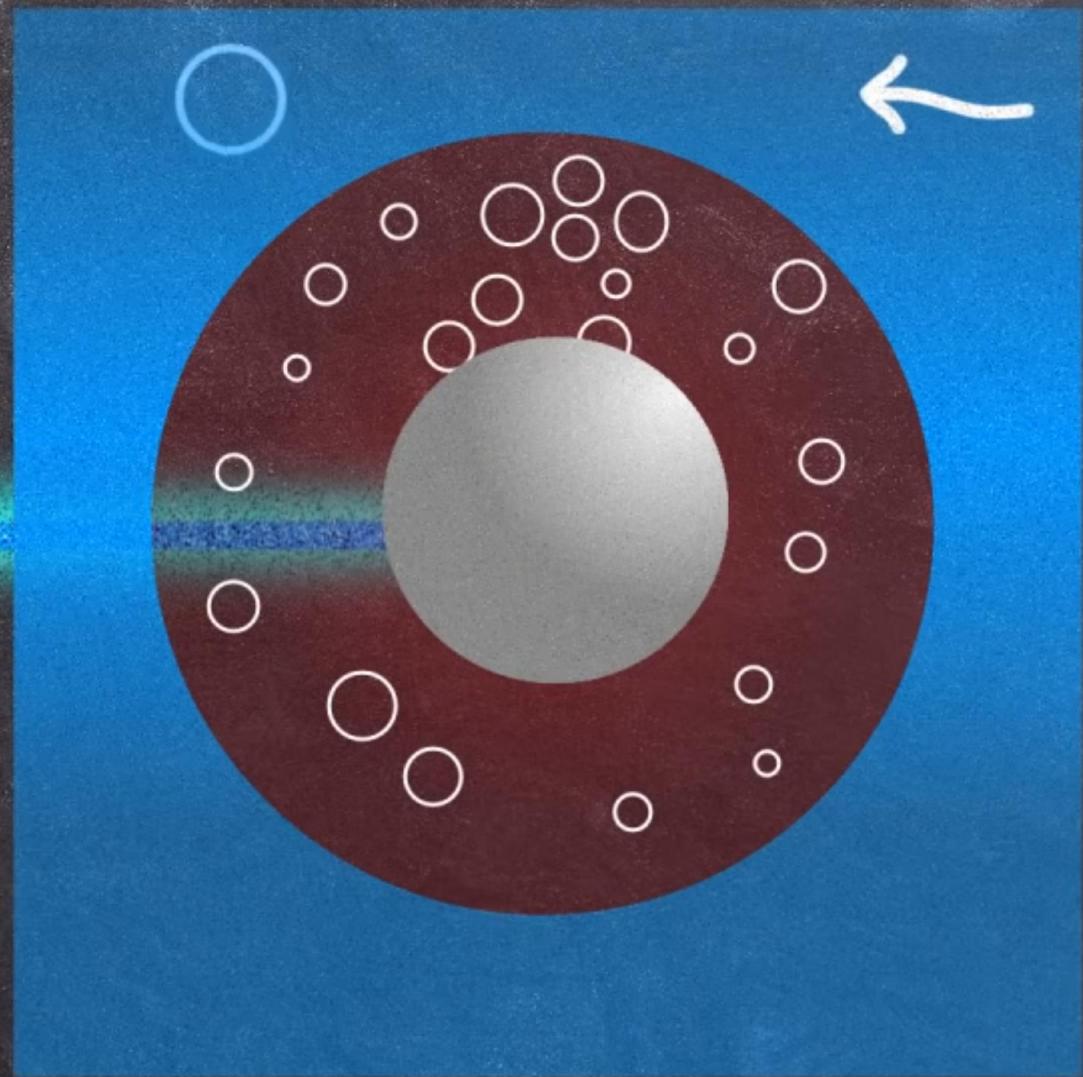
Even at ROOM TEMPERATURE!





Steam bubble!

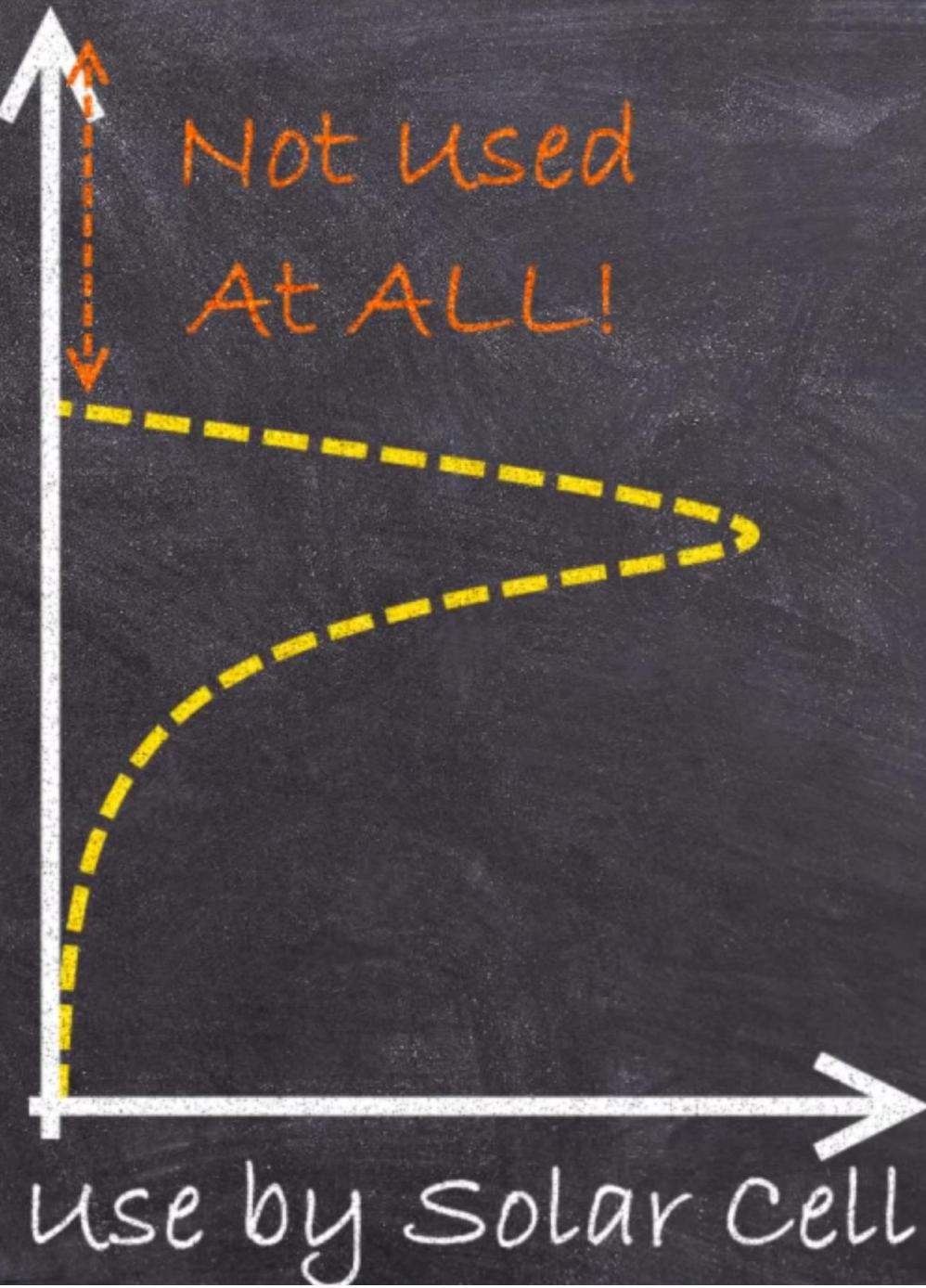




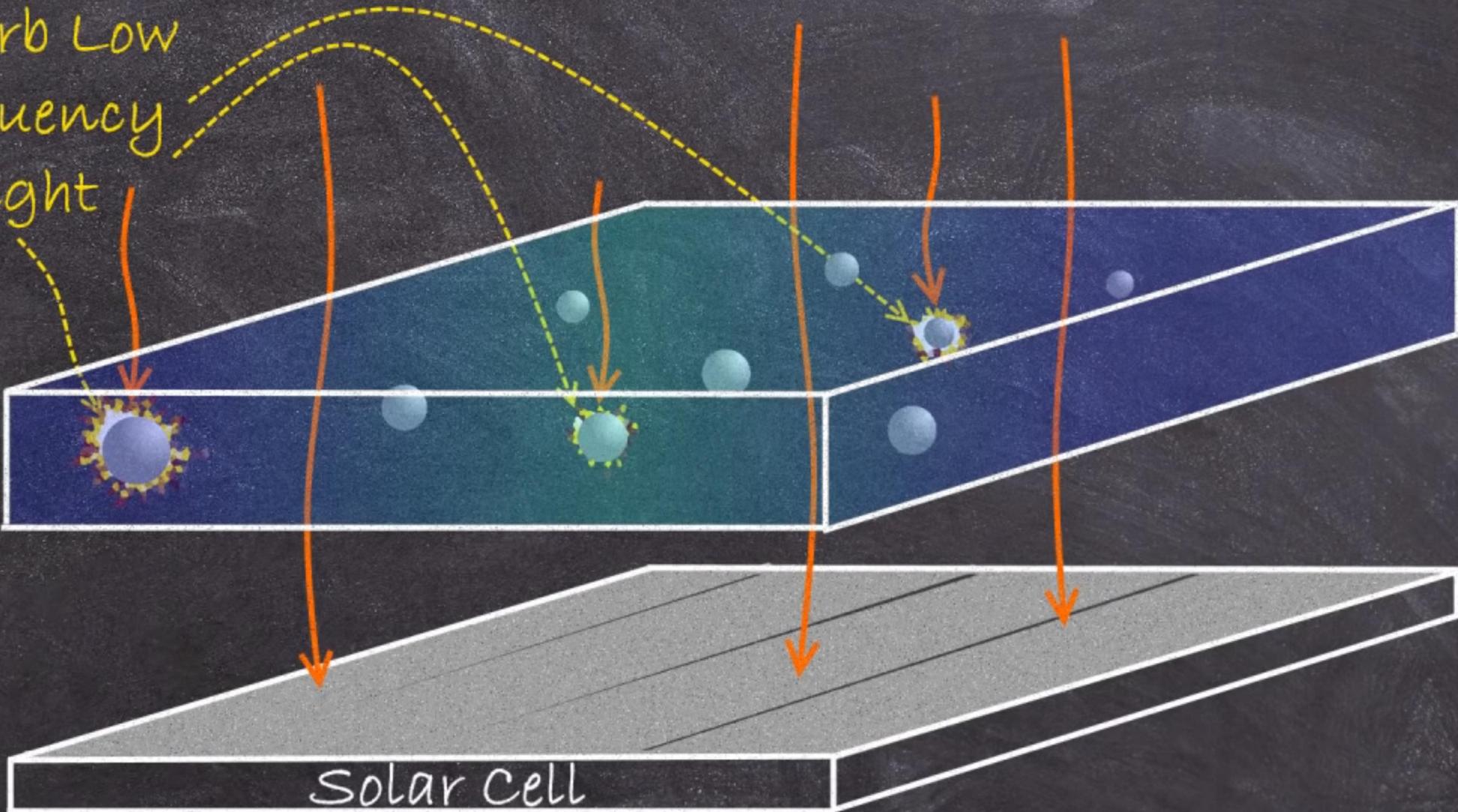
could be a
chemical
reaction!

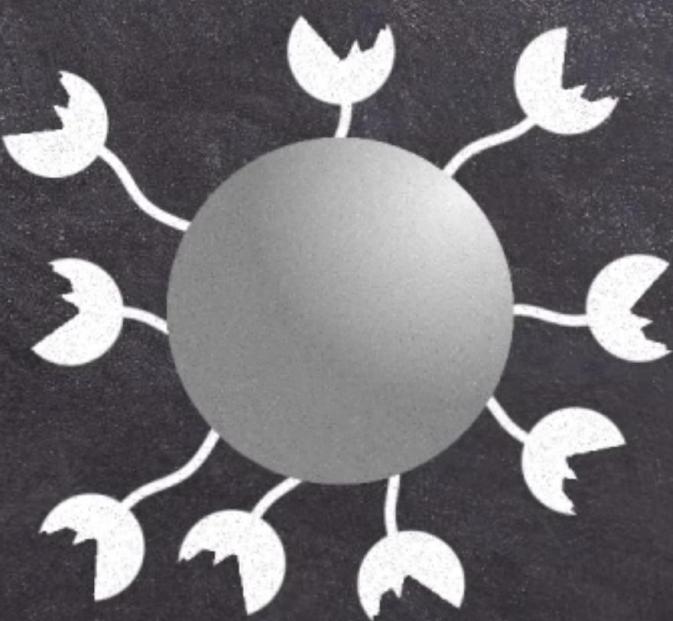
Hybríd
Photo-
Voltaíc
Thermal
(HPVT)

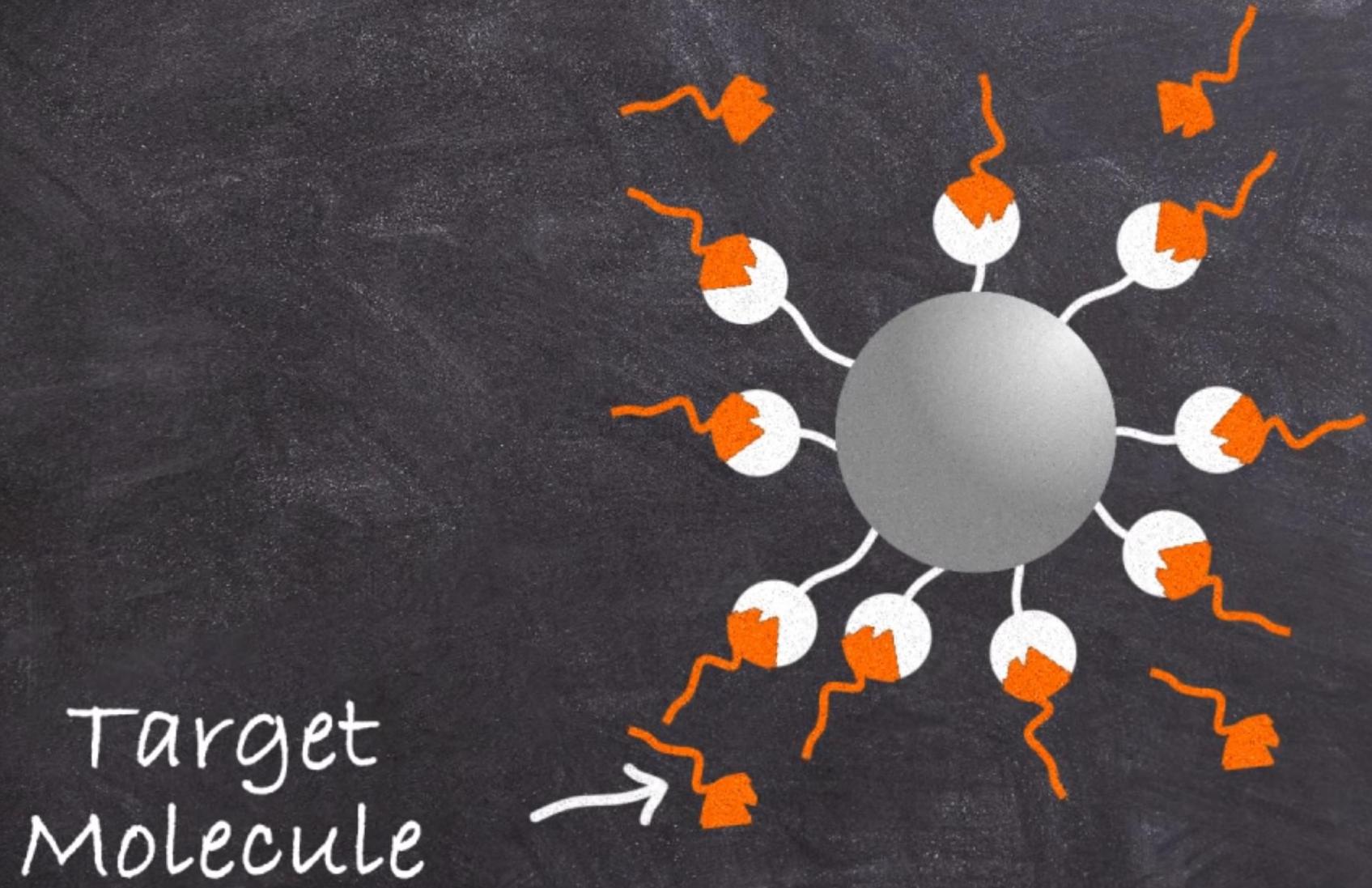
wavelength
of
Light



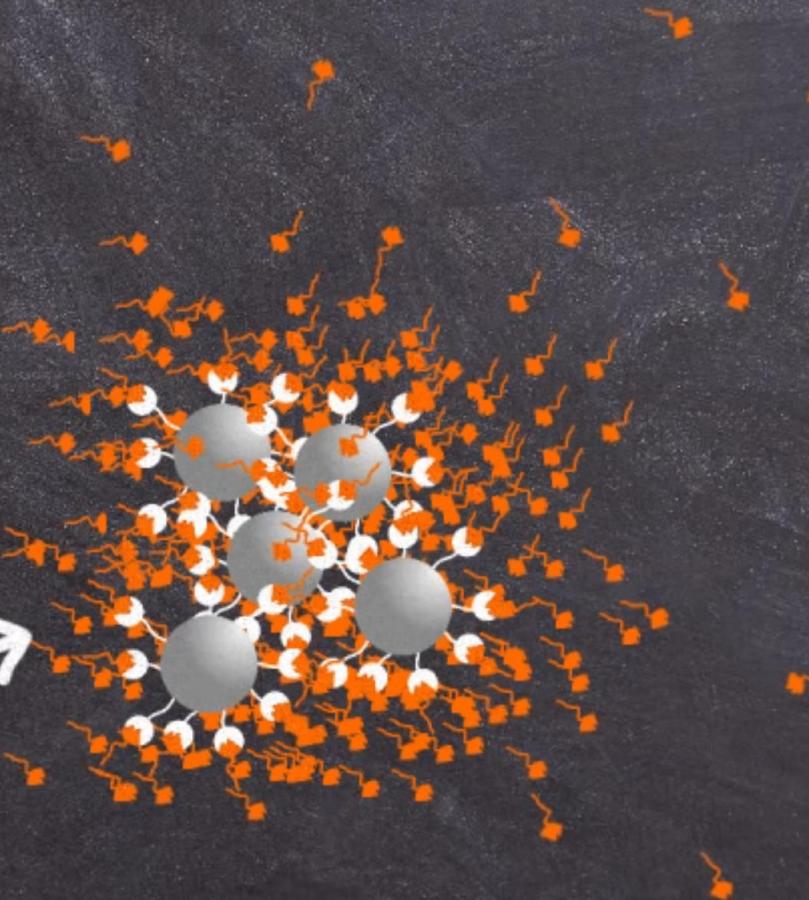
Nanoparticles
Absorb Low
Frequency
Light

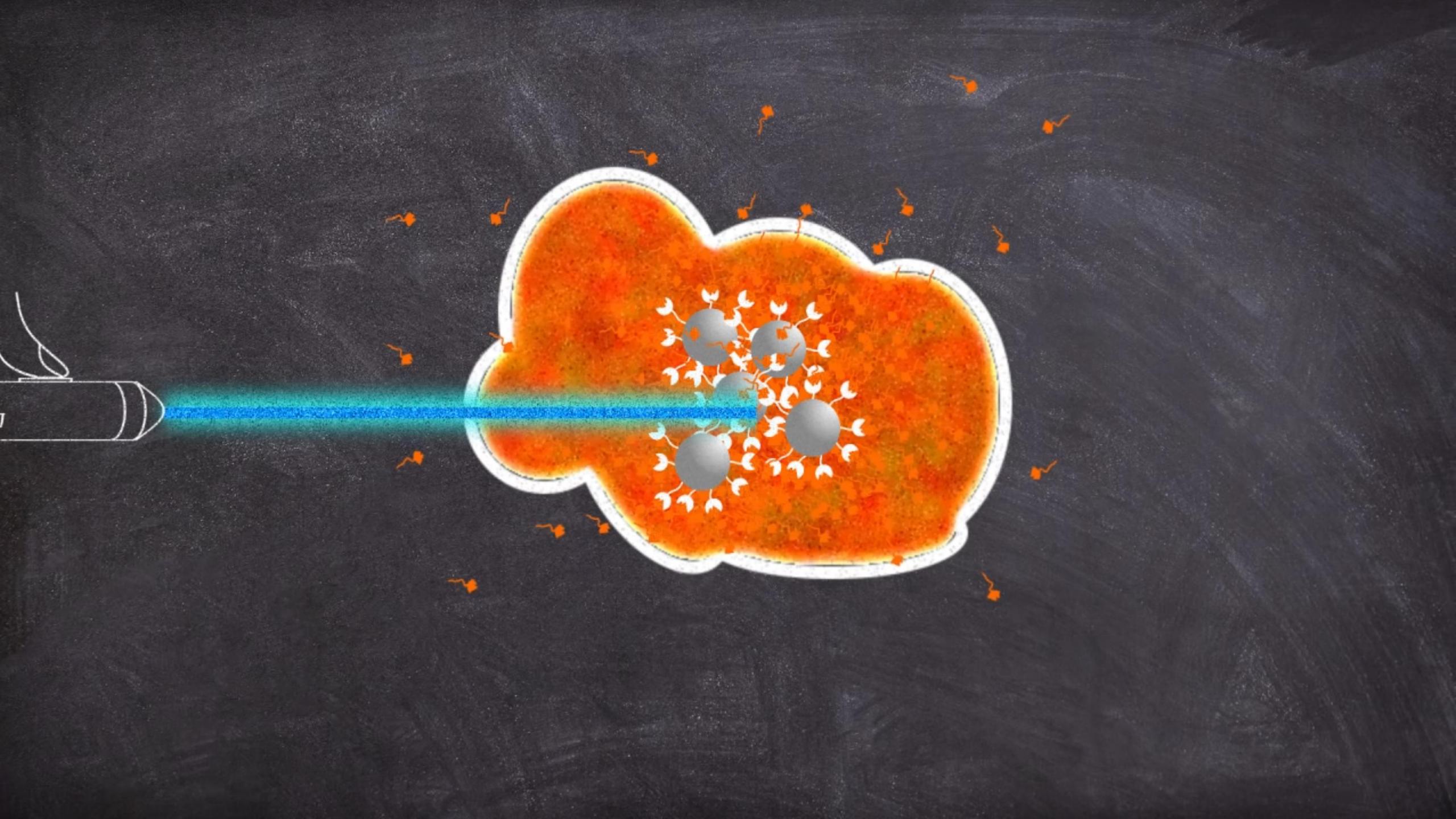






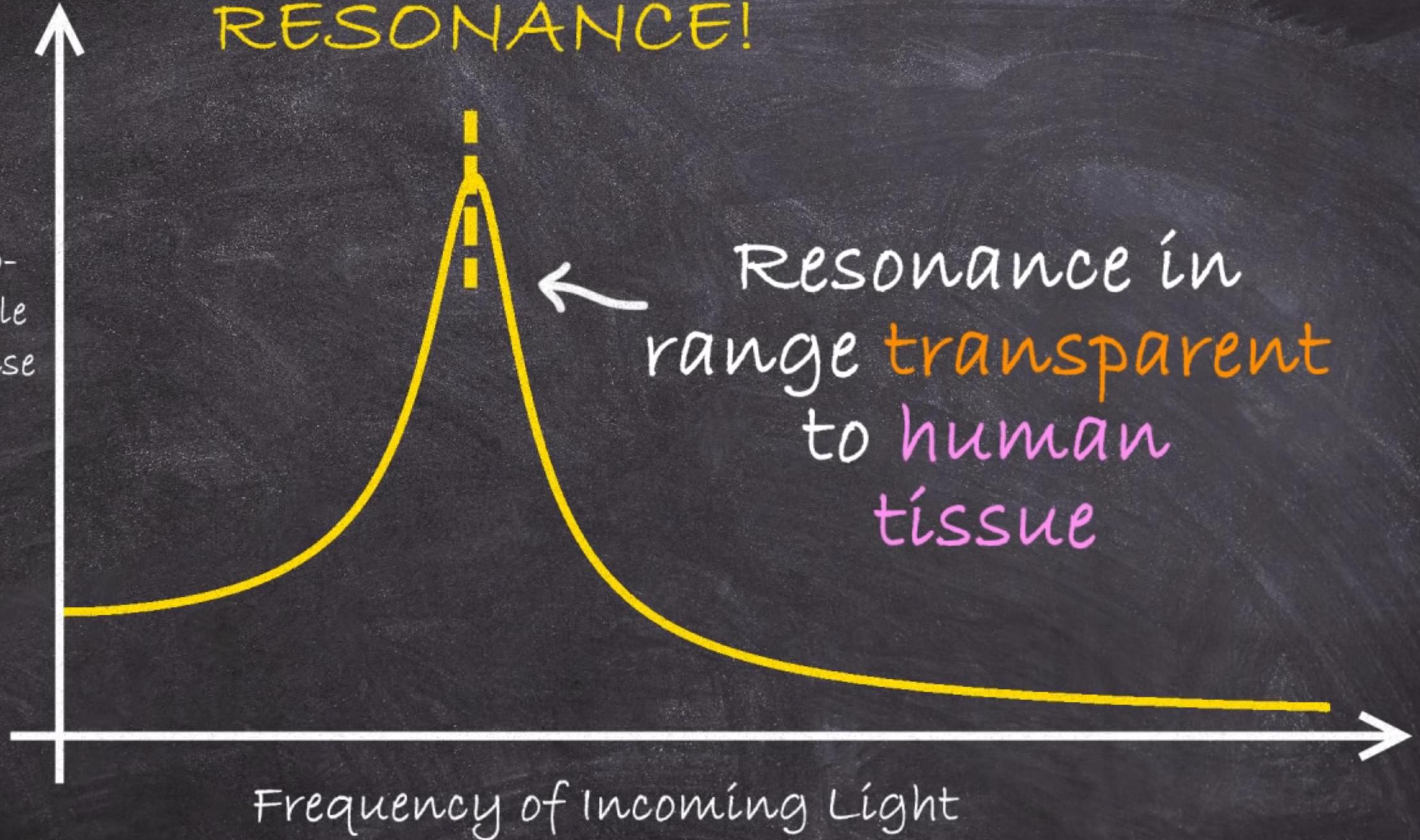
Concentration
of target
molecule

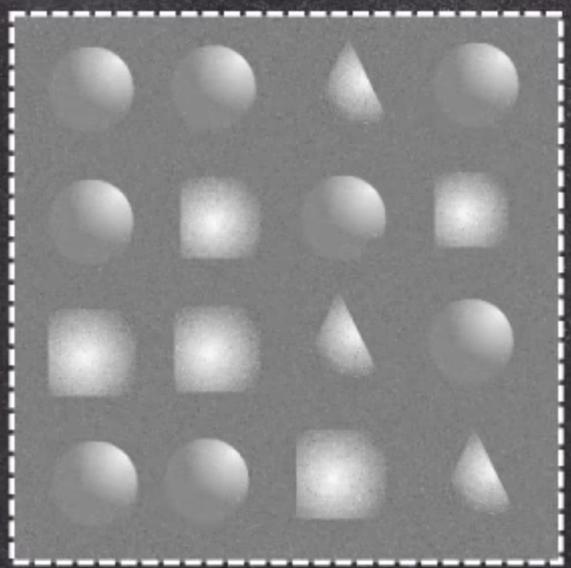




RESONANCE!

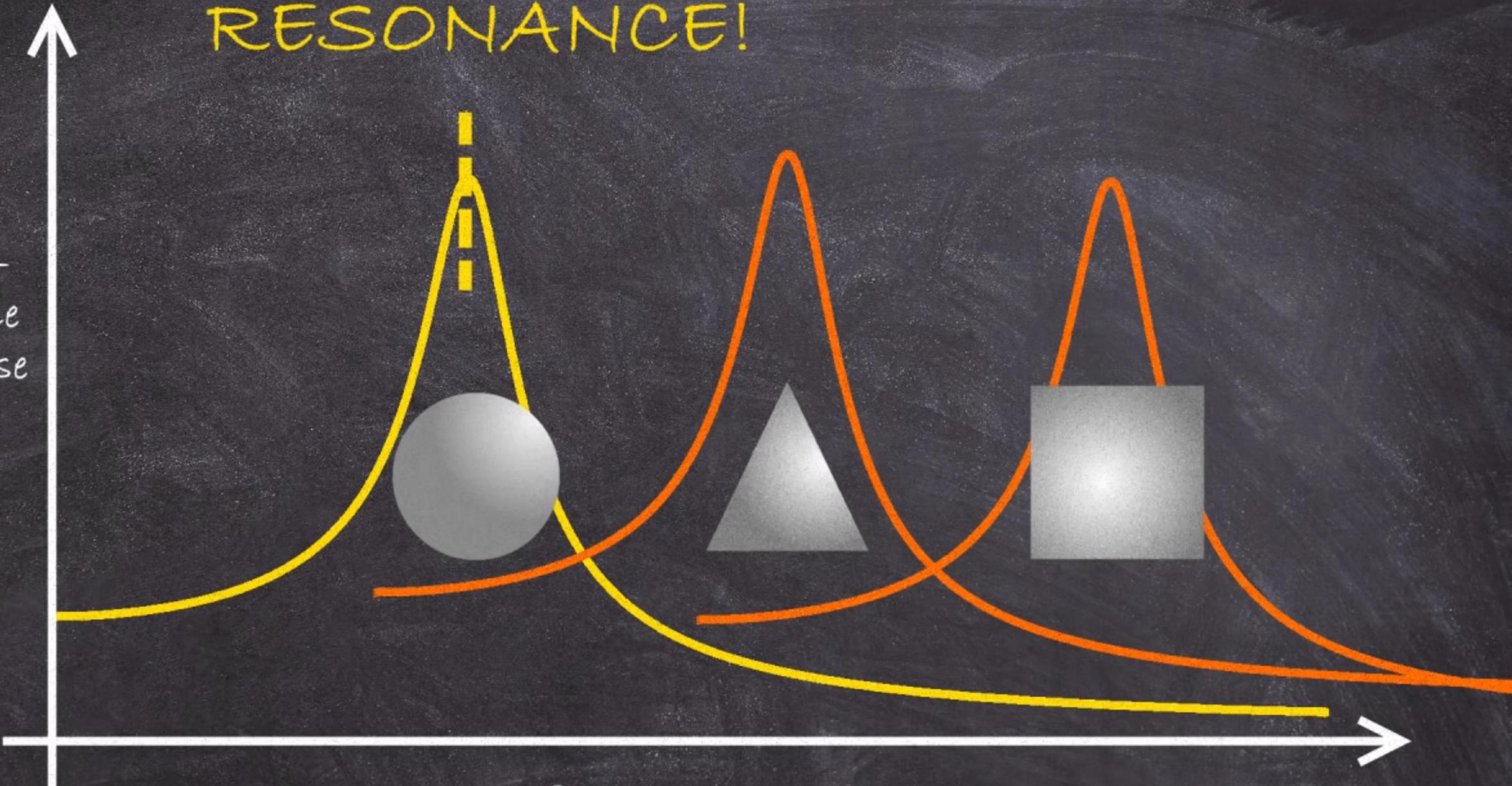
Nano-
particle
response





RESONANCE!

Nano-particle response



Frequency of Incoming Light

DYNAMIC plasmonic
displays

aka

“Electronic paper”

Silver-atom-containing
-GEL



Electro-chromic polymers

Surface Plasmon Resonance (SPR)

At an interface between two transparent media of different refractive index (glass and water), light coming from the side of higher refractive index is partly reflected and partly refracted. Above a certain critical angle of incidence, no light is refracted across the interface, and total internal reflection is observed.

While incident light is totally reflected the electromagnetic field component penetrates a short (tens of nanometers) distance into a medium of a lower refractive index creating an exponentially detenuating evanescent wave.

If the interface between the media is coated with a thin layer of metal (gold), and light is monochromatic and p-polarized, the intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow (called surface plasmon resonance) due to the resonance energy transfer between evanescent wave and surface plasmons.

The resonance conditions are influenced by the material adsorbed onto the thin metal film. Satisfactory linear relationship is found between resonance energy and mass concentration of biochemically relevant molecules such as proteins, sugars and DNA.

The SPR signal which is expressed in resonance units is therefore a measure of mass concentration at the sensor chip surface. This means that the analyte and ligand association and dissociation can be observed and ultimately rate constants as well as equilibrium constants can be calculated.

Plasmonics: merging photonics and electronics at nanoscale dimensions.

Science. 2006 Jan 13;311(5758):189-93

Ozbay E.

Nanotechnology Research Center, Bilkent University, Bilkent, Ankara 06800 Turkey. ozbay@bilkent.edu.tr

Electronic circuits provide us with the ability to control the transport and storage of electrons. However, the performance of electronic circuits is now becoming rather limited when digital information needs to be sent from one point to another. Photonics offers an effective solution to this problem by implementing optical communication systems based on optical fibers and photonic circuits. Unfortunately, the micrometer-scale bulky components of photonics have limited the integration of these components into electronic chips, which are now measured in nanometers. Surface plasmon-based circuits, which merge electronics and photonics at the nanoscale, may offer a solution to this size-compatibility problem. Here we review the current status and future prospects of plasmonics in various applications including plasmonic chips, light generation, and nanolithography.

PMID: 16410515 [PubMed]

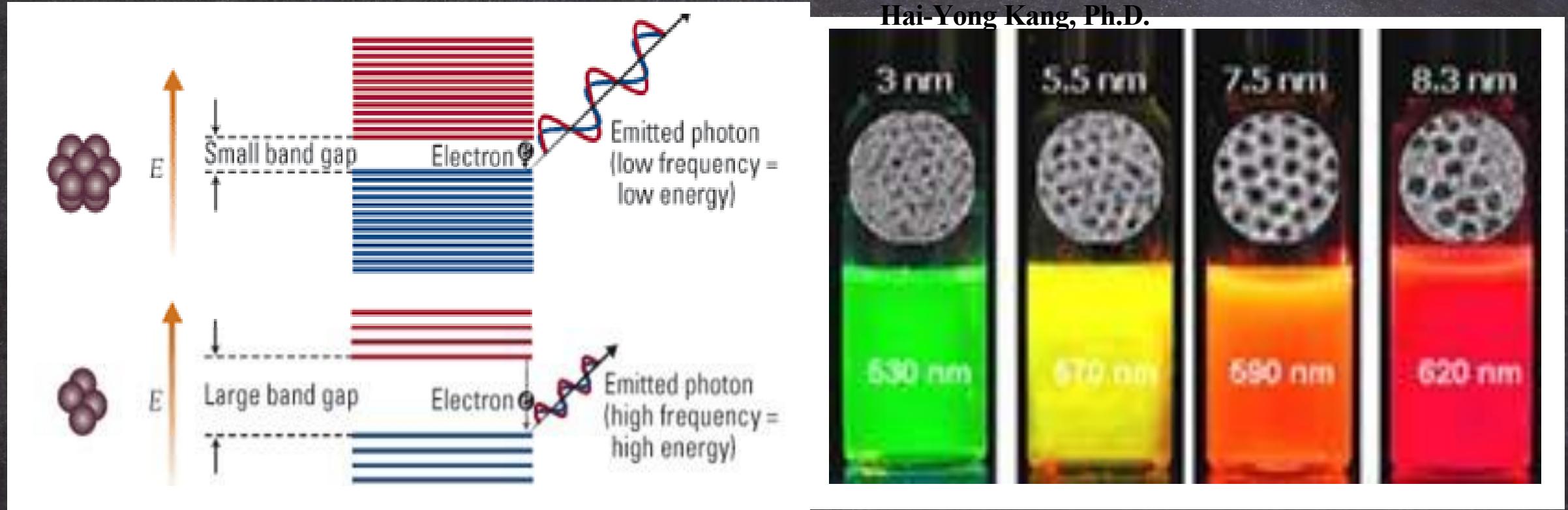
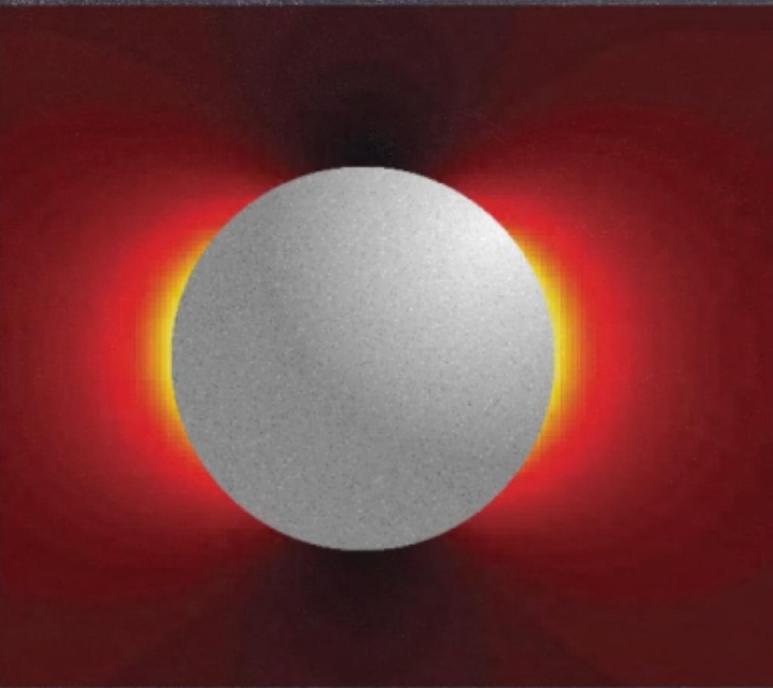
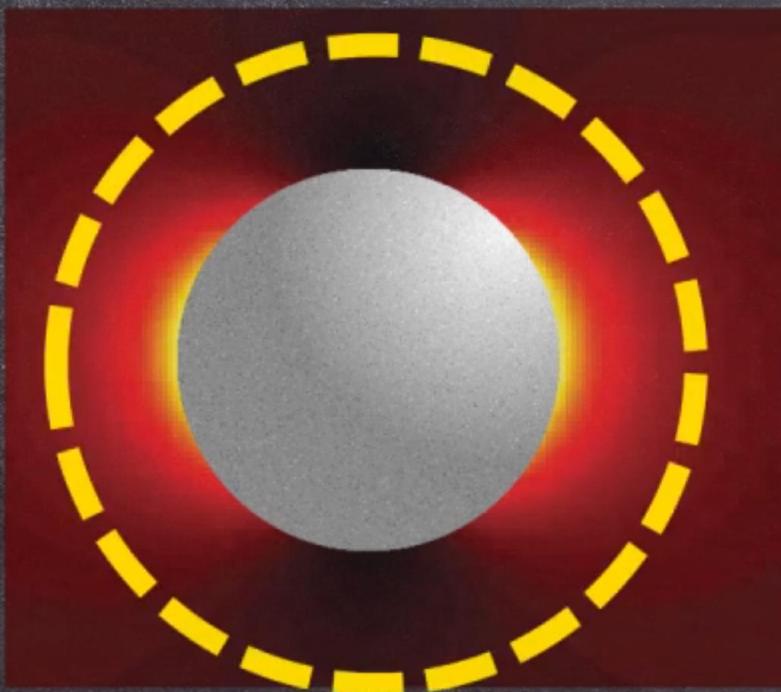


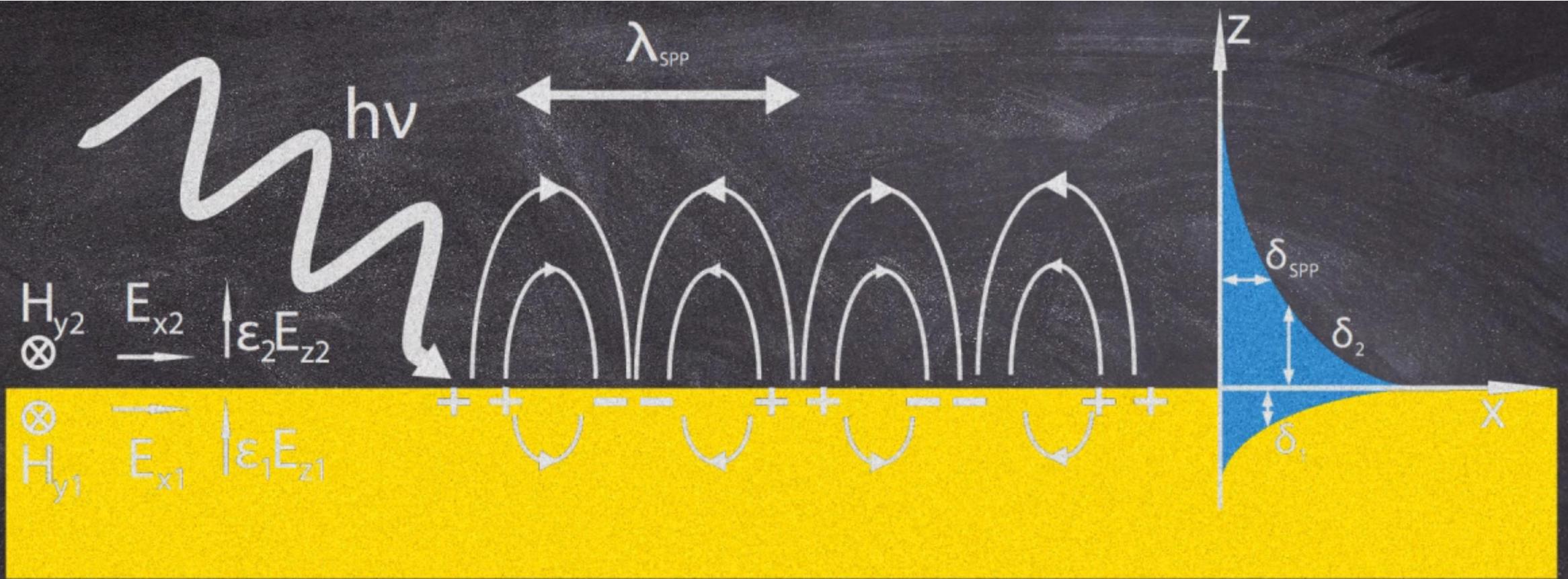
Figure 4.2 Schematic diagrams of band gap and photon energy (Rogers 2008), and changing color of quantum dots according to size of dots (Ocean NanoTech).



This is a LOCALIZED
Surface PLASMONIC RESONANCE
(LSPR)

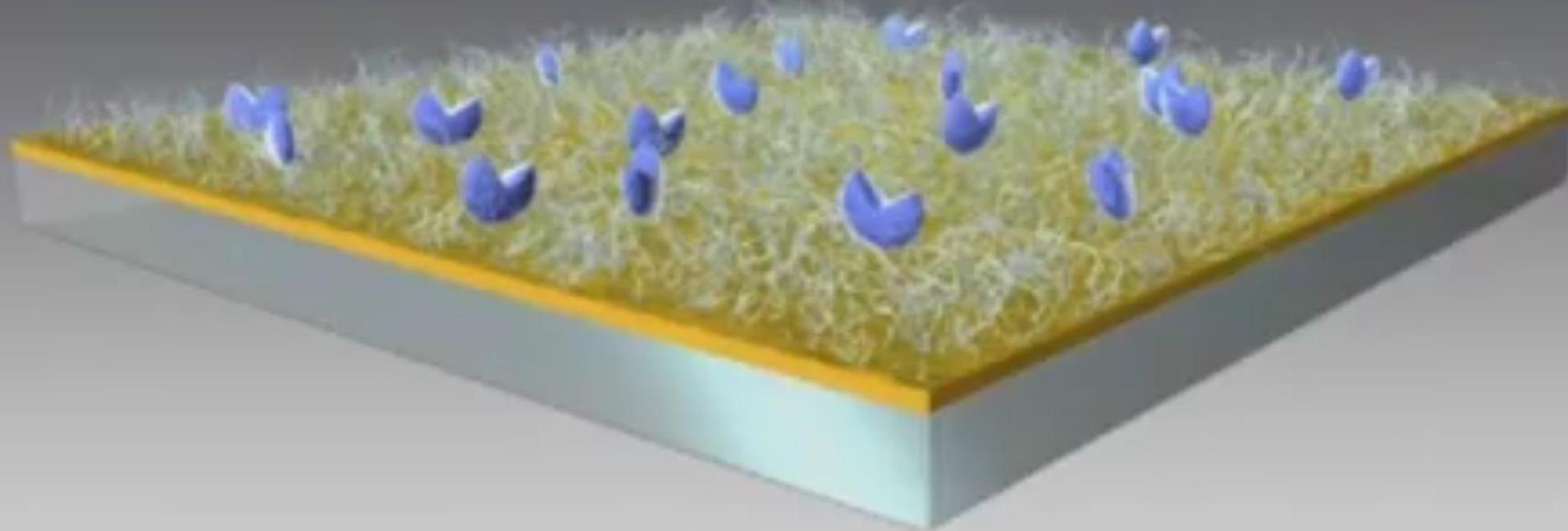


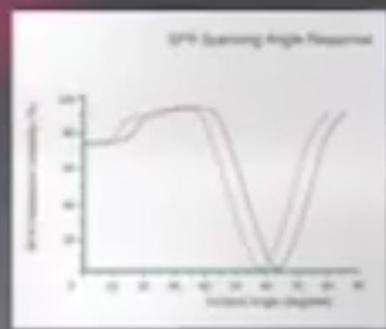
This is a LOCALIZED
Surface PLASMONIC RESONANCE
(LSPR)



Source: https://en.wikipedia.org/wiki/File:Sketch_of_surface_plasmon.png

Surface Plasmoníc Polarítónics! (SPPs)





RECORDED WITH
SCREENCASTOMATIC