École polytechnique fédérale de Lausanne

Neuro X Institute

Laboratory of Chemical Nanotechnology

Applications
Lesson 11

MSE 304

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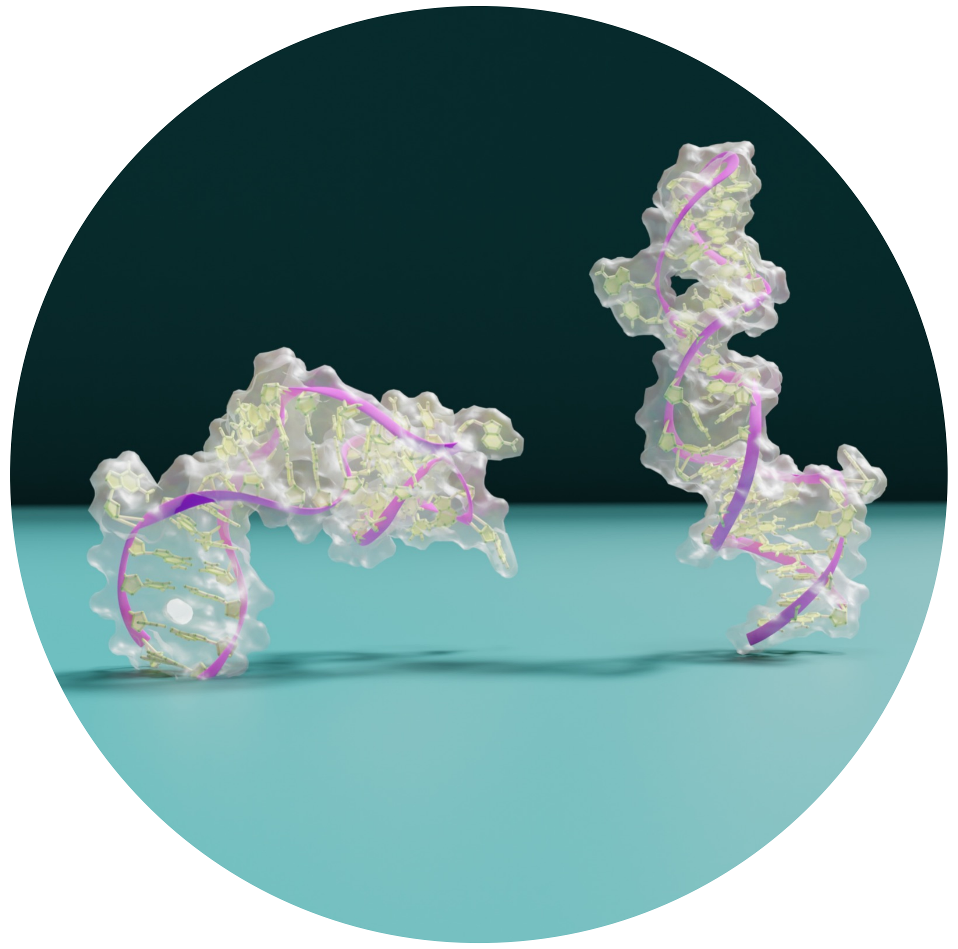
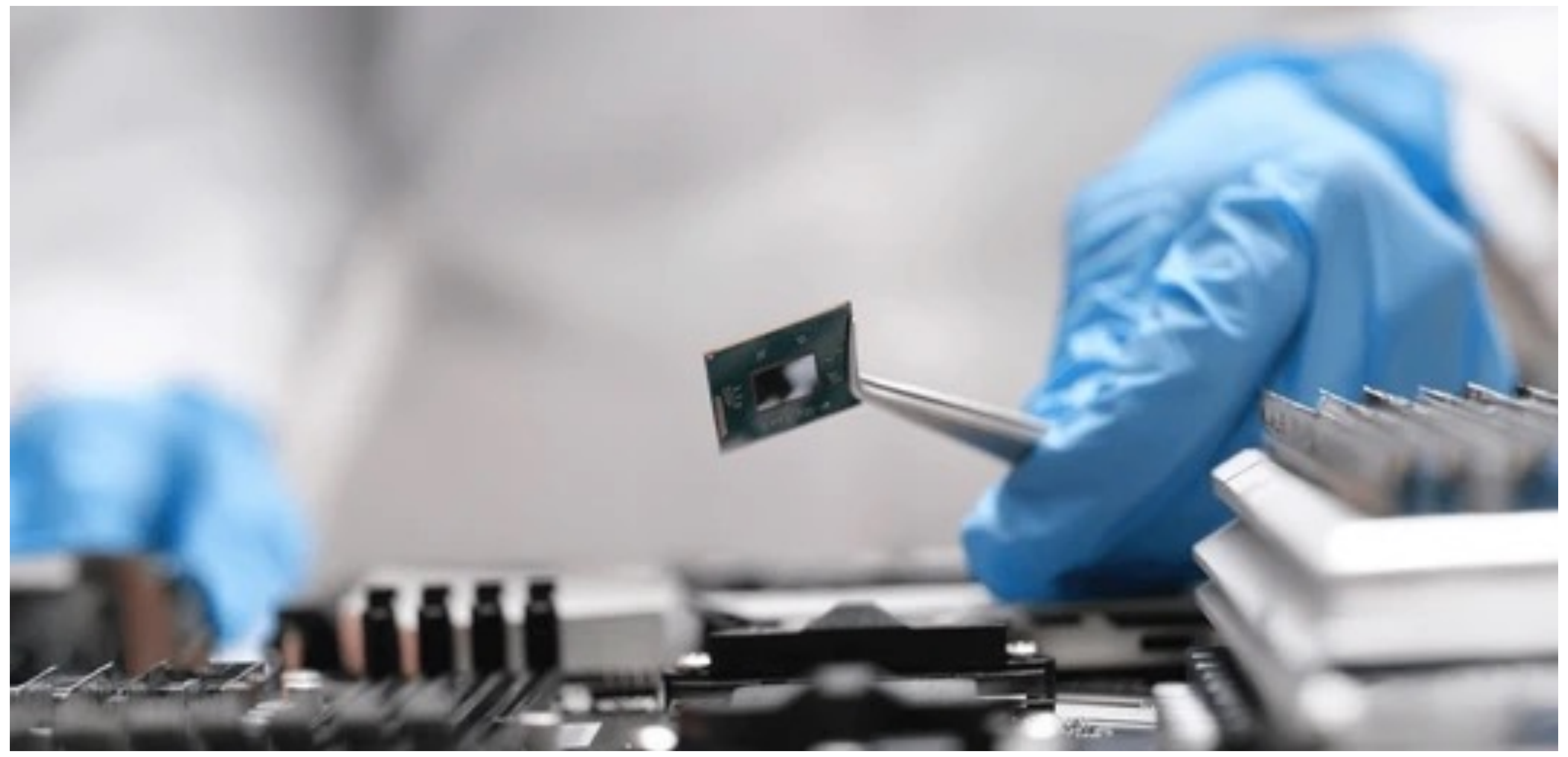
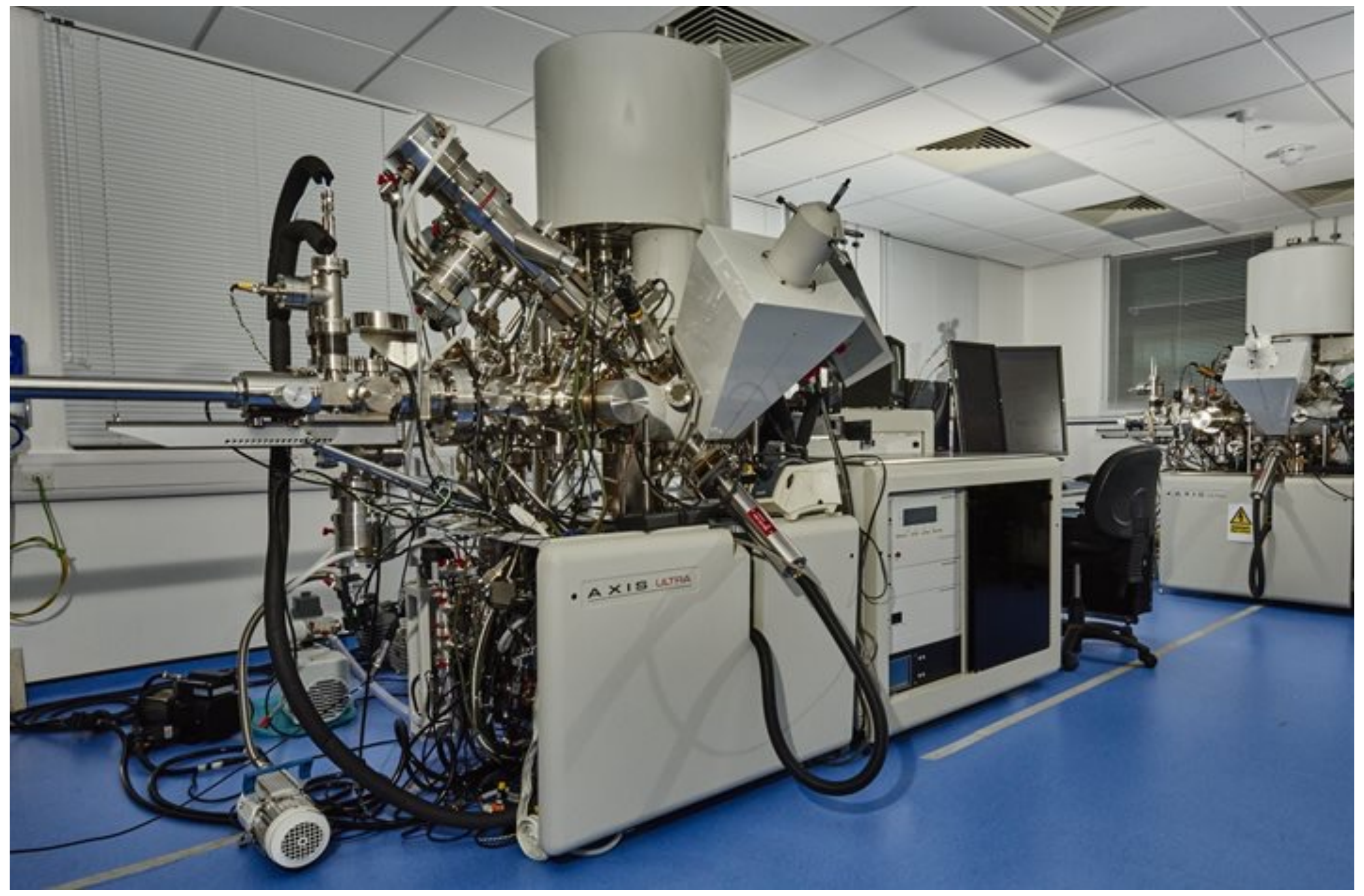
November 29th 2024



Recap of Last Week's Class on Applications

- Surfaces and Interfaces in Nature – how geckos stick to walls
- Artificial Surfaces– the challenge of cleaning and importance of UHV
- Techniques to Monitor Surfaces – contact angle and XPS
- Introduction to Self-Assembled Monolayers



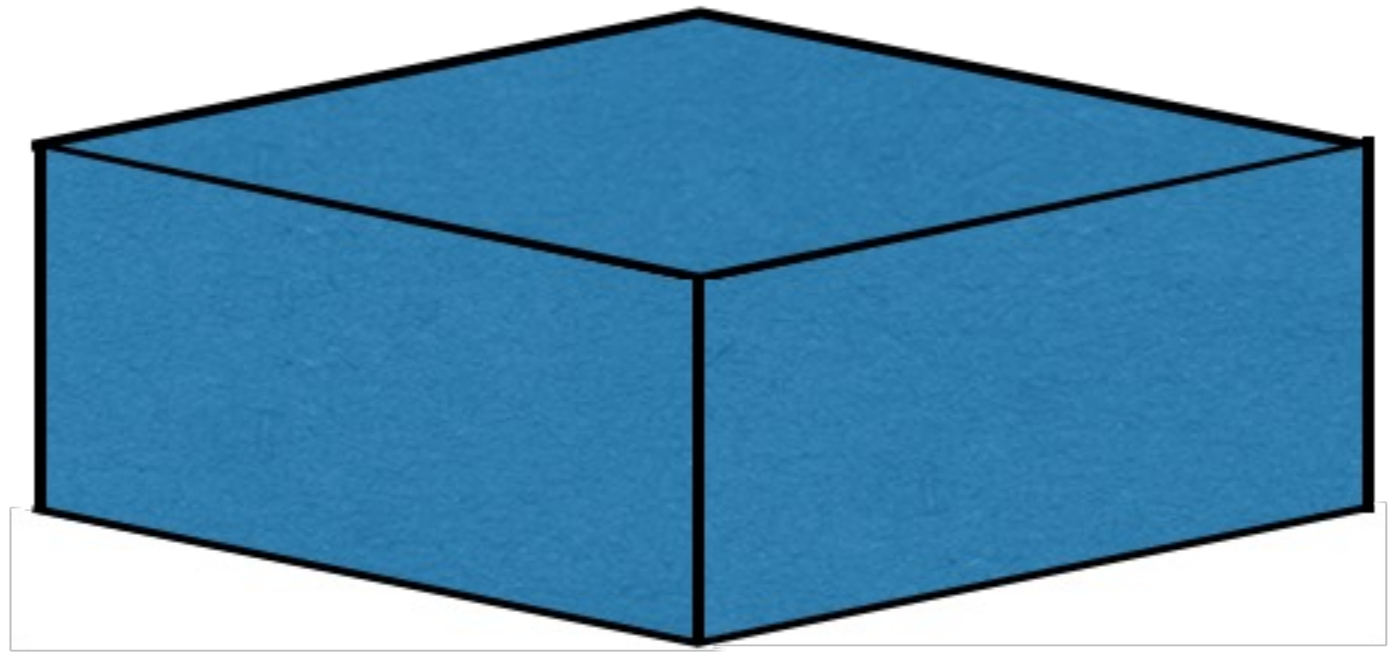


What We Cover in Today's Class

- Surface Chemistry – recap and go more in-depth from the end of last class
  - Alkanethiols – how they assemble on surfaces
  - Alkylsilanes – modifying surfaces beyond metals
  - Polymers – Antifouling mechanisms
- AFM to Visualize Surfaces – with unique advances like FluidFM
- Intro to Nanoscience – recap on work function and band theory
- STM for Higher Resolution Imaging of Surfaces – tunneling effect
- Nanoscale Interactions with Light – recap on plasmon resonance

Surface Chemistry – Why Functionalize Surfaces?

The goal is to combine ideal bulk properties with ideal surface properties



Bulk Properties

Reflect behavior of atoms/molecules within interior of material

Porosity

Thermal conductivity

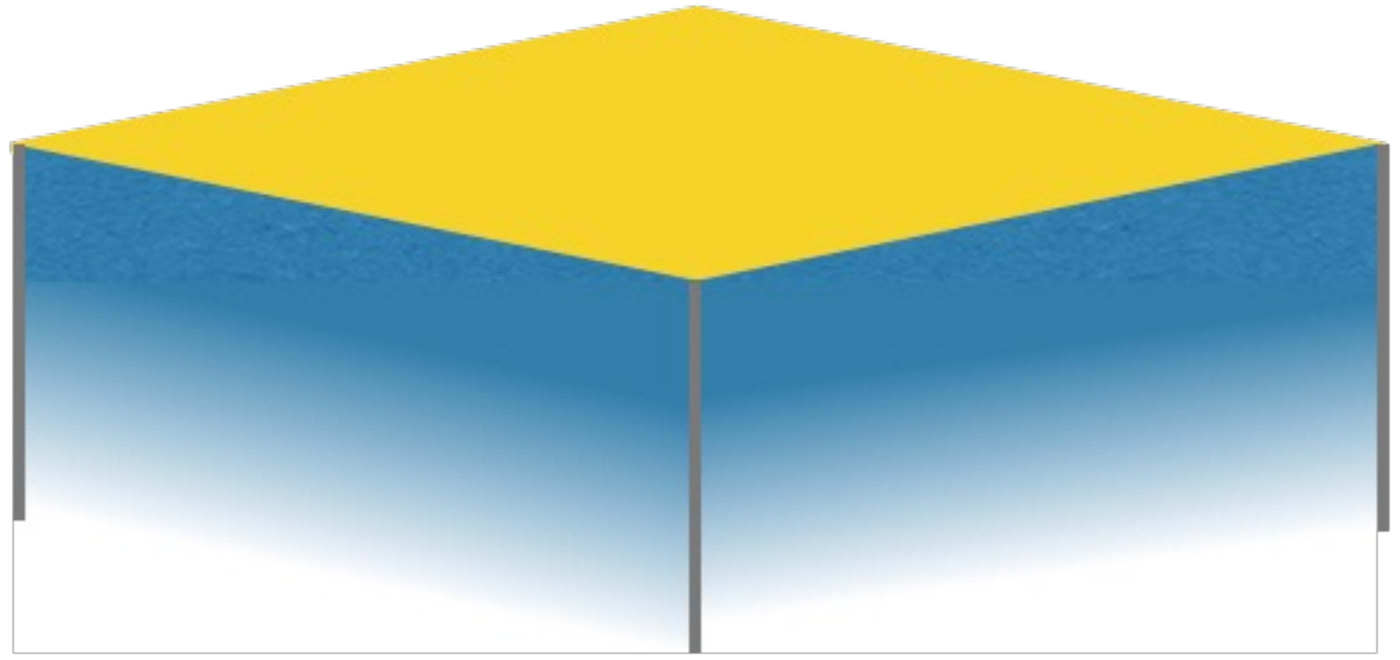
Electrical conductivity

Density

Elasticity

Tensile strength

Magnetism



Surface Properties

Properties unique to atoms on material's surface where they are less coordinated and experience different forces

Wettability

Biocompatibility

Corrosion resistance

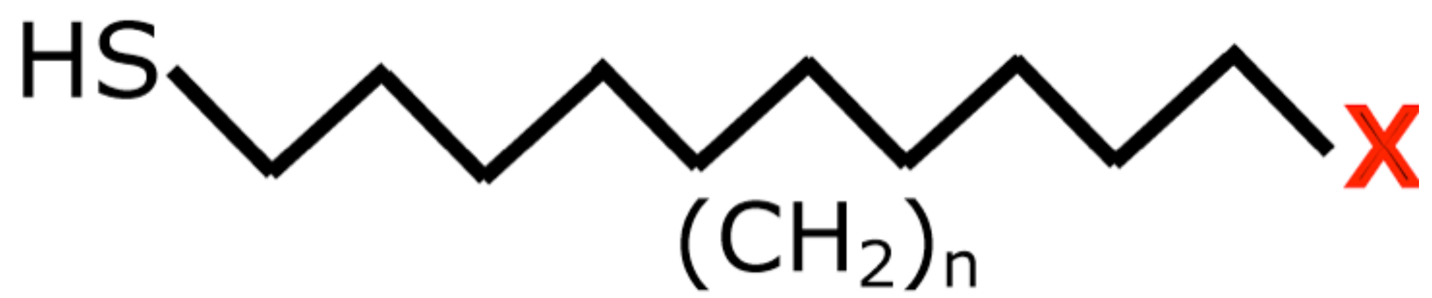
Roughness

Lubricity/ease-of-cleaning

Catalytic activity

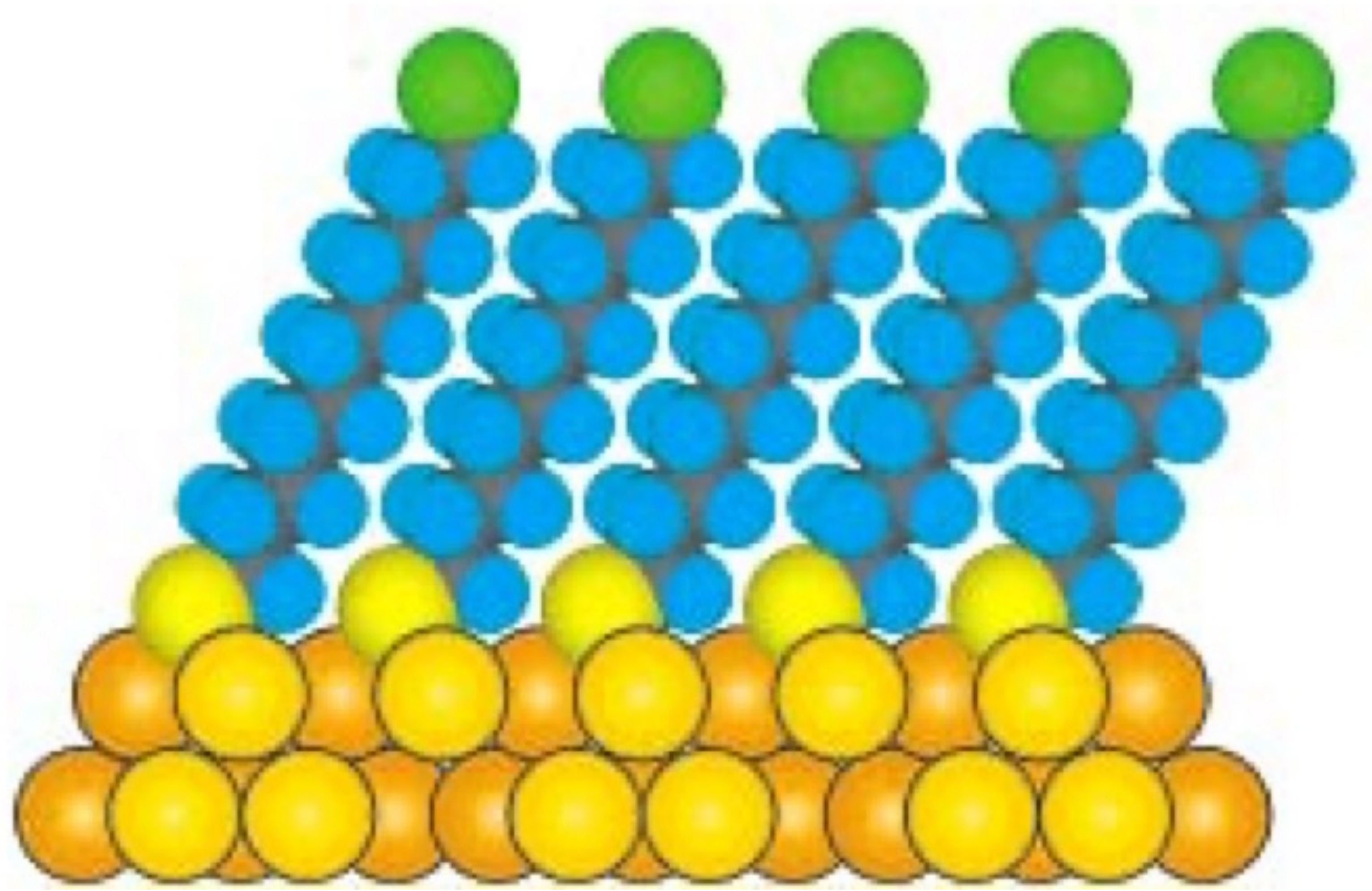
How to Functionalize Surfaces? Self-Assembled Monolayers

Examples of alkanethiols that spontaneously self-assemble on surfaces:



X = tail group/functional group

CH_3, OH, COOH, NH_2, *etc.*



Functional group: mainly determines surface properties

Hydrocarbon chain: interchain van der Waals interactions

Head/anchoring group: interacts with substrate (chemisorption)

Spontaneously adsorbed, single layer of species with a high degree of lateral organization

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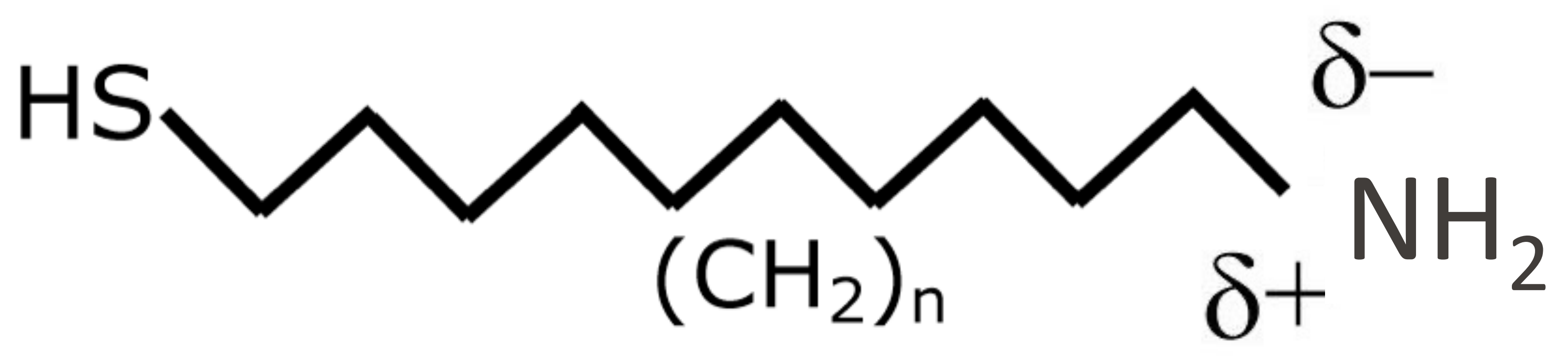
Hydrophilic *vs.* Hydrophobic Terminal Groups

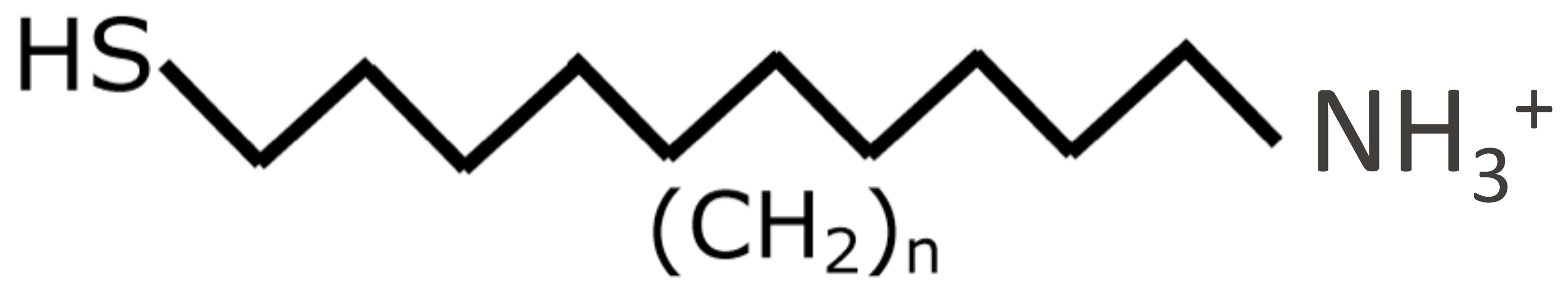
Hydrophilic terminal groups

- OH (hydroxyl)
- COOH (carboxyl)
- NH_2 (amine)

Polar

Hydrogen-bonds or ionic interactions with H_2O



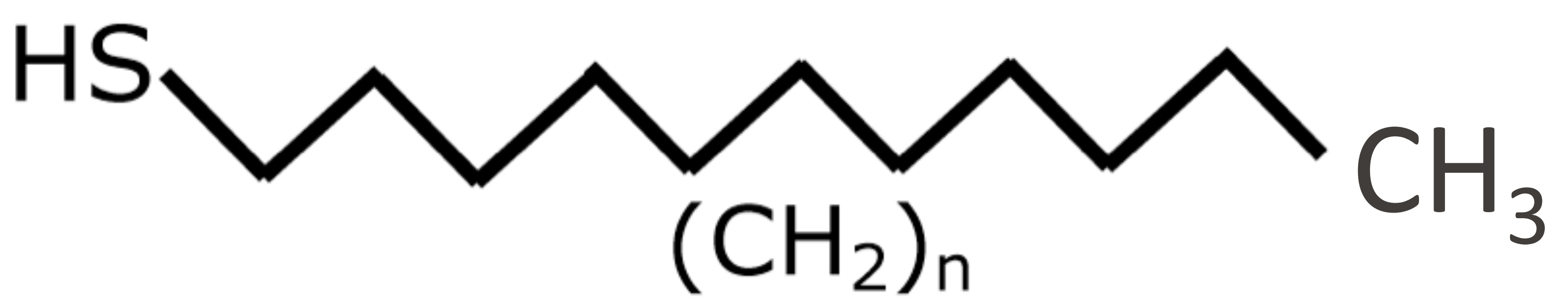


Hydrophobic terminal groups

- CH_3 (methyl)
- CF_3 (triflyoromethyl)
- C_6H_5 (phenyl group)`

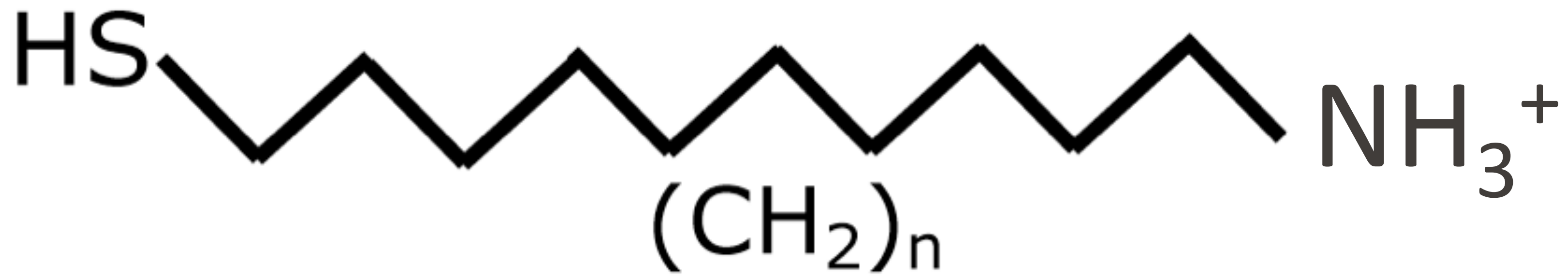
Non-polar

Minimal interactions with water due to low polarity



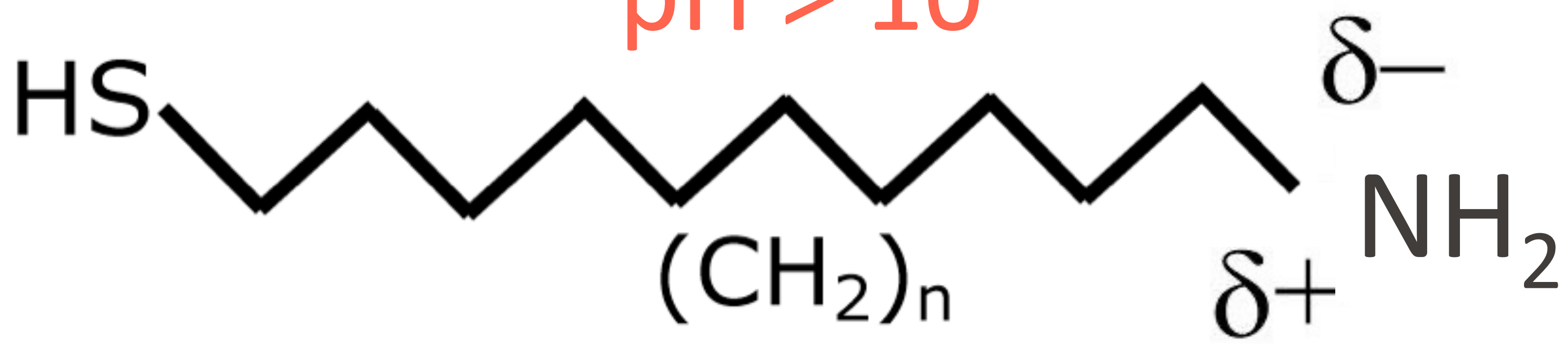
Recall the Strength of Intermolecular Interactions/Forces

pH < 10



pKa ~ 10

pH > 10



Acid dissociation

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

Intermolecular Forces	Formed by attraction between:
Ion-dipole	Ion + polar molecule
Hydrogen bond	Molecules with H, N, O, F atoms
Dipole-dipole	Two polar molecules
Ion-induced dipole	Ion + nonpolar molecule
Dipole-induced dipole	Polar + Nonpolar molecule
Van der Waals forces	Two nonpolar molecules

Strength of force

Henderson-Hasselbach equation

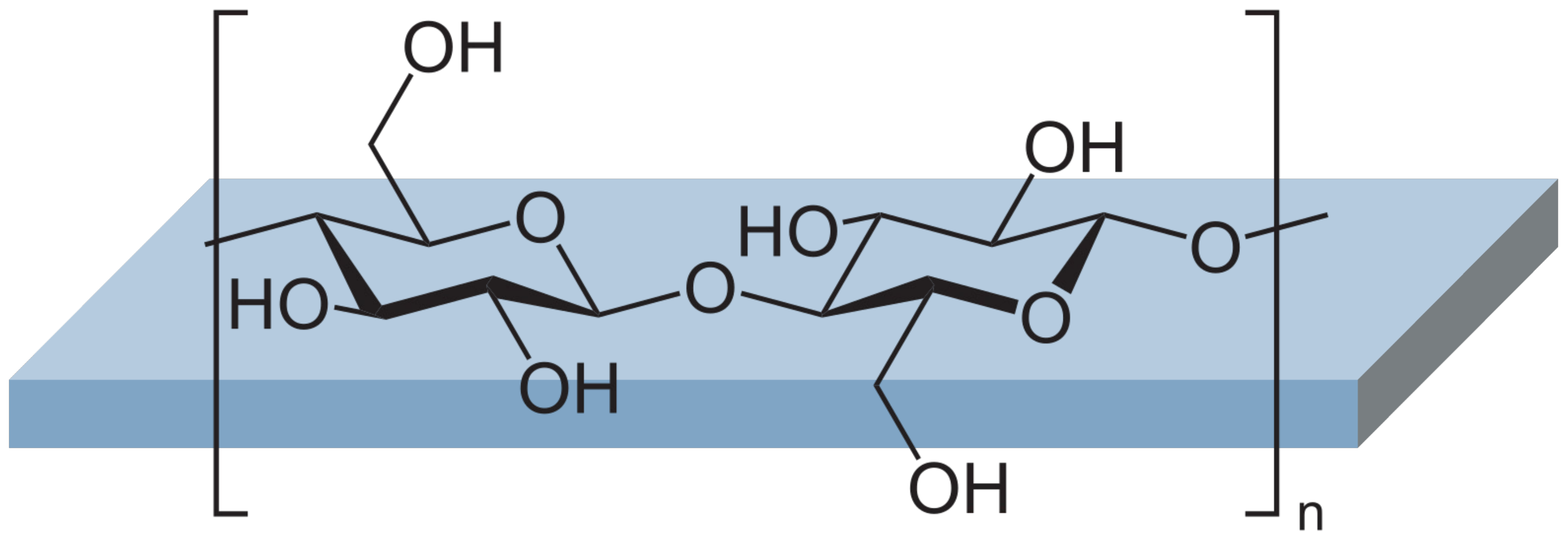
$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

pH < pKa ➔ protonated
pH > pKa ➔ deprotonated

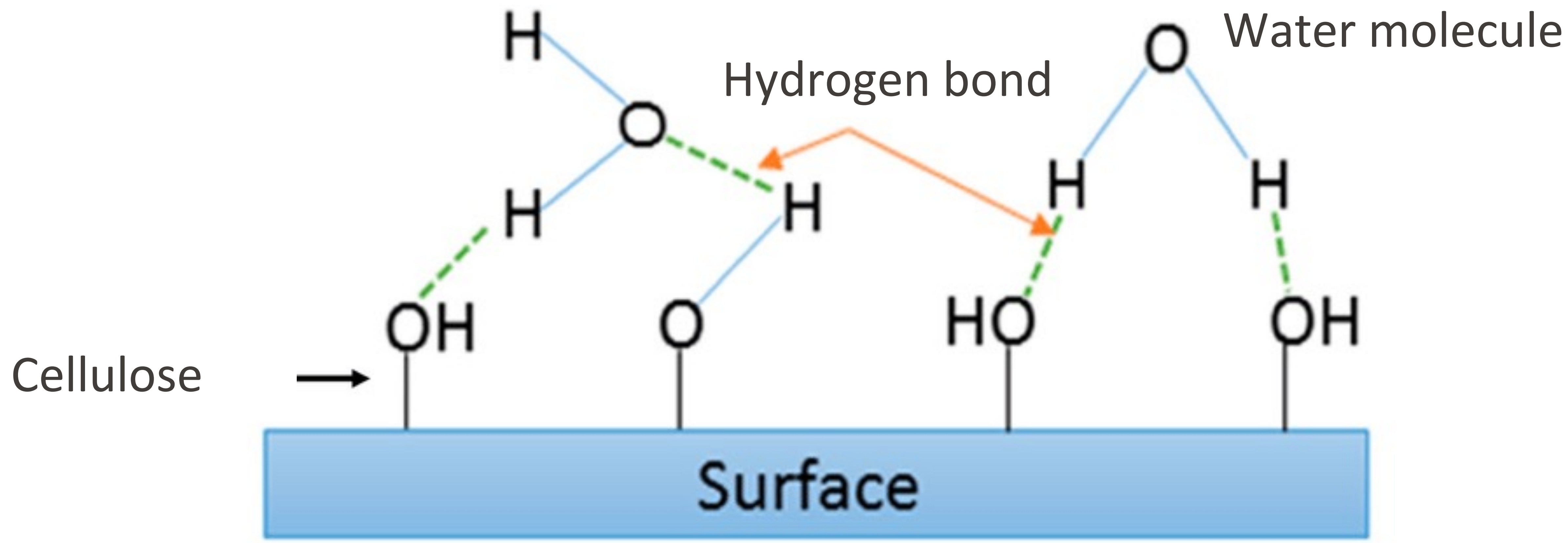
Hydrophilic *vs.* Hydrophobic Terminal Groups

Hydrophilic terminal groups

- OH (hydroxyl)



Cellulose on a surface



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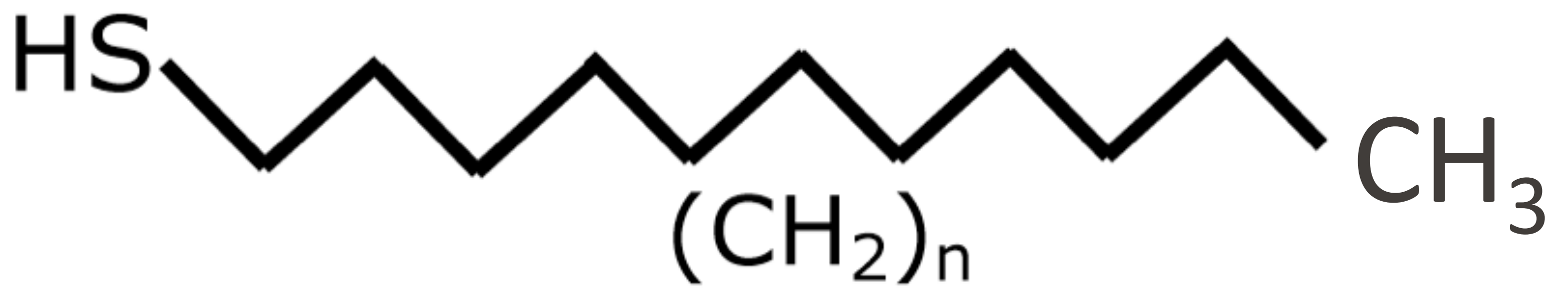

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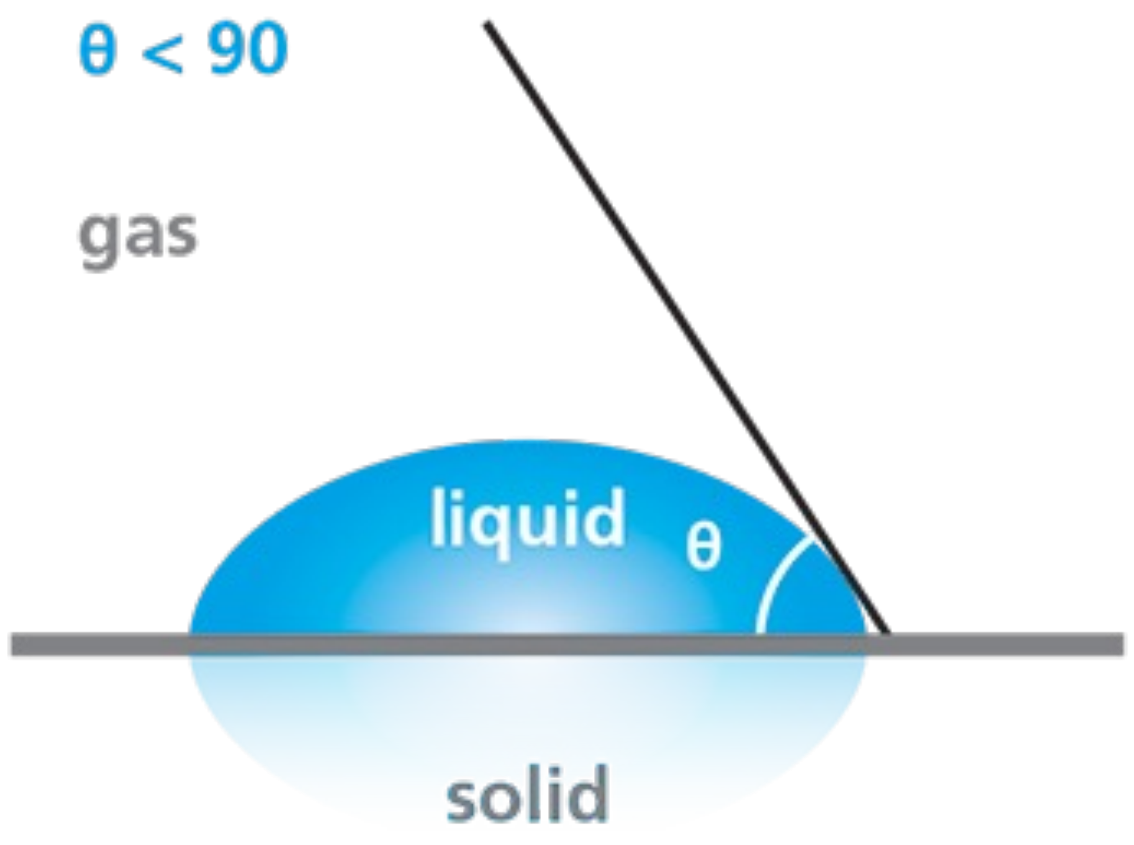

Hydrophobic terminal groups

- CH_3 (methyl)
- CF_3 (triflyoromethyl)
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Non-polar

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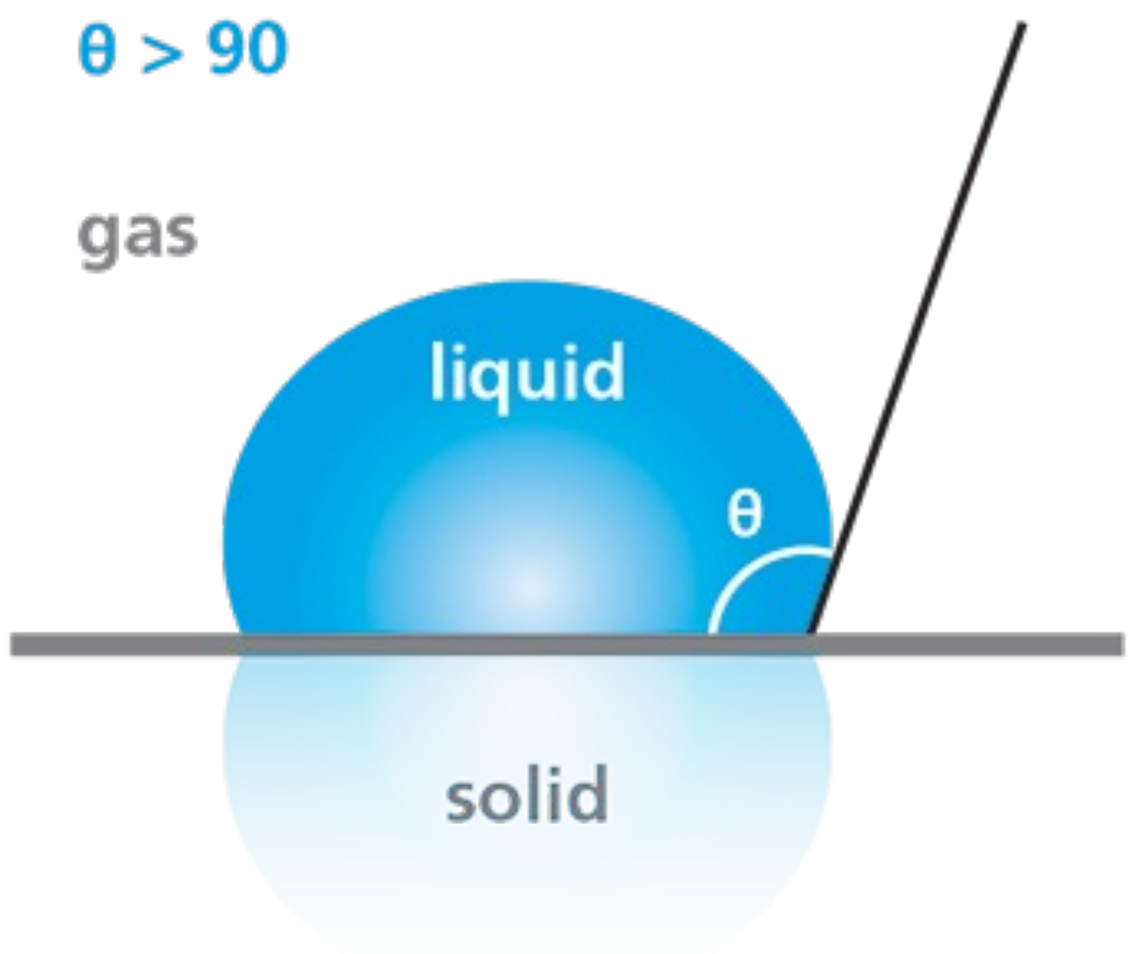
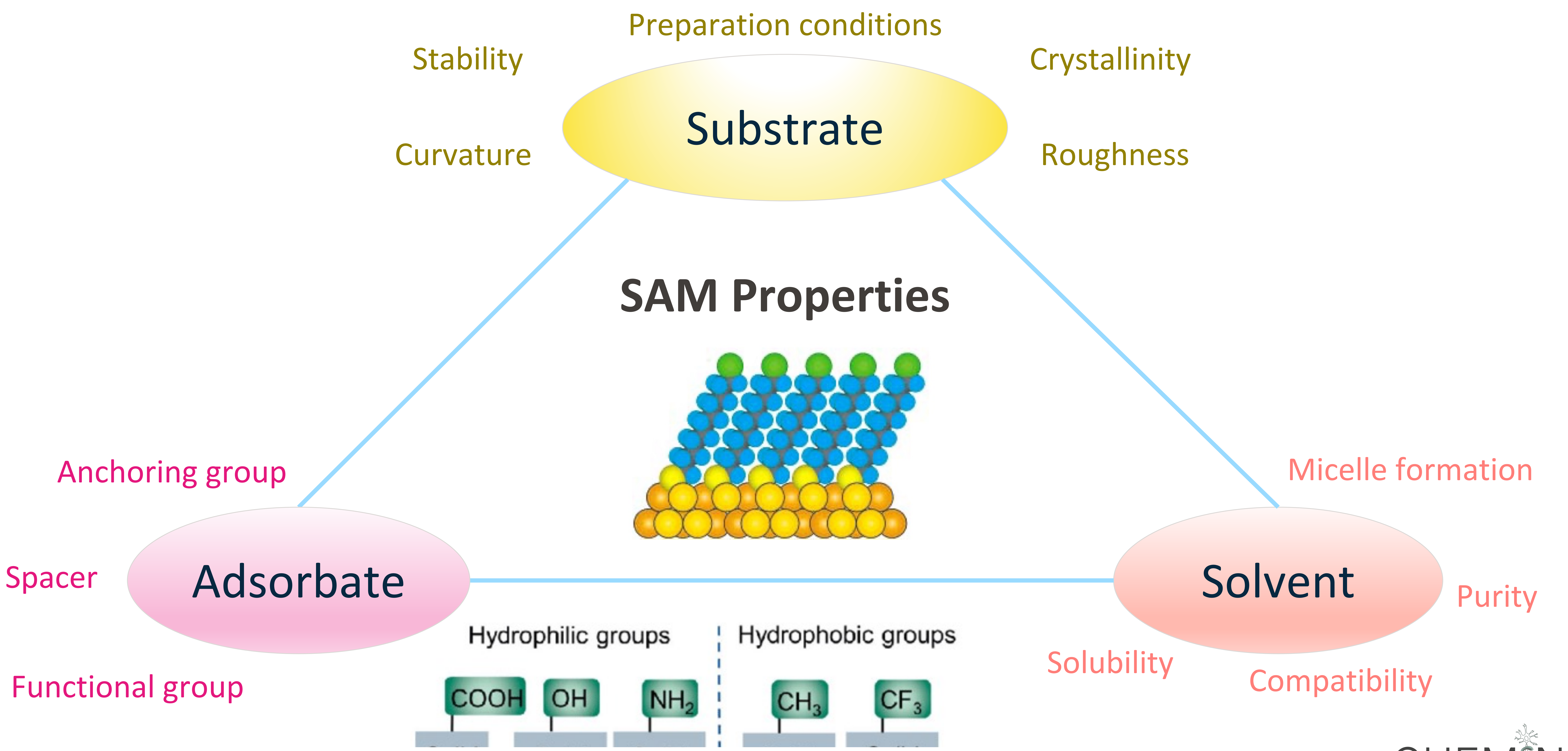
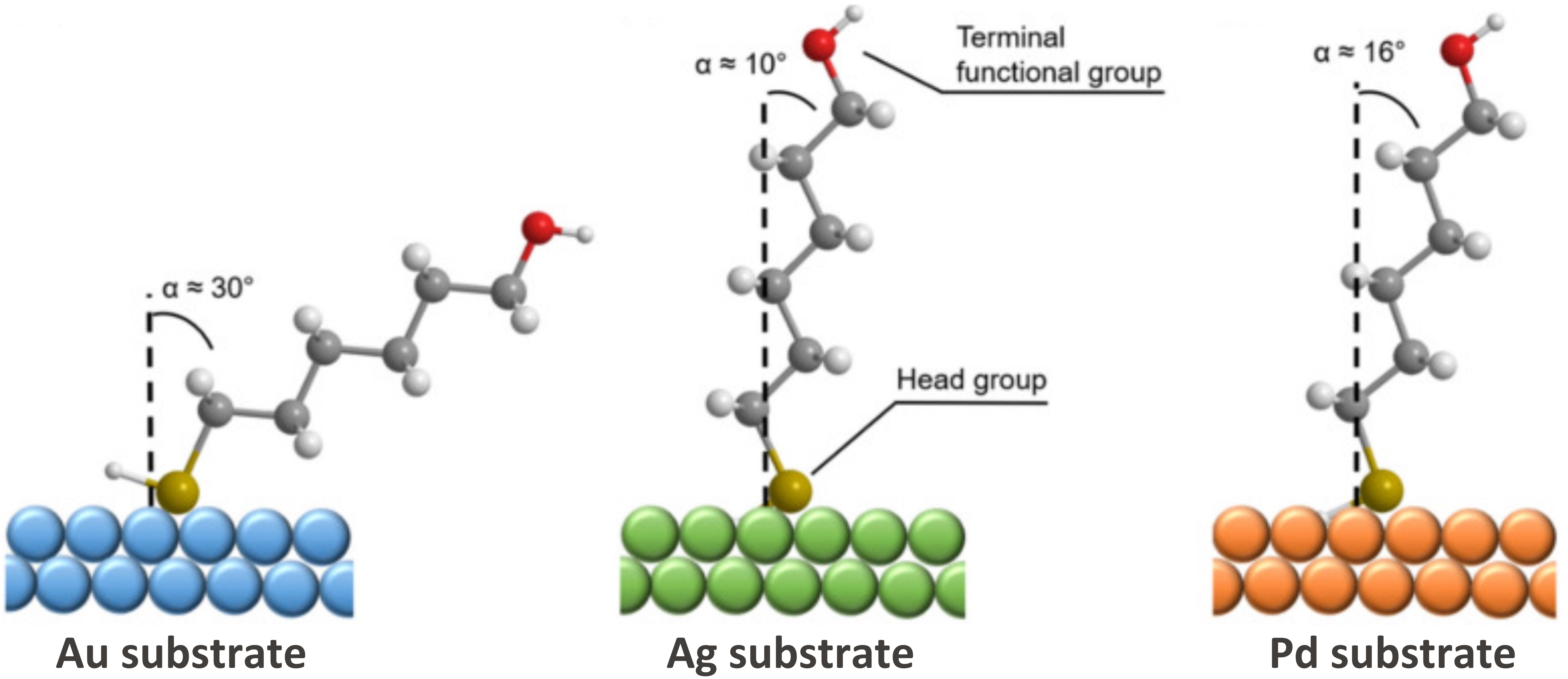
Contact angle



Factors Governing Self Assembly



Alkanethiols Structure on Different Substrates



Lattice mismatch between the gold substrate and the natural packing density of alkanethiols, requiring higher tilt to achieve stable van der Waals interactions

Güvener *et al.*, *Fundamentals of Sensor Technology*, **2023**

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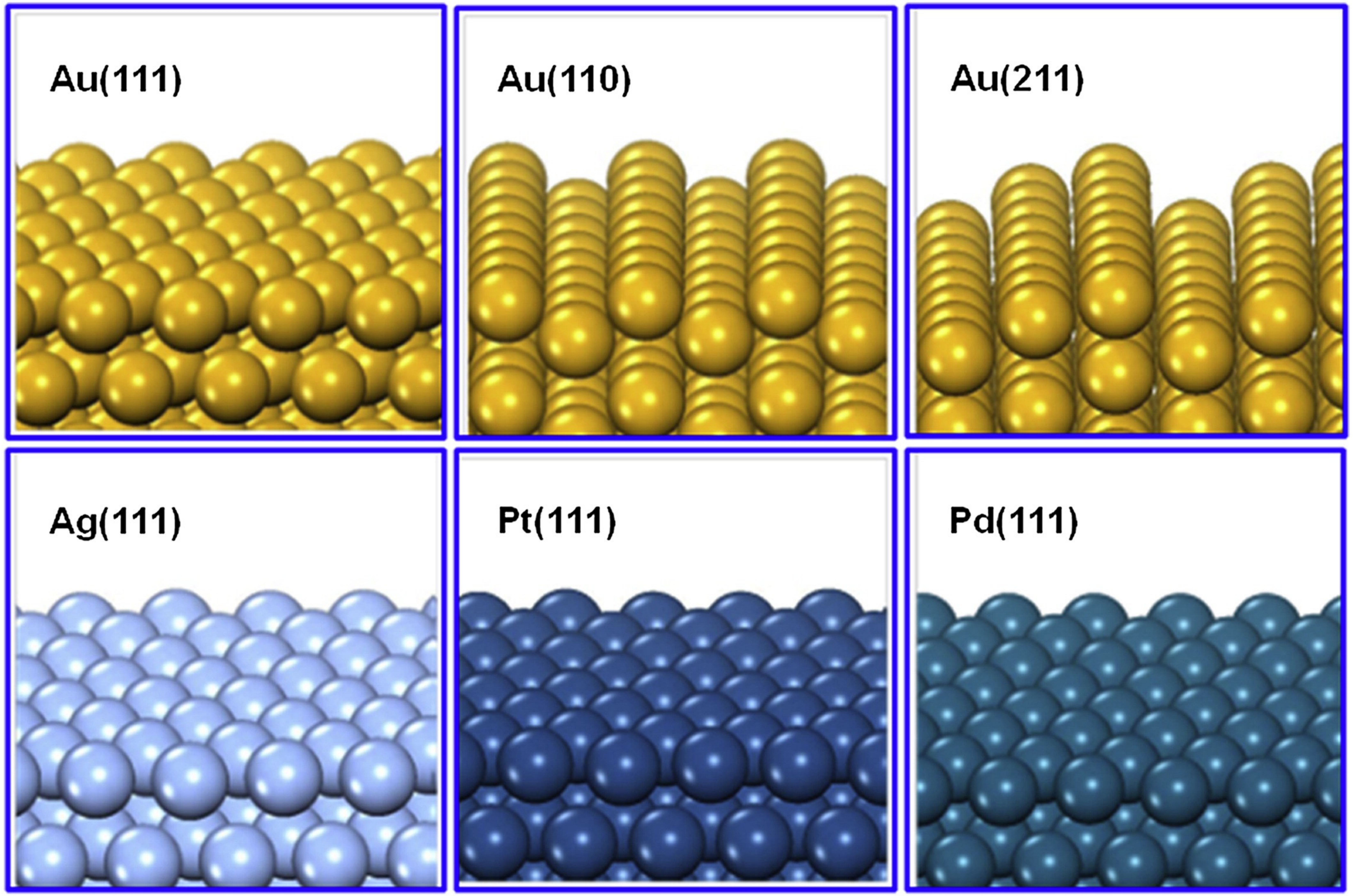
Atomic Arrangements of Atoms on Different Planes

Miller indices describe crystallographic planes in crystalline material

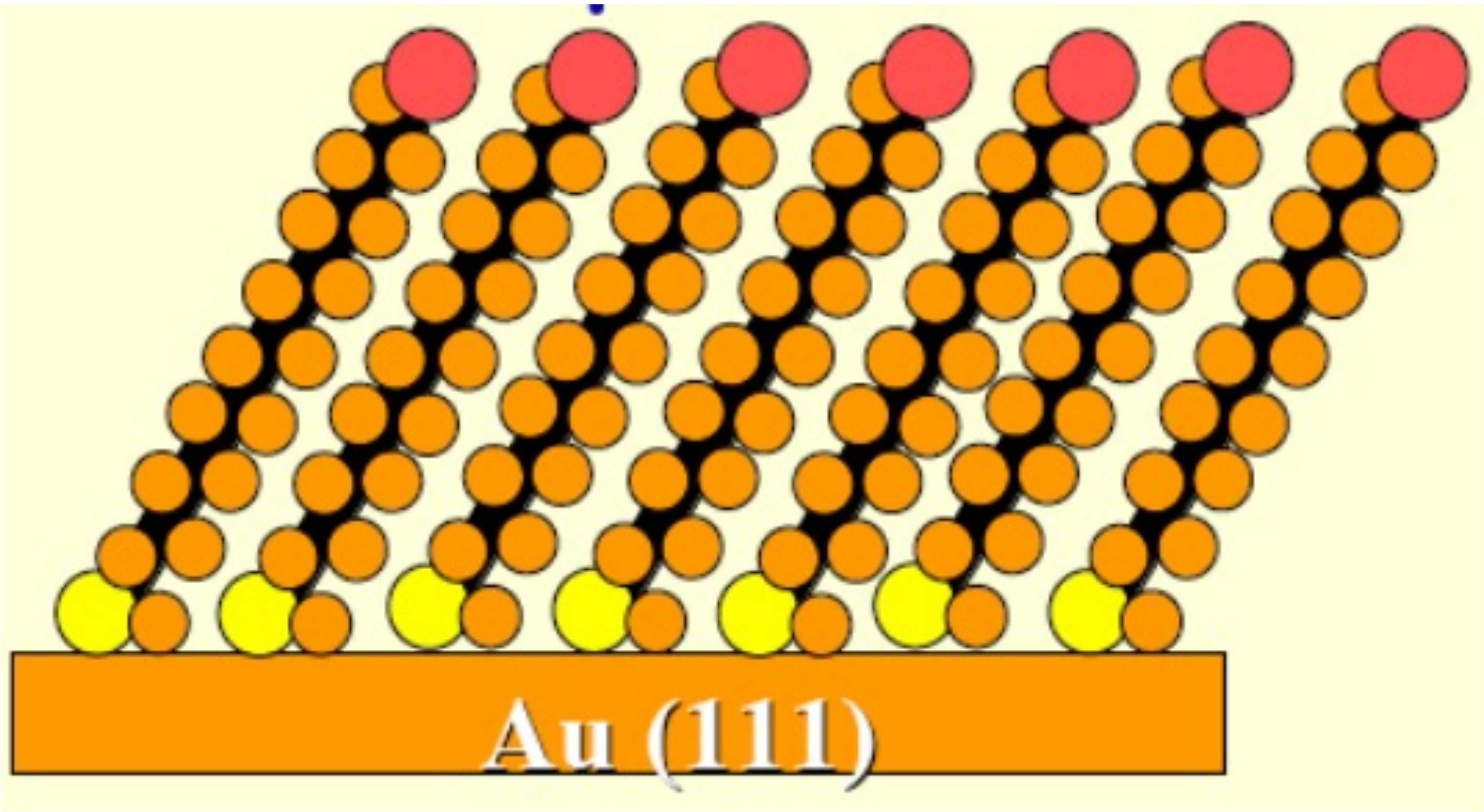
Each orientation represents specific arrangement of atoms on the surface of the crystal lattice, with distinct geometric and chemical properties

Variations in:
- Atomic density
- Surface energy
- Geometry
- Stability



Li *et al.*, *Biomaterials*, *48*, 37, **2023**

Alkanethiols Adopt Specific Arrangements on Surfaces

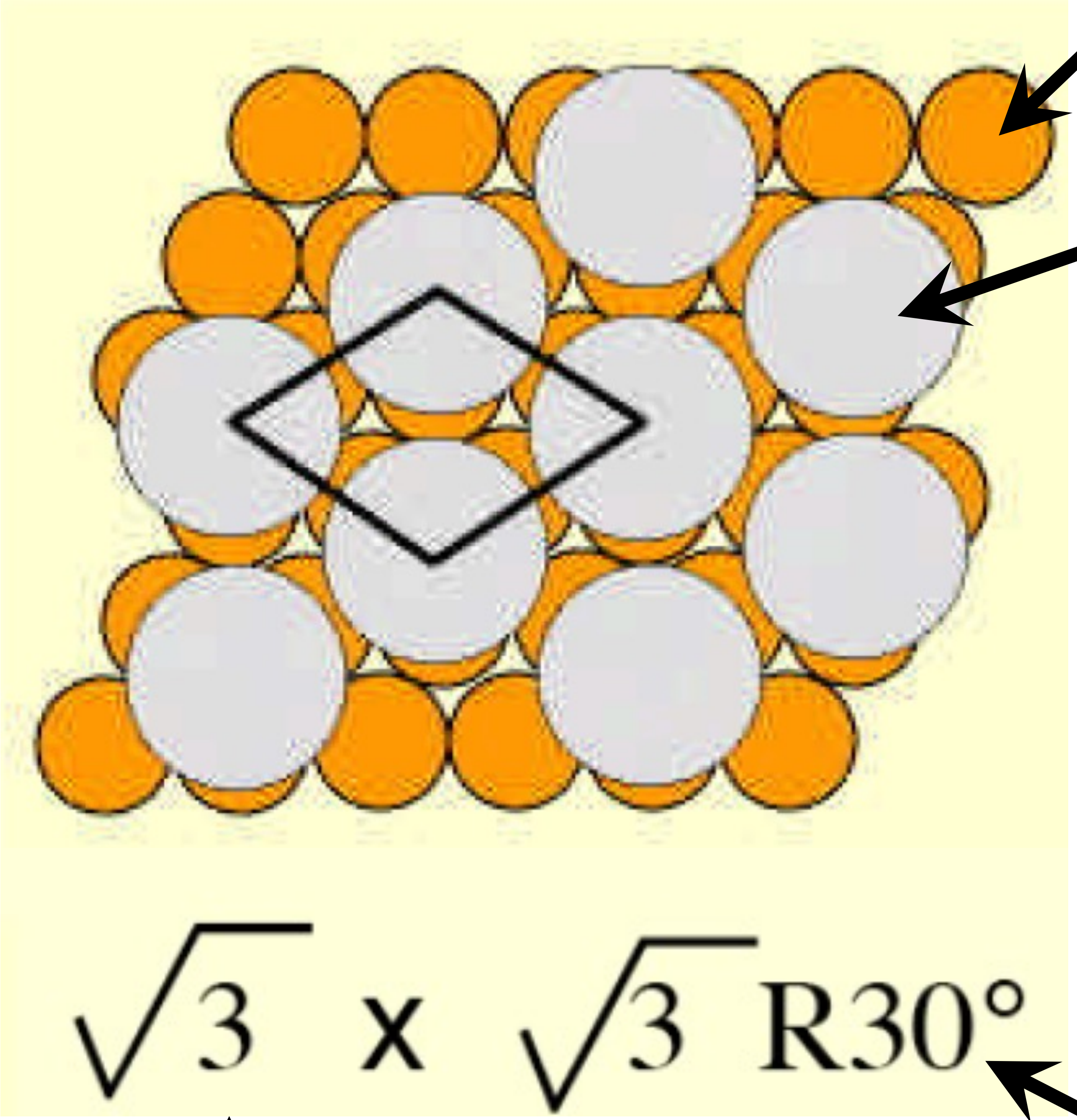


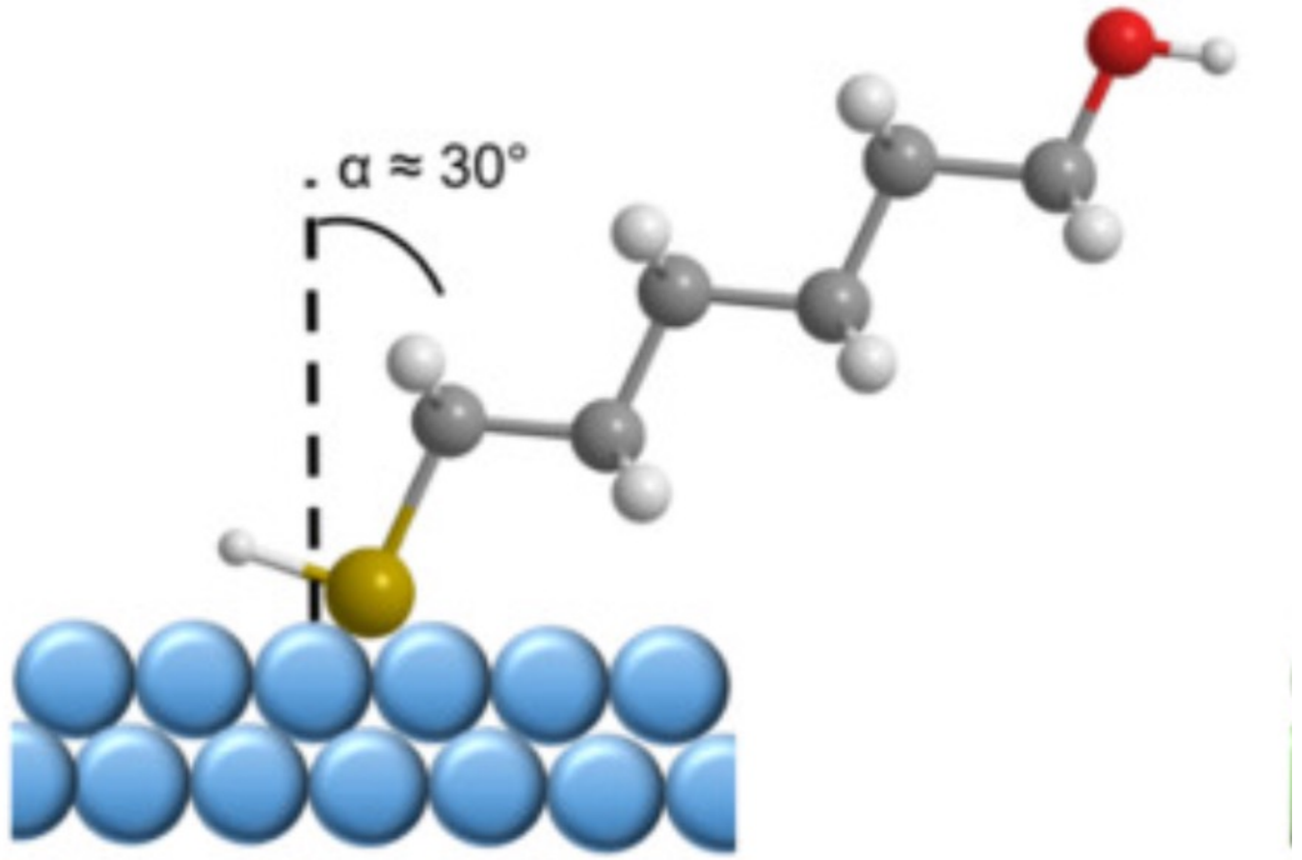
Face-centered cubic (FCC)
Close-packed hexagonal lattice
d_{Au} ~0.29 nm

Alkanethiols form covalent bond with the gold atoms and adopt a superlattice structure

Au

Alkanethiol





Rotation
Alignment of adsorbed lattice relative to gold lattice

Every 3rd Au atom is a binding site

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Intrinsic and Extrinsic Defects Found in Polycrystalline SAMS

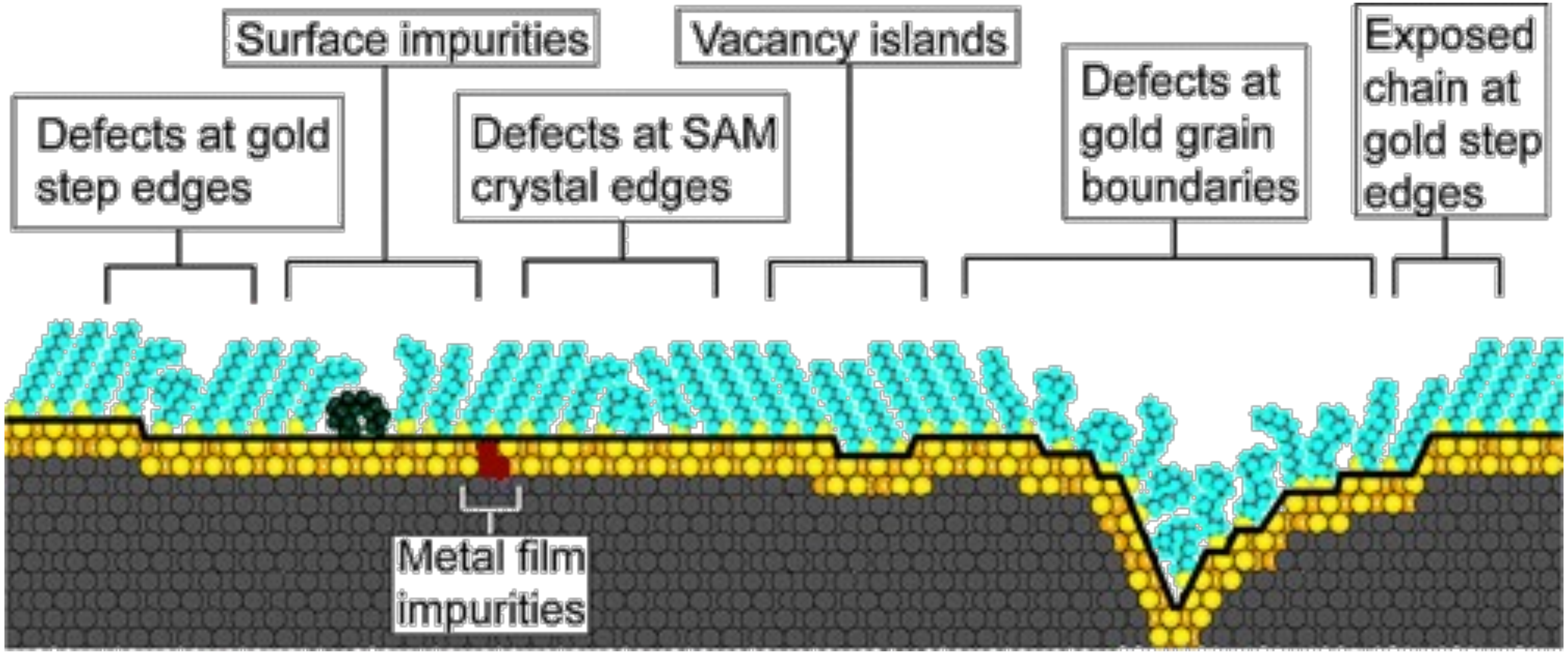
Chem. Rev. **2005,** *105,* 1103–1169 **1103**

Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology

J. Christopher Love,† Lara A. Estroff,† Jennah K. Kriebel,† Ralph G. Nuzzo,*,‡ and George M. Whitesides*,†

Department of Chemistry and the Fredrick Seitz Materials Research Laboratory, University of Illinois–Urbana–Champaign, Urbana, Illinois 61801 and Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Cited > 10,000 times!



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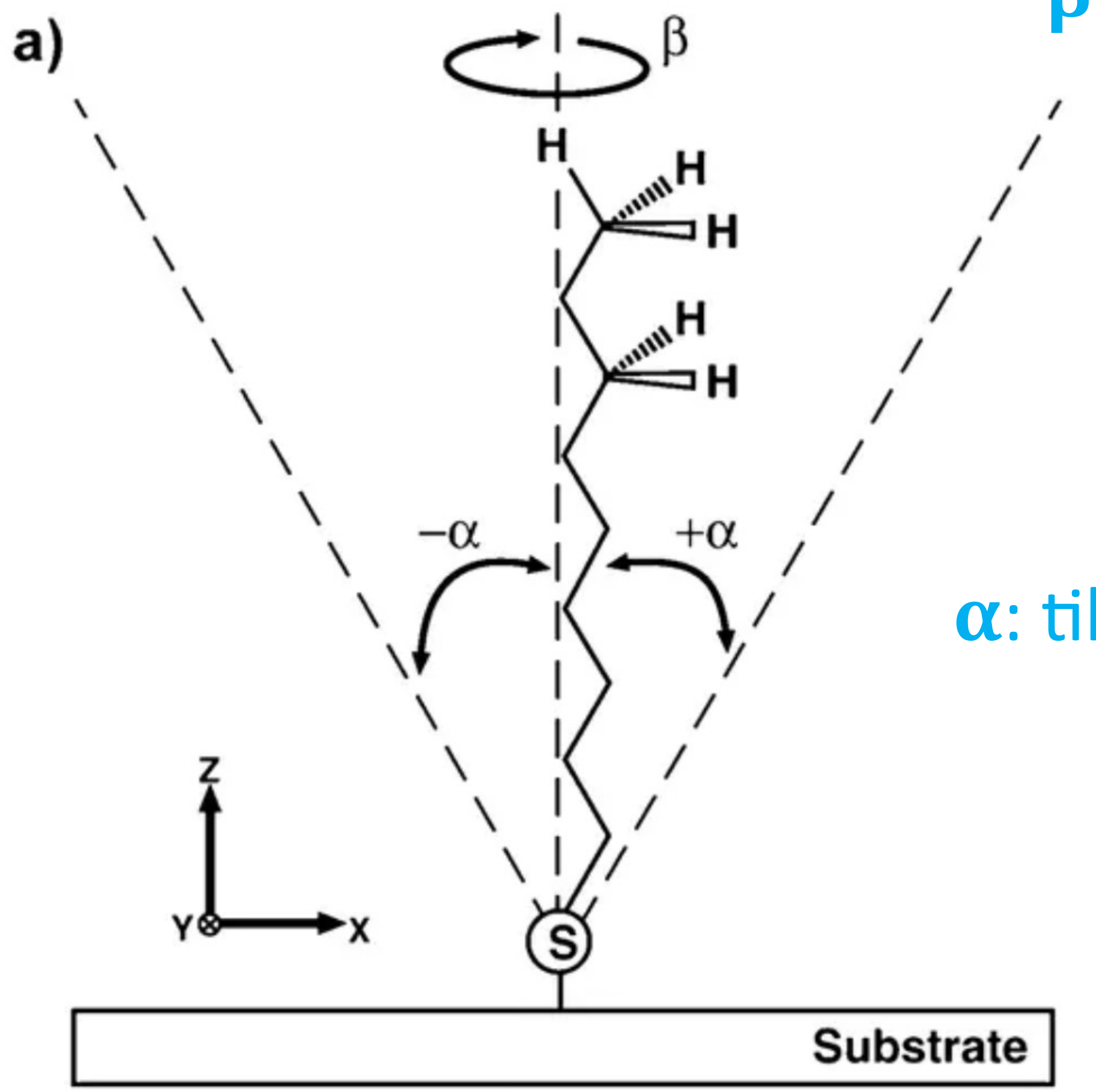

β: rotation of C-C bond

α: tilt angle

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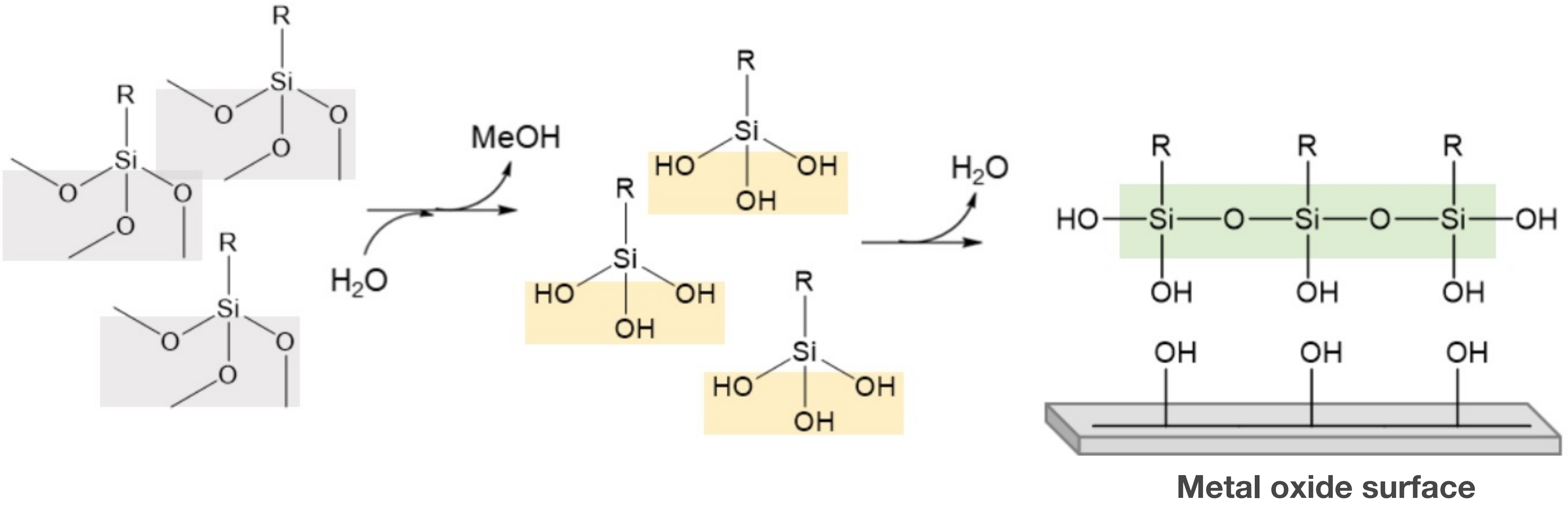
Beyond Alkanethiol-Gold Surface Chemistry

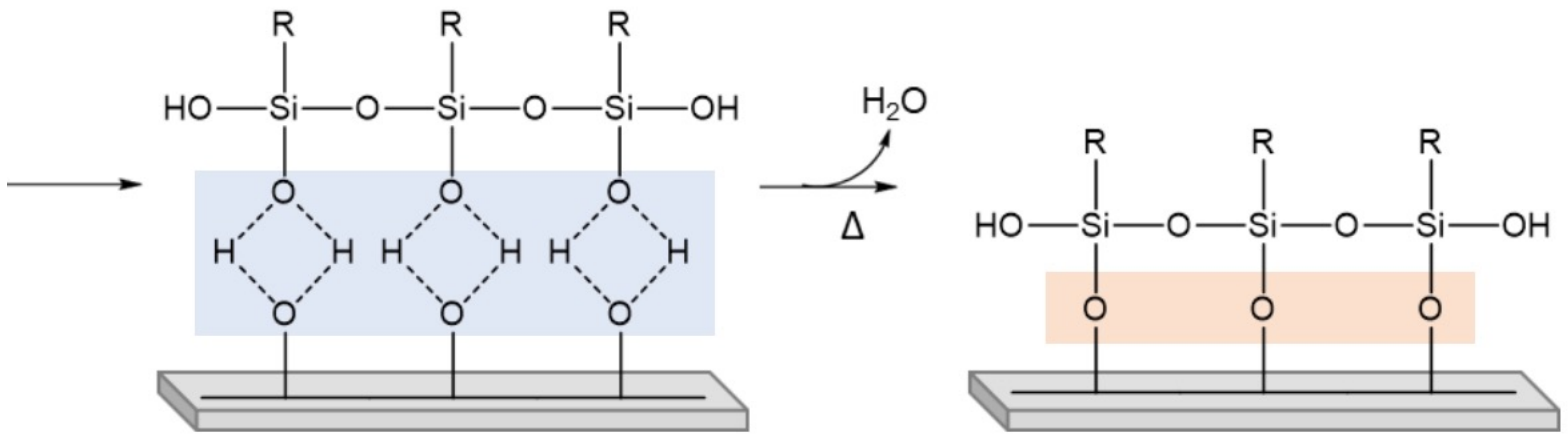
Silane chemistry for surfaces with –OH groups (*e.g.,* metal oxides)

*The precise mechanism of assembly is unknown



Hydrolysis

Condensation

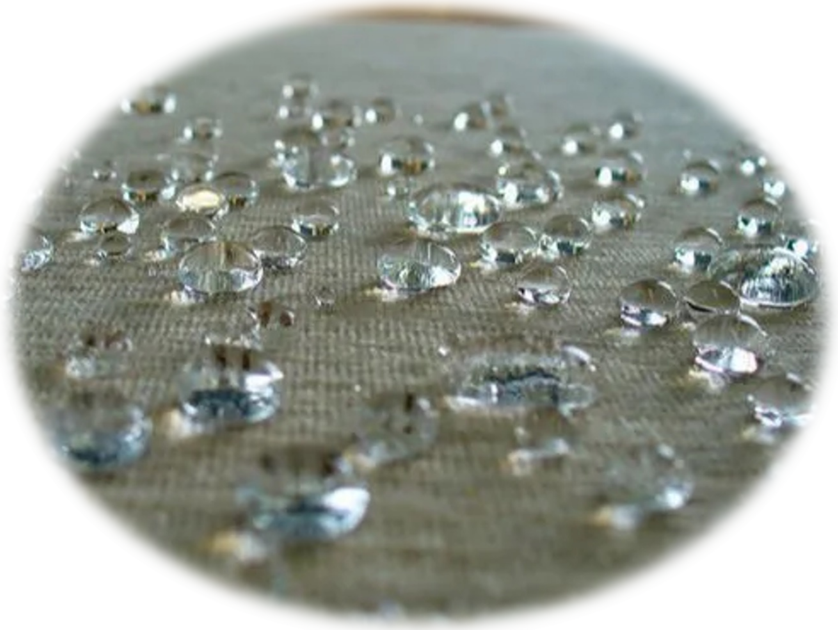


Hydrogen bonding

Covalent bond formation

Arkles, *CHEMTECH, 7,* 766, **1977**

Applications of silane chemistry



Water repellant coatings

Adhesives, primers, paints

Antifog

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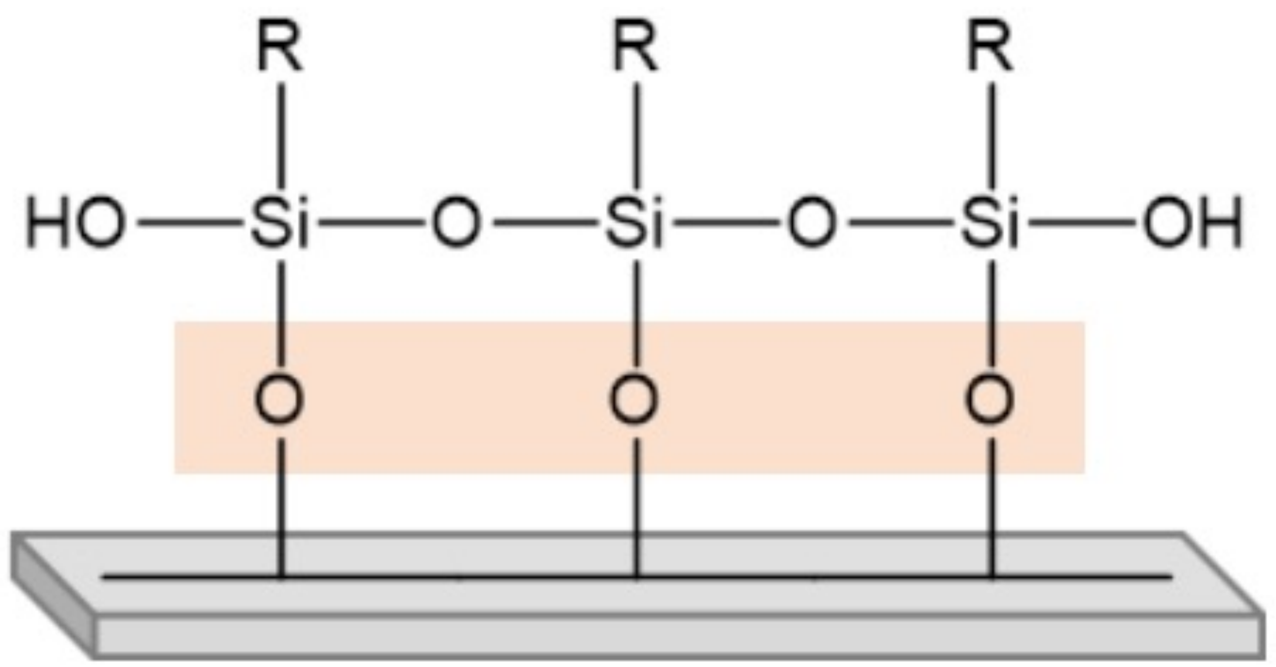
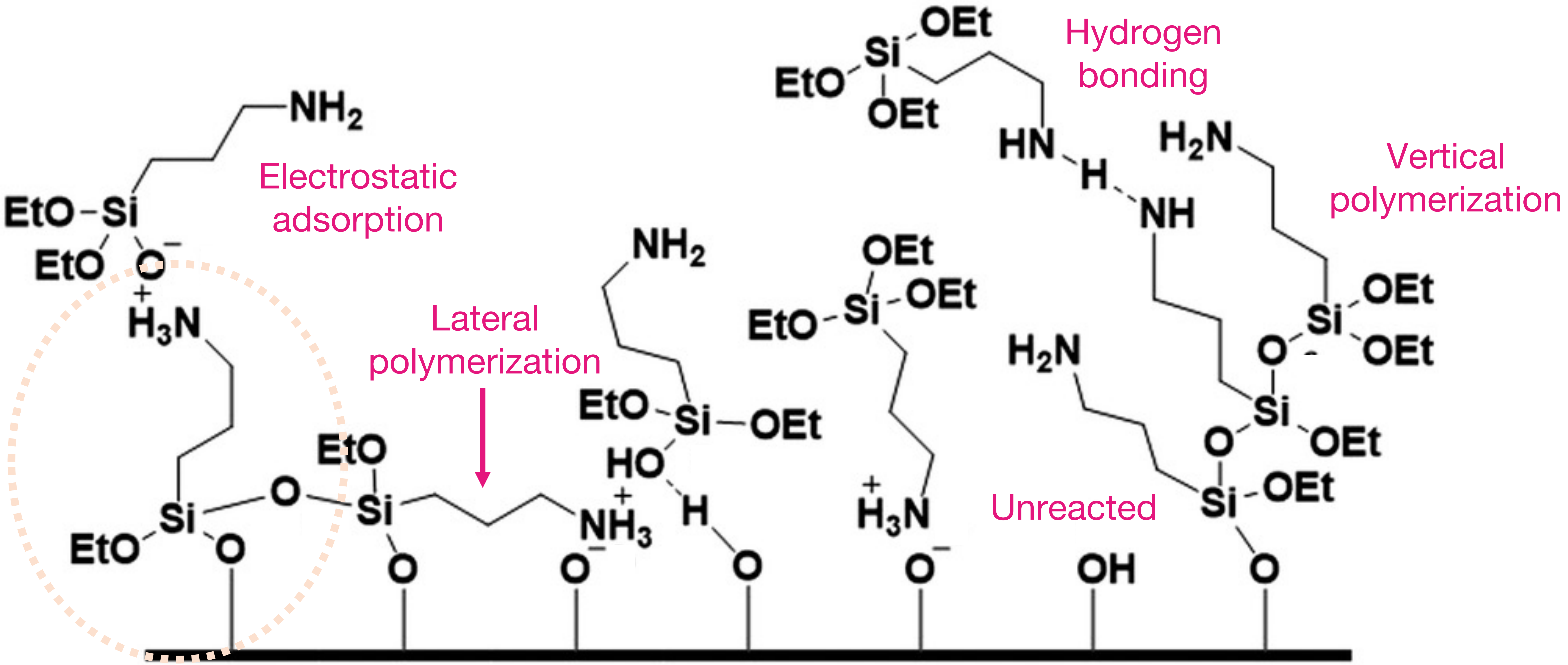
Challenges of Homogenous and Reproducible Silane Chemistry

Expectation ☺



Metal oxide surface

Reality ☹



Layer characteristics are heavily influenced by solvent, water content, environmental humidity, pH, silane concentration, reaction time, temperature, etc.

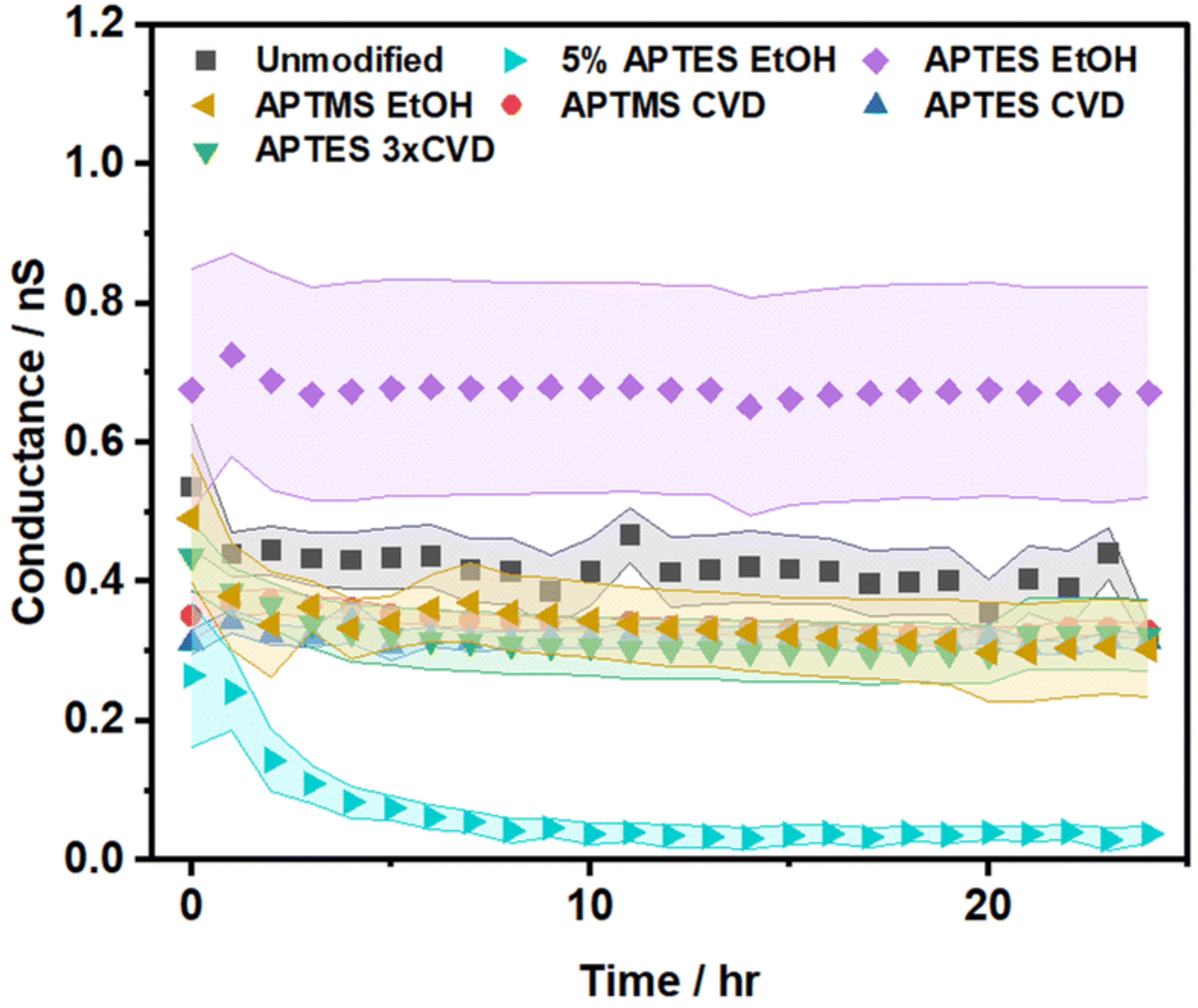
Duleba *et al., Phys. Chem. Chem. Phys.,26, 15452,* **2024**

Achieving Reproducible Silane Layers in the Lab

Modifying the surface of quartz surfaces

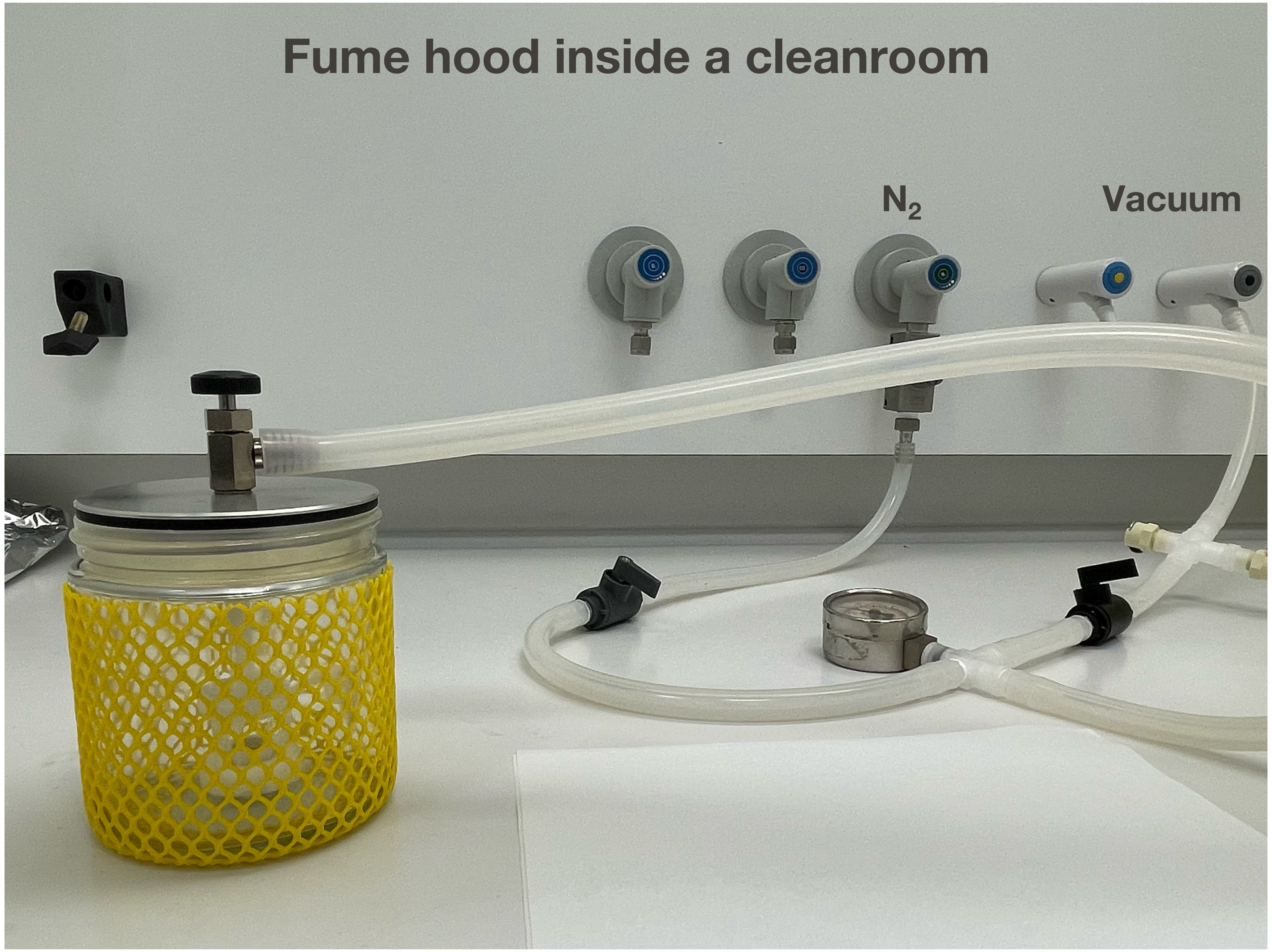
Pre-treatment	Silane	Concentration	Solvent	Reaction	Post-treatment
Piranha	APTES	5%	Ethanol	2 h	120 °C for 1 h
Piranha	APTES	5%	Ethanol	1 h	120 °C for 1 h
	APTES	1%	Ethanol	2 h	110 °C for 1 h (vacuum)
	APTES	1%	Ethanol		120 °C for 2 h
Piranha (0.5 h)	APTES	0–1.1%,	Ethanol	0–4 h	110 °C for 0.5 h
	APTMS	1%	Acetone	4 °C for 12 h	120 °C for 1 h
Boiling H_2O_2 (0.5 h)	APTMS	11%	Acetone	Overnight	120 °C for 1 h
	APTMS	Vapour-phase	Vapour-phase	40 °C for 1 h	
	TESPG	2.5%	Ethanol	Overnight	N_2 dry
Piranha (24 h)	DHITES	0.74 mM	Ethanol	Overnight	
	DHITES	17%	Ethanol	Overnight	
Piranha (24 h)	ATMS	1 mM	Ethanol	Overnight	
Piranha (2 h)	TESP-SA	1%	Isopropanol	1 h	60 °C for 1.5 h (vacuum)
Piranha	TESBA	5%	Ethanol, acetate buffer (pH 4.7)	20 h	
	MPTES	0.01%	Ethanol	15 min	60 °C for 2–3 h
Boiling H_2O_2 (20 min)	MPTMS	10%	Ethanol	4 h	120 °C

Solution deposition yields higher variability



Duleba *et al.*, *Phys. Chem. Chem. Phys.,26, 15452*, **2024**

How We Conduct Silane Chemistry in our Lab



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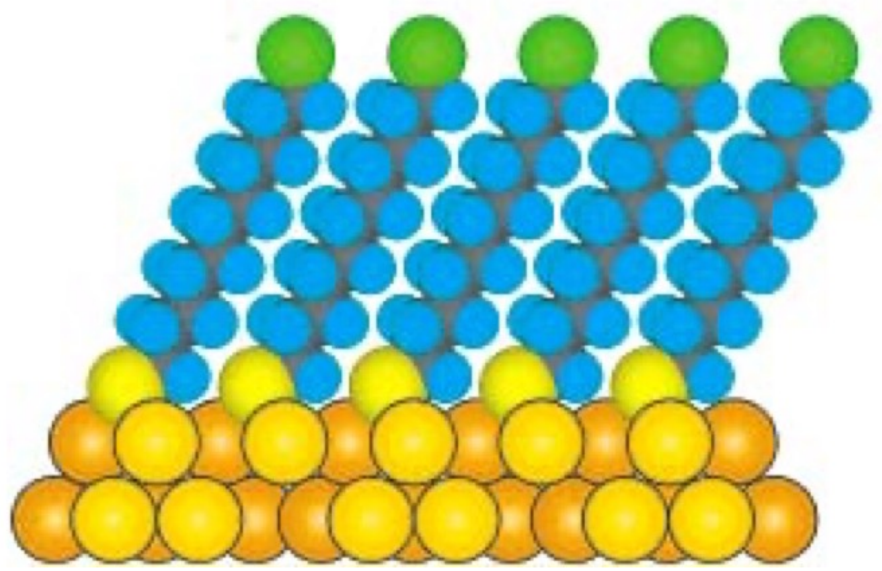
The Pros and Cons of Alkanethiols vs. Alkylsilanes

Alkanethiols



Metal surface *(e.g.,* Au*)*

Selective bonds formed with noble metal surfaces

Many different functional end groups commercially available

Easy to prepare (Au chemically inert)

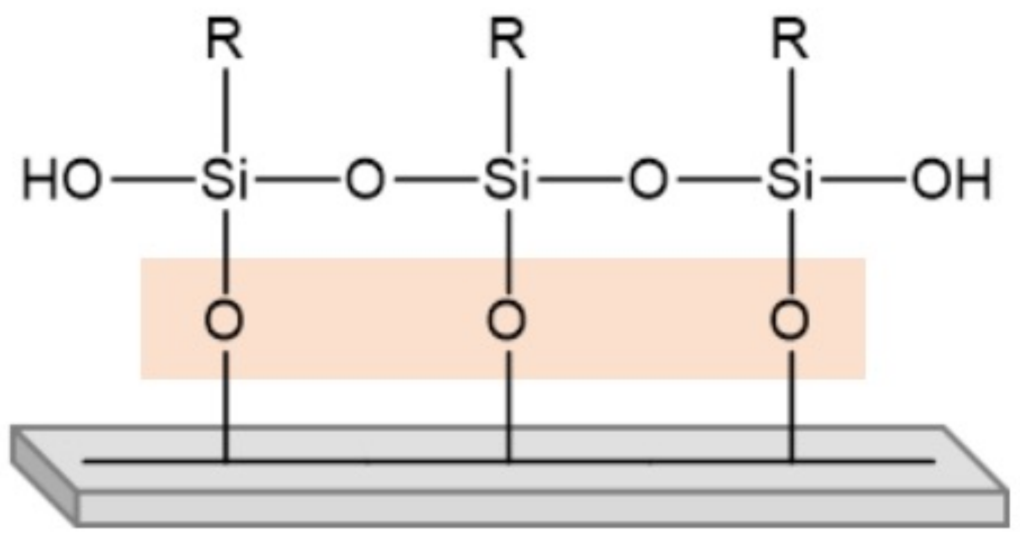
Very well studied (order and packing well known)

Patterning is possible

Do not absorb on most technologically important materials

Sensitivity to oxidation leads to low stability

Alkylsilanes



Metal oxide surface (-OH)

Only requirement for substrate is presence of –OH groups

Many functionalized silanes commercially available

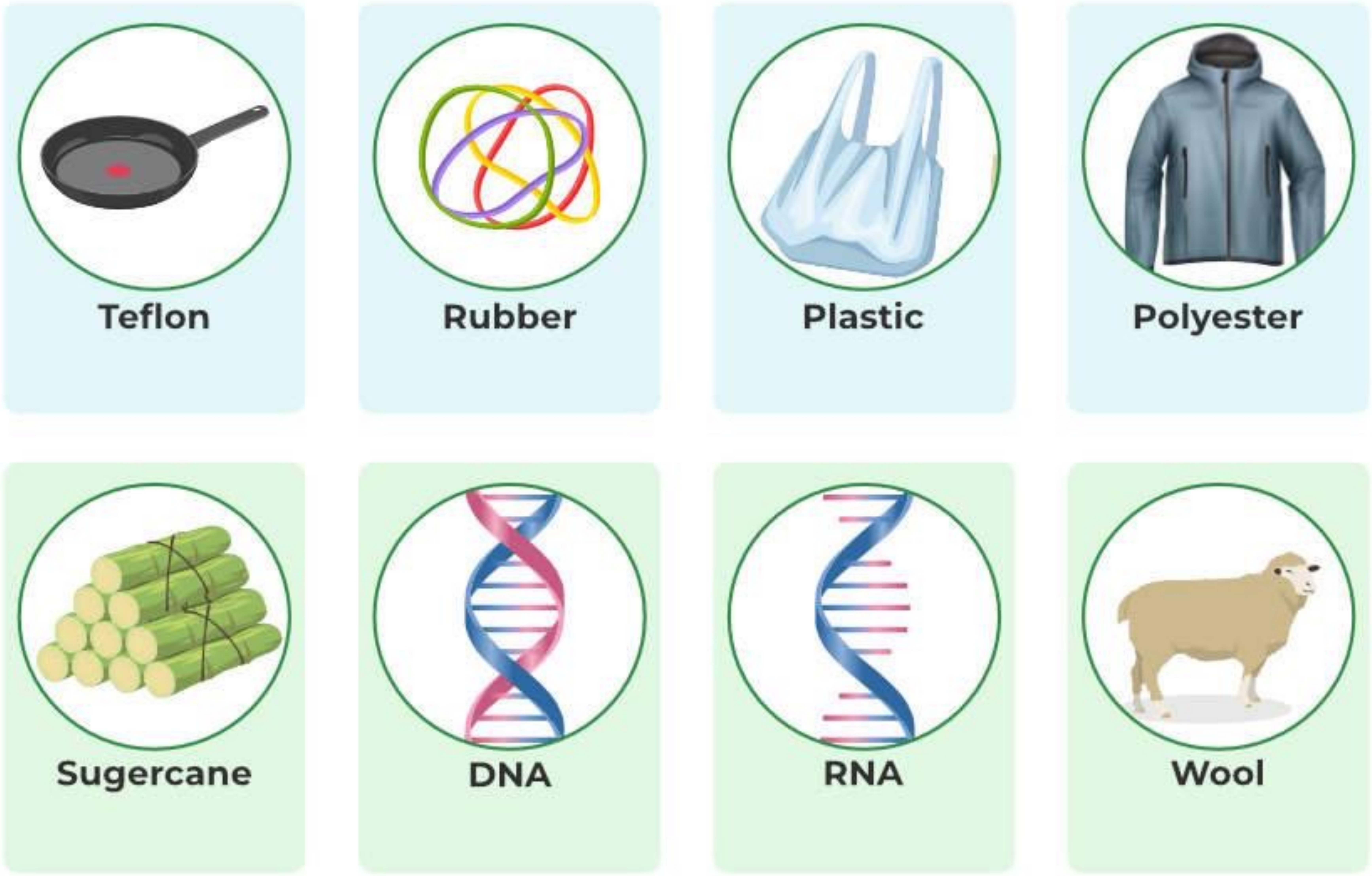
High stability due to polysiloxane formation

Limitation in functional groups due to possible reactivity with head/anchor group

Reproducible sample prep can be difficult

Multilayer formation is possible (and common)

Polymers are All Around Us



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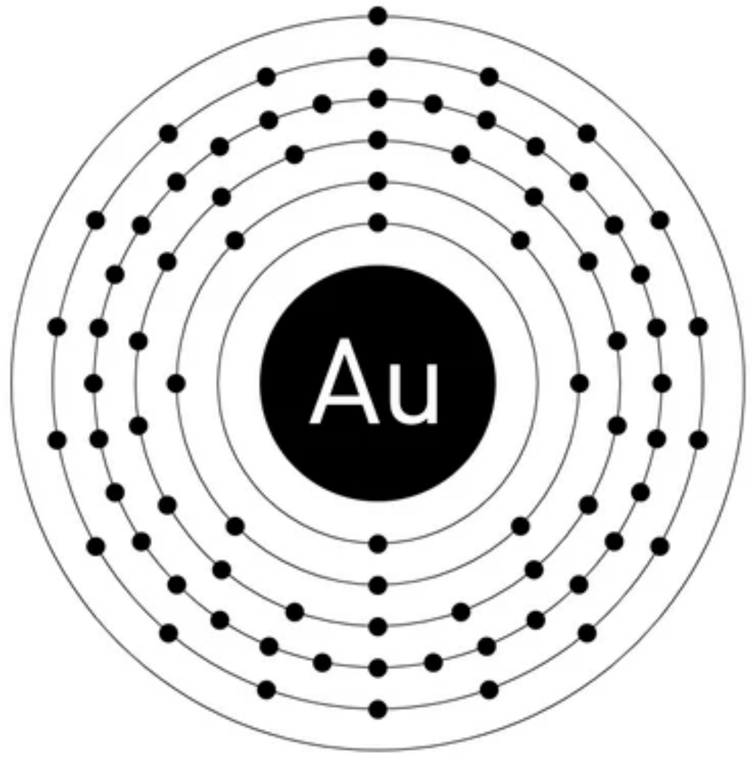
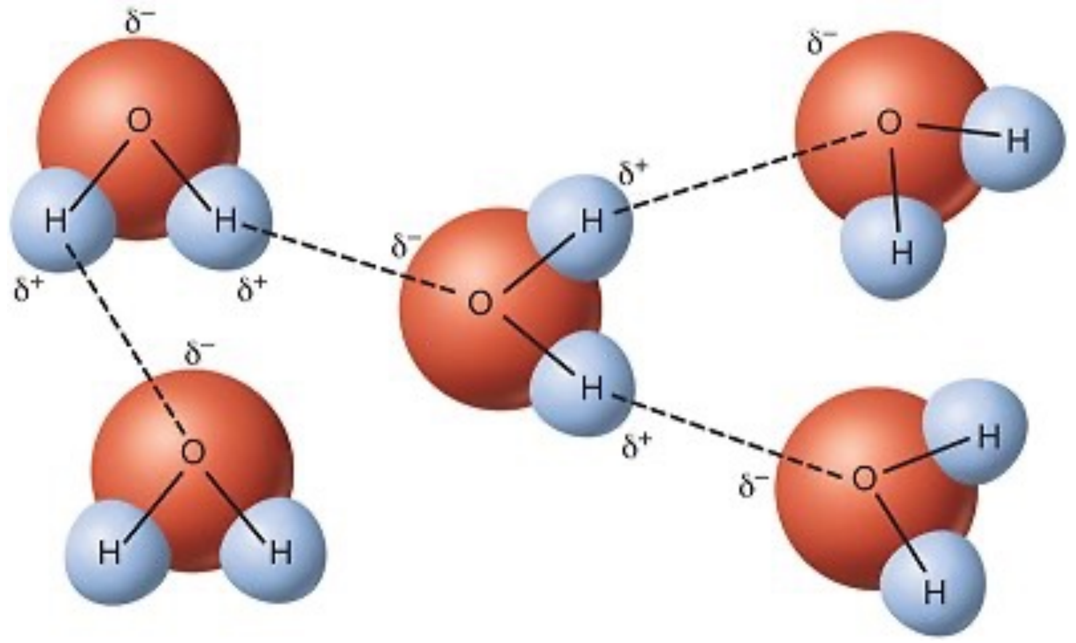
Surface Assembly of Polymers

Metal



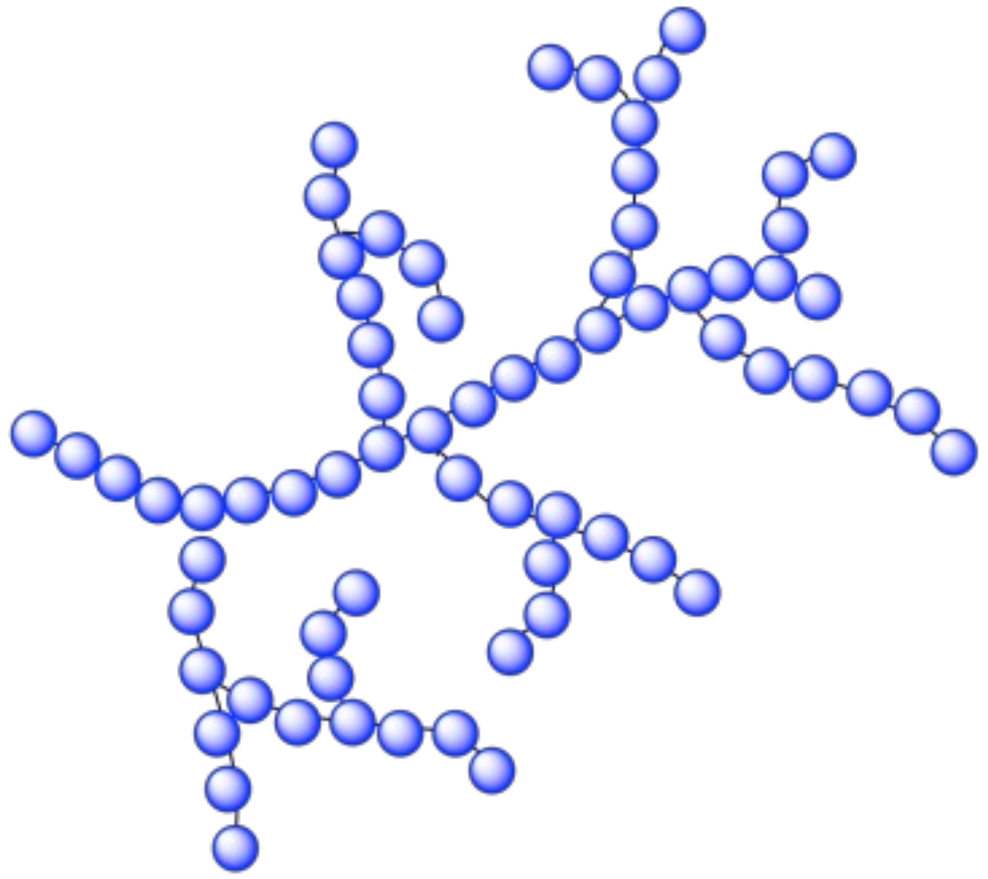
Atoms

Water



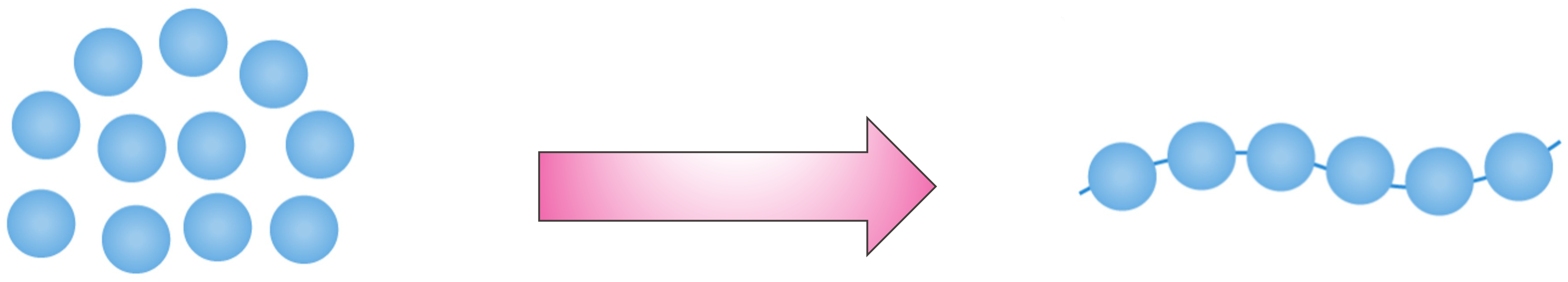
Molecules

Polymer

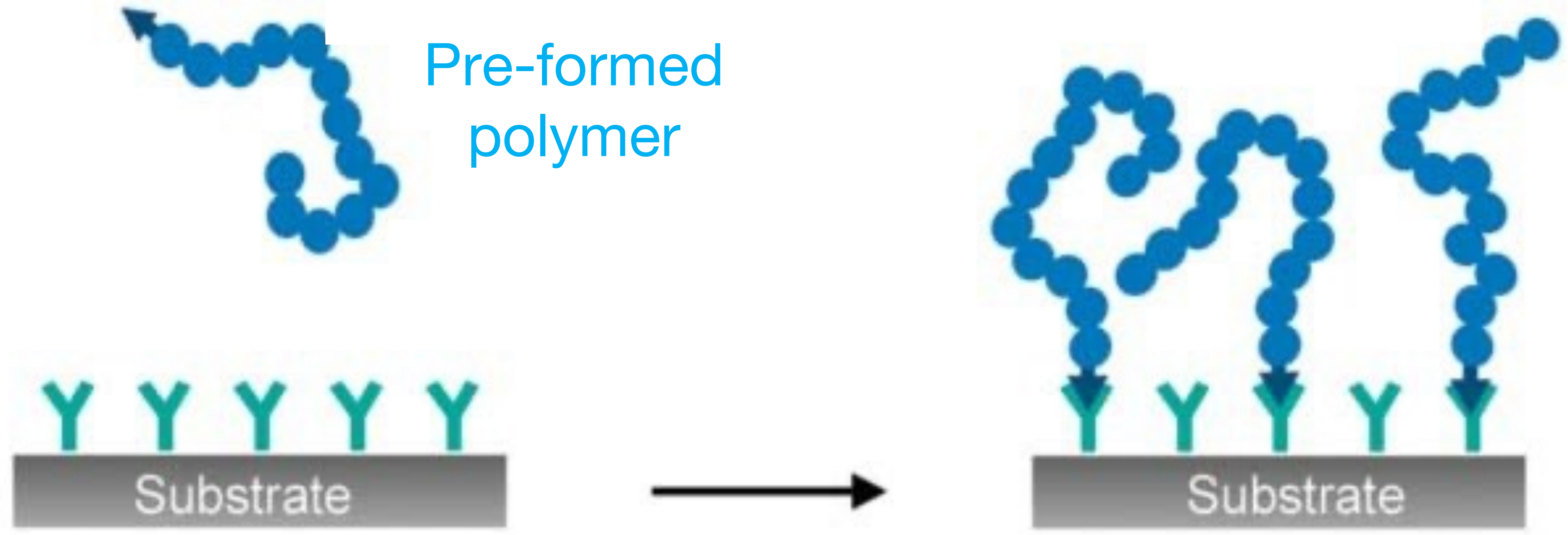


Chains of molecules

Surface Assembly of Polymers



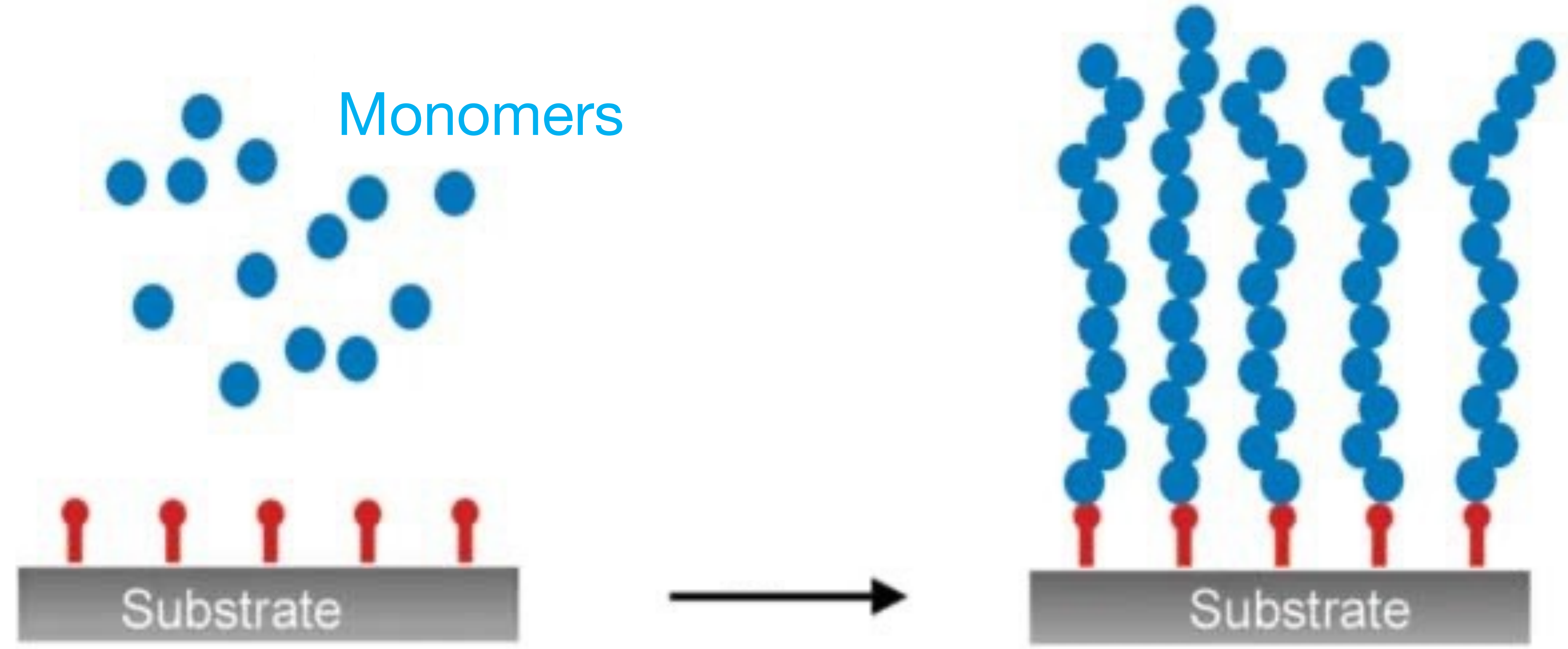
Top-down:
Grafting-to approach



Control over polymer properties

Limited surface density steric hindrance

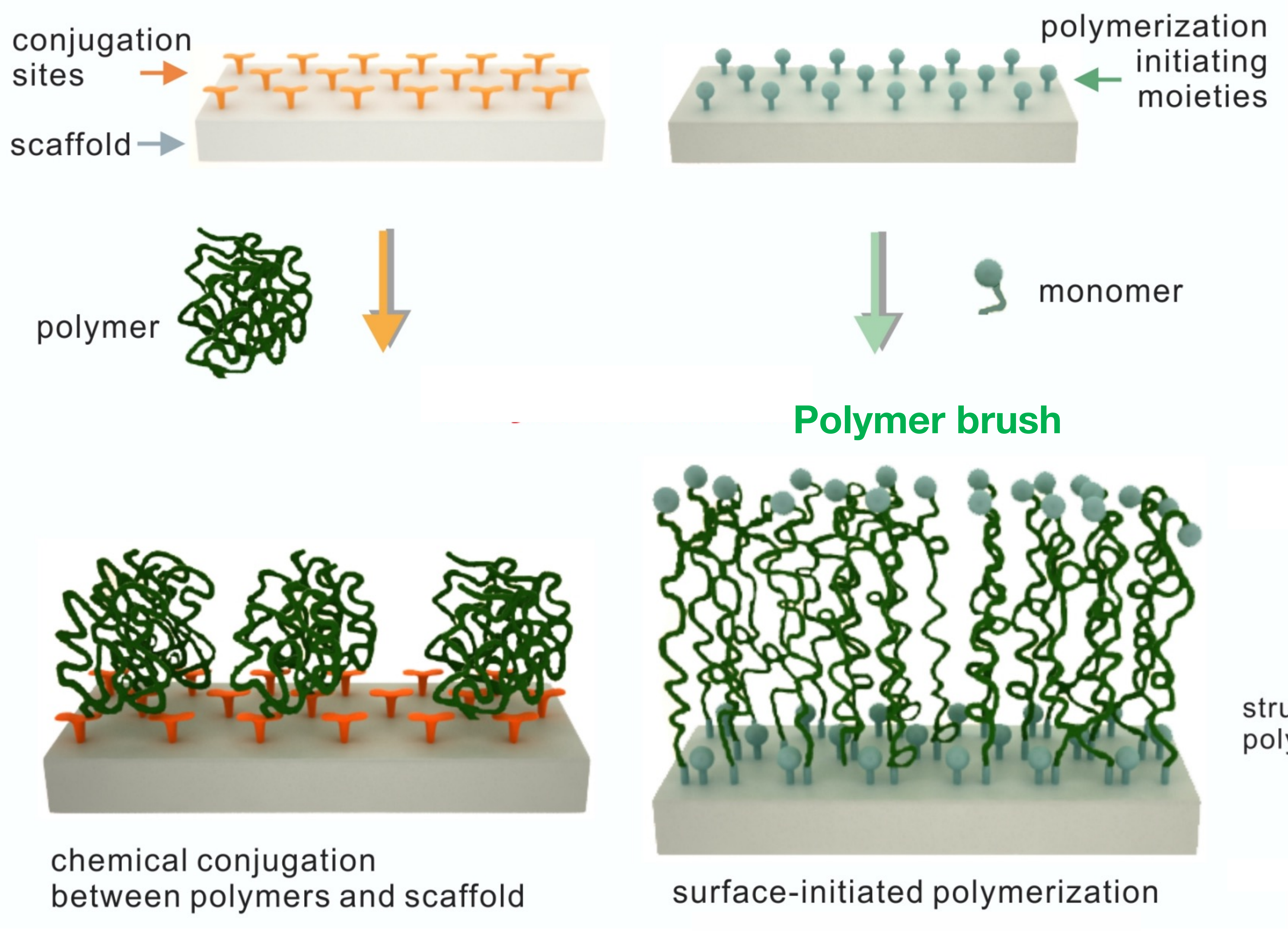
Bottom-up:
Grafting-from approach



High grafting density and stronger bonding

Less control over polymer properties

High Density Polymer Layers (Polymer Brushes) Add Functionality

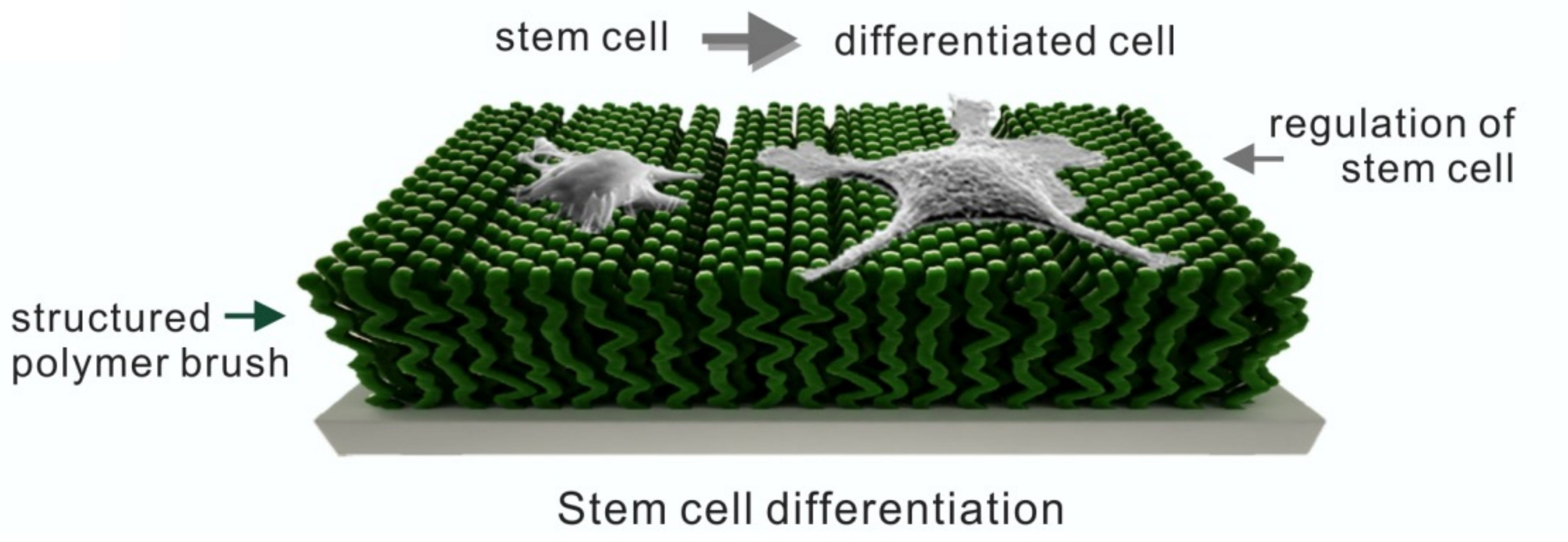


Polymer brush

$$D < 2R_g$$

Distance between adjacent grafting points

Radius of gyration of polymer



Kim & Jung, *Phys. BMB Rep.,49, 12*, **2016**

Comparing Polymer Brushes to SAMs

	Polymer brush		SAM (self-assembled monolayer)
	Grafting-to	Grafting-from	
Grafting molecule	Almost all types of polymers		Mainly alkanethiol & alkyl silnae
Micro-architecture	Various and complex polymeric structures		Well assembled molecular monolayer
Scaffold materials	Glass, titanium, gold, silver, silicon, etc		Gold thin film, oxide-formed substrate
Thickness	High tenability by adjusting polymer chain length		Thin: one molecular layer
Coating defects	Presence: short polymer chain Self-healing of defects: long polymer chain		Presence of defects and pinhole
In vivo stability	High stability		Low stability
Coating density	Loosely packed	Densely packed	Densely packed
Fabrication approach	Various chemical coupling between polymer and surface	Various polymerization on the surface	Thiol-gold bond & silane linkage

Kim & Jung, *Phys. BMB Rep.,49, 12*, **2016**

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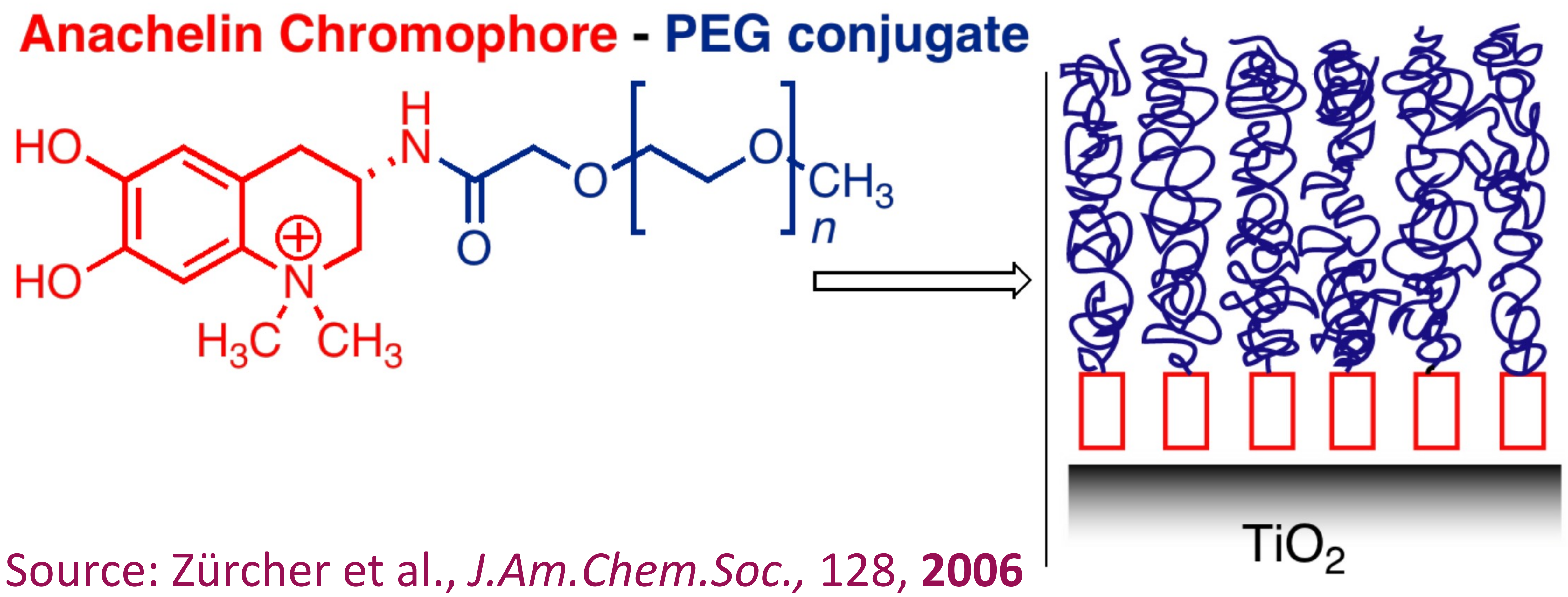
Is this Catechol-Based Assembly of PEG Molecules a SAM?

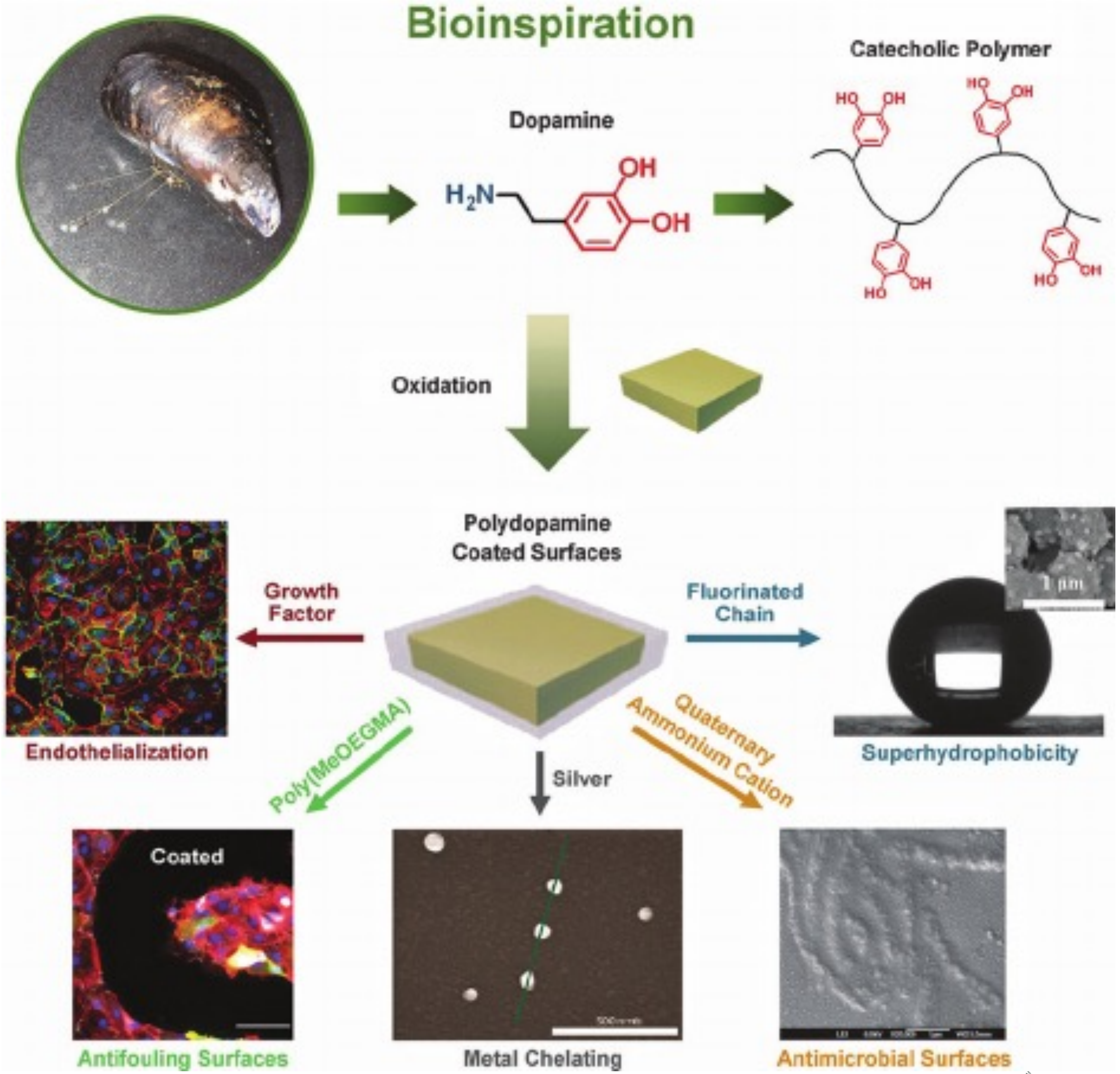


Source: Zürcher et al., *J.Am.Chem.Soc.*, 128, **2006**

Catechol groups have high affinity for metal oxide surfaces

Formation of **stable**, **oriented**, and **packed monolayer**

Application: Protein-resistant, antifouling surfaces



Wei et al., *Mater. Horiz.*, 2, **2015**

Is this Grafted Polymer Assembly of PEG Molecules a SAM?

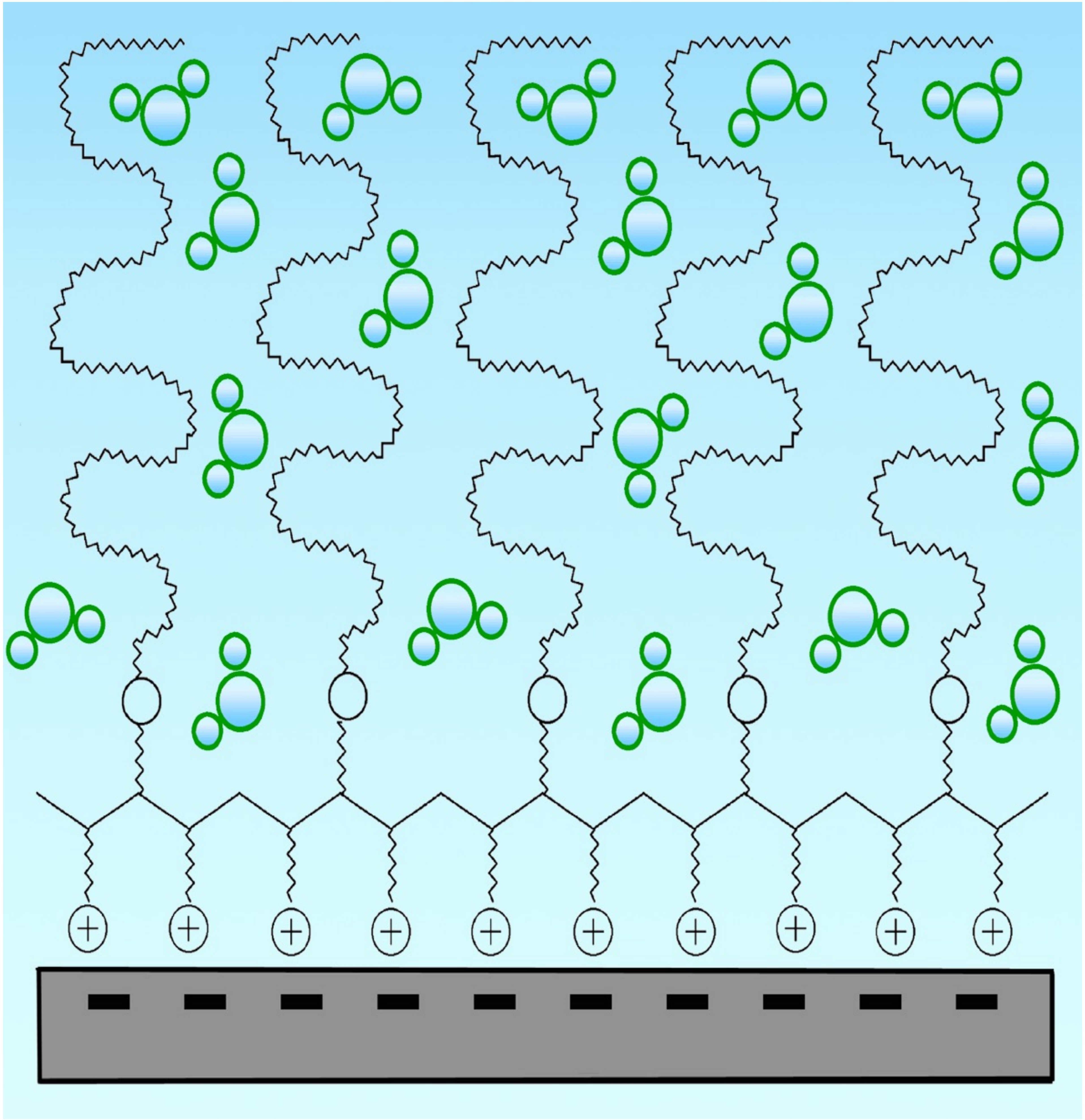
Poly(*L*-lysine)-*graft*-poly(ethylene glycol)
(PLL-*g*-PEG)

Monolayer formed on metal oxide surfaces due to electrostatic interactions

No!

PLL-*g*-PEG is grafted along the positively charged backbone of PLL to attach through electrostatic interactions to negative oxide surfaces

SAMs are dense, highly ordered monolayers. Alternatively, PLL-*g*-PEG forms a more flexible, brush-like structure leading to more hydration.



SuSoS SURFACE TECHNOLOGY

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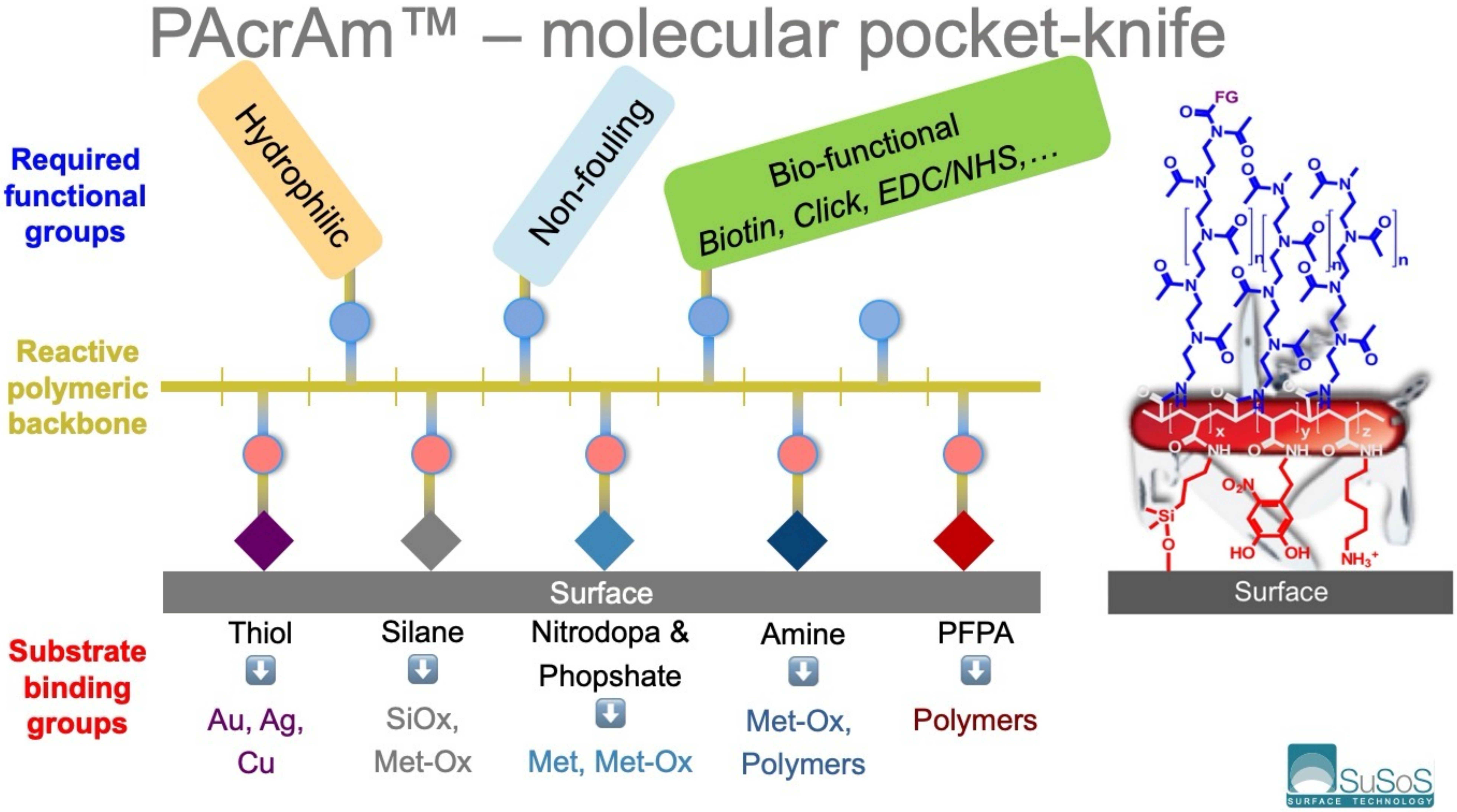
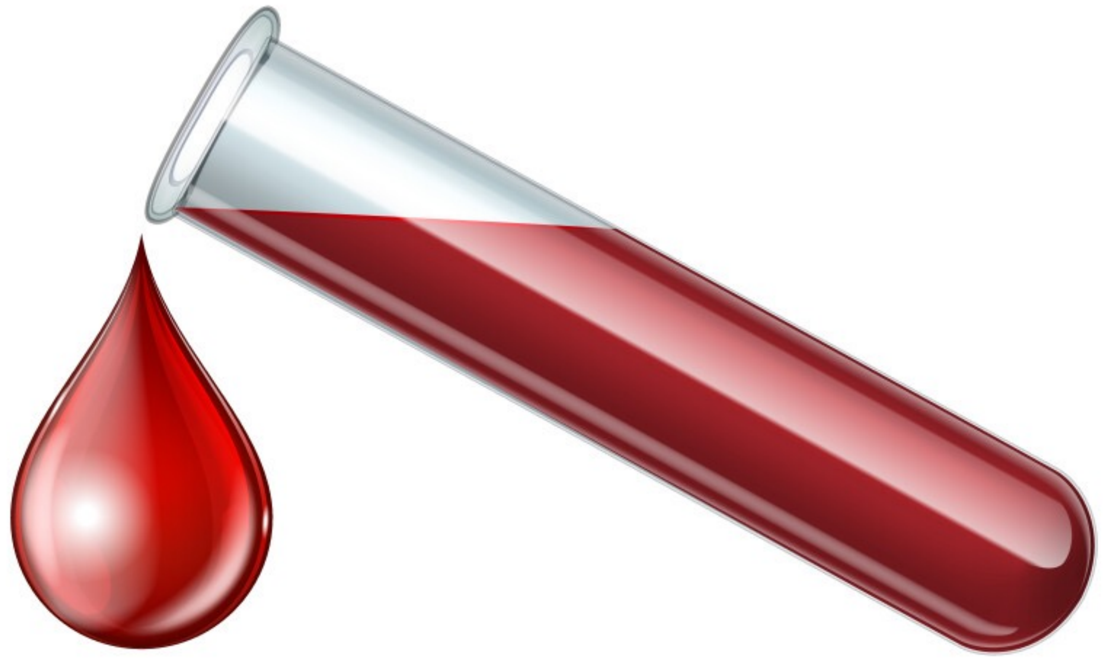
The “Swiss Army Knife” of Surface Chemistry with Polymers



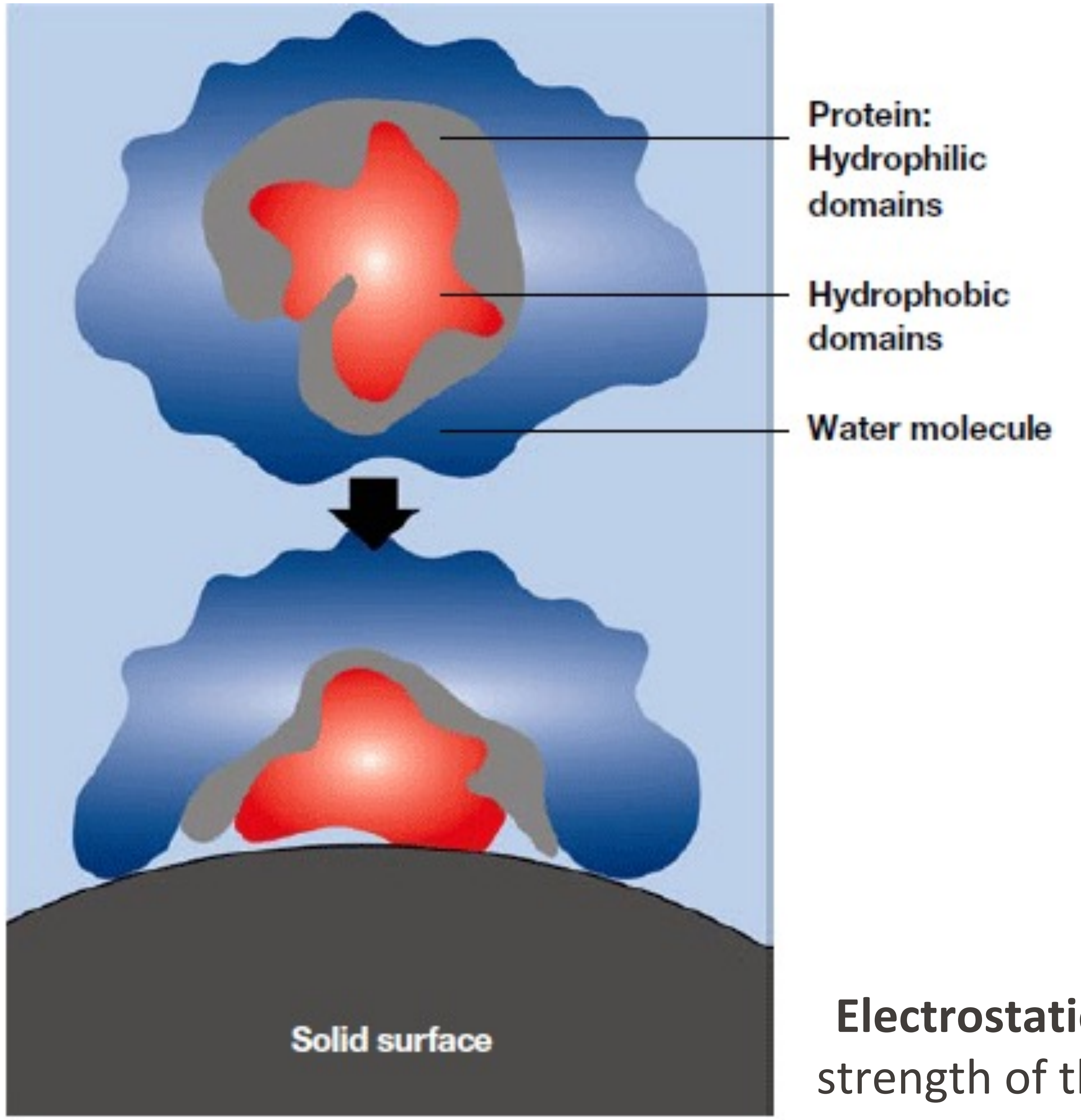
What Can Such Polymer Layers be Used For in Surface Science?

Nonspecific protein adsorption in complex environments/biofluids



Proteins on Surfaces – Adsorption and Denaturation

Proteins adsorb on surfaces in order to lower the free energy of the system



Hydrophobic interactions

Hydrophobic groups on the protein: tend to be located inside of the overall protein structure

↓

shielded from the aqueous surroundings

Upon encountering a hydrophobic surface, it is energetically favorable for the hydrophobic amino acids to be close to the surface

↓

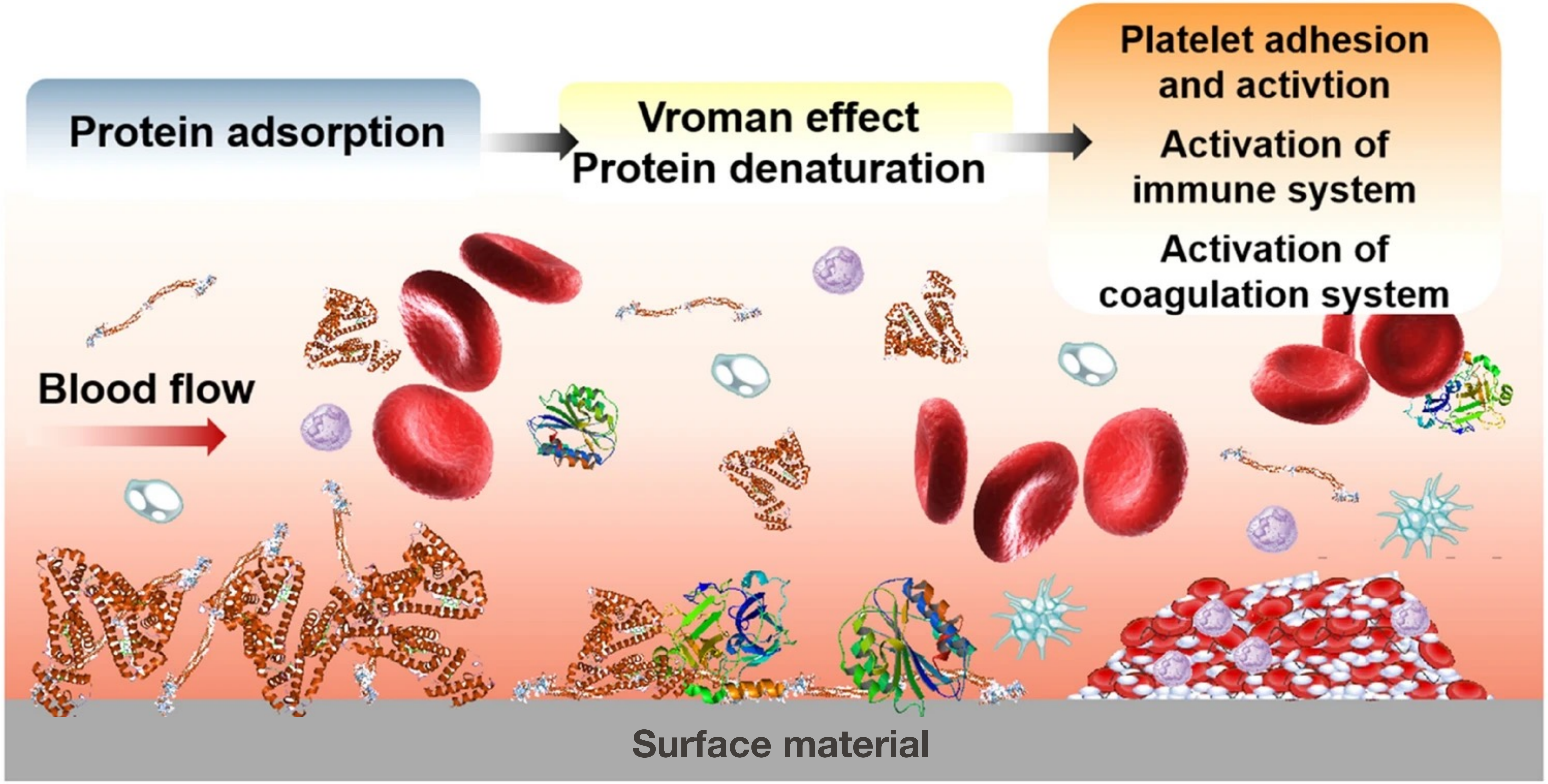
Unfolding or denaturation of the protein

Electrostatic interactions with the surface are often important → pH and ionic strength of the surroundings can have a significant influence on protein adsorption

Proteins on Surfaces – Vroman Effect

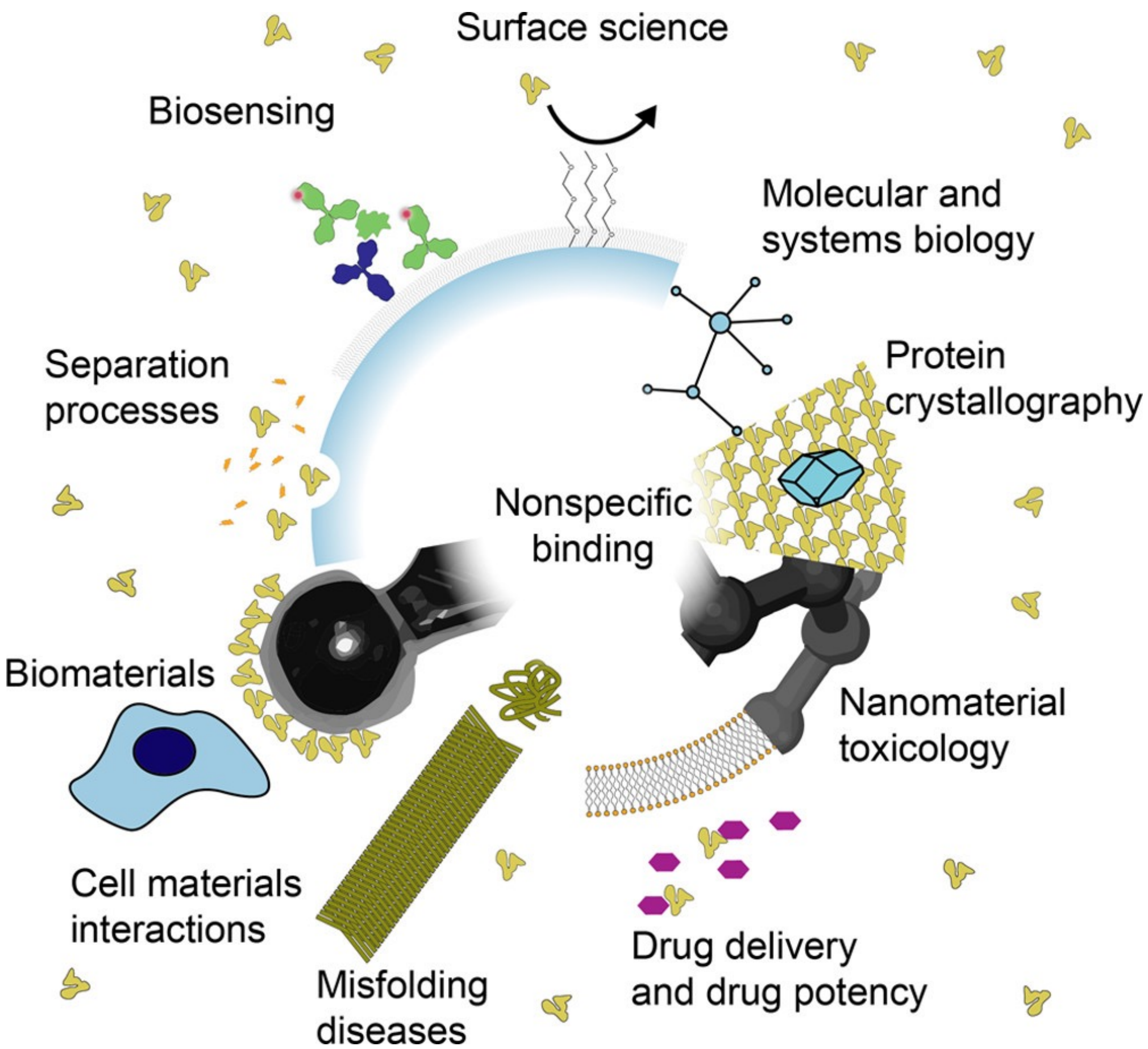
Small, abundant molecules (albumin, fibrin) will rapidly and reversibly coat a surface, gradually being replaced by larger molecules with higher affinity for the surface

Conformational change of many proteins upon nonspecific adsorption to the interface



Ji, *et al.*, *Adv. Fiber Mater.* *5*, 1198, **2023**

Fields of Study where Nonspecific Binding has Major Implications

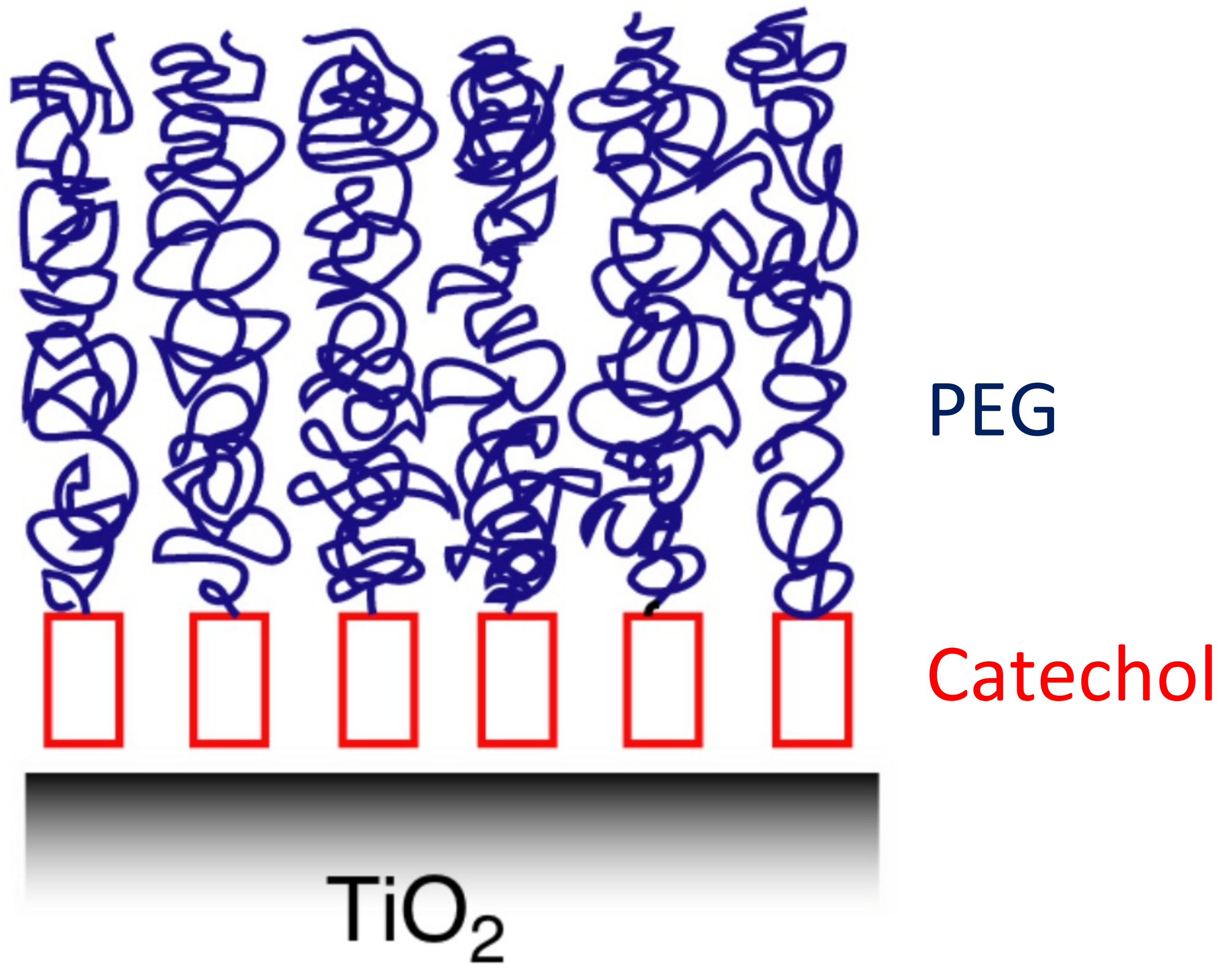


Frutiger, *et al., Chem. Rev. 121*, 13, **2021**

Antifouling Mechanisms of Polymer Layers on Surfaces

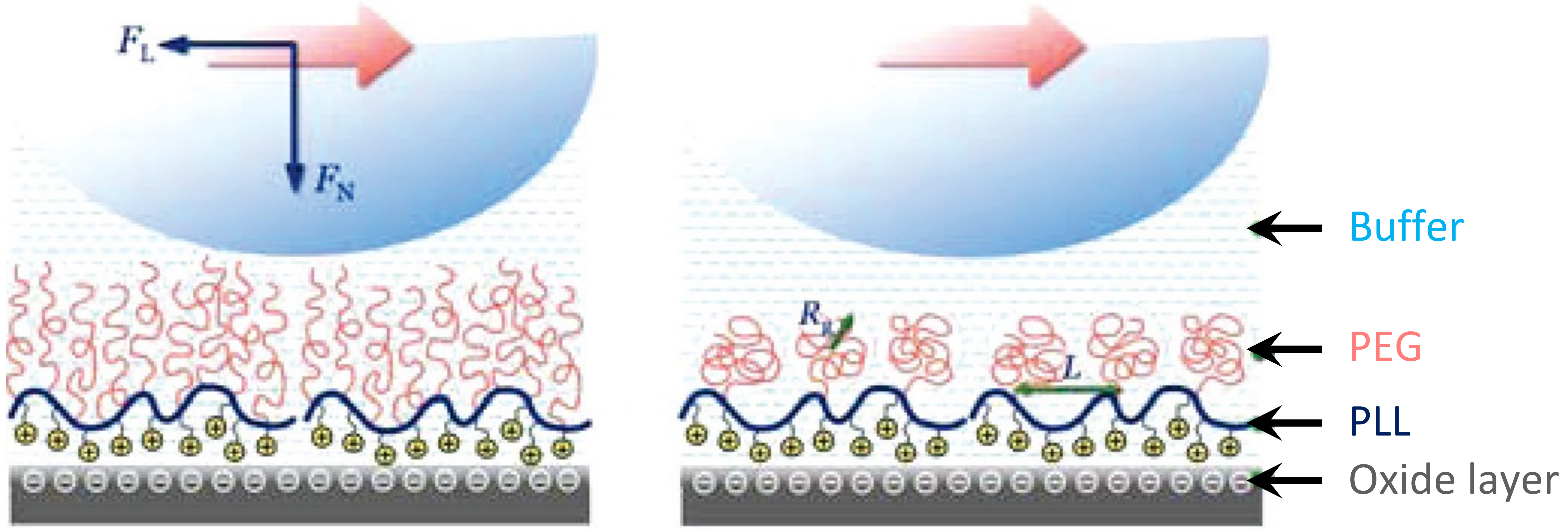
Dense PEG layer

Strong steric barrier



Hydration and dynamic flexibility of PEG brush

Frictional properties vary with polymer architecture

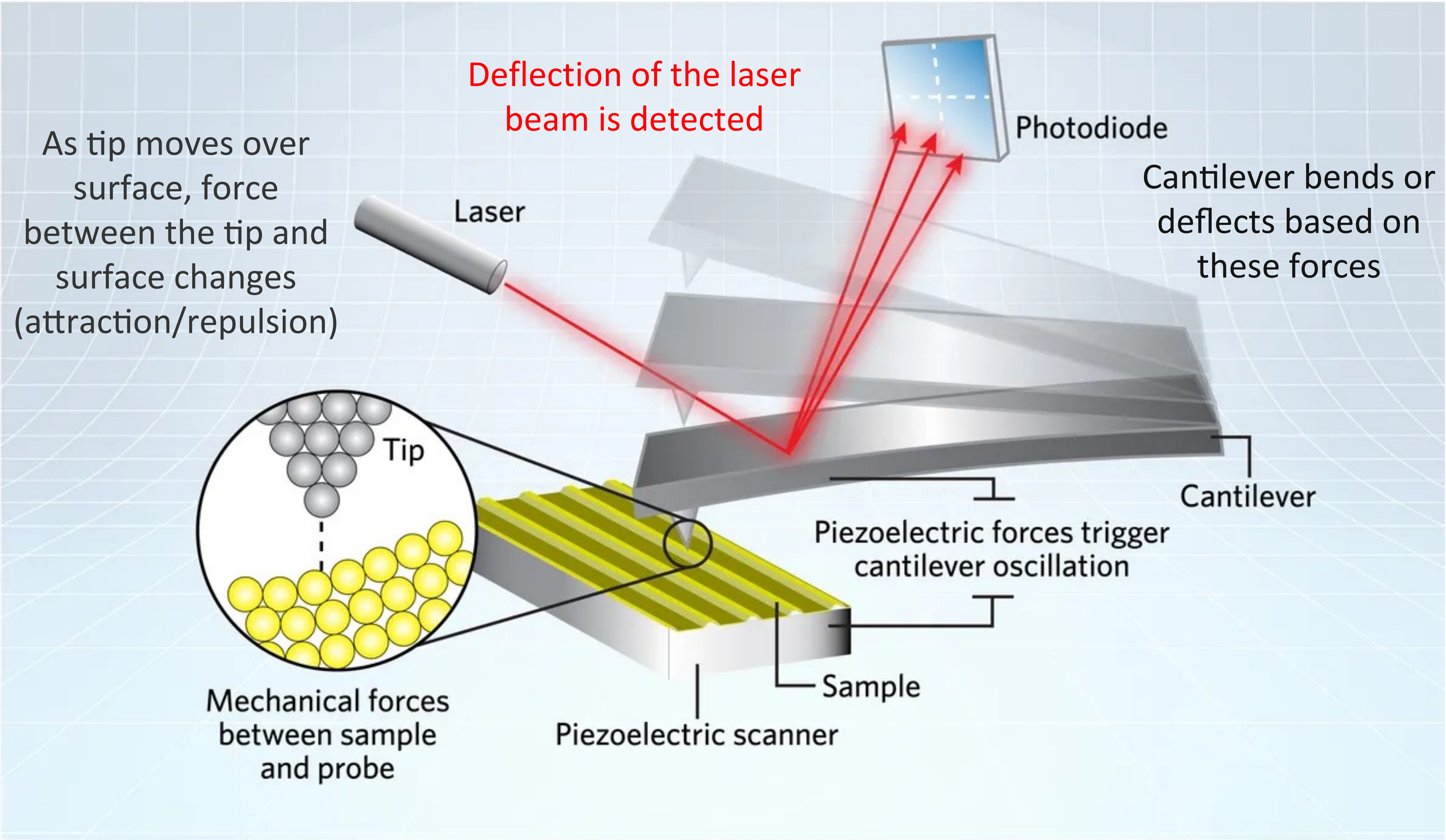


Spatial density of PEG side chains based on the distance between PEG chains (L) and radius of gyration (R_g) of side chains

Wei et al., *ACS. Appl. Mater. Interf.*, 1, 6, **2009**

How Can We “See” What is Happening on Surfaces?

Atomic Force Microscopy (AFM)



TheScientist

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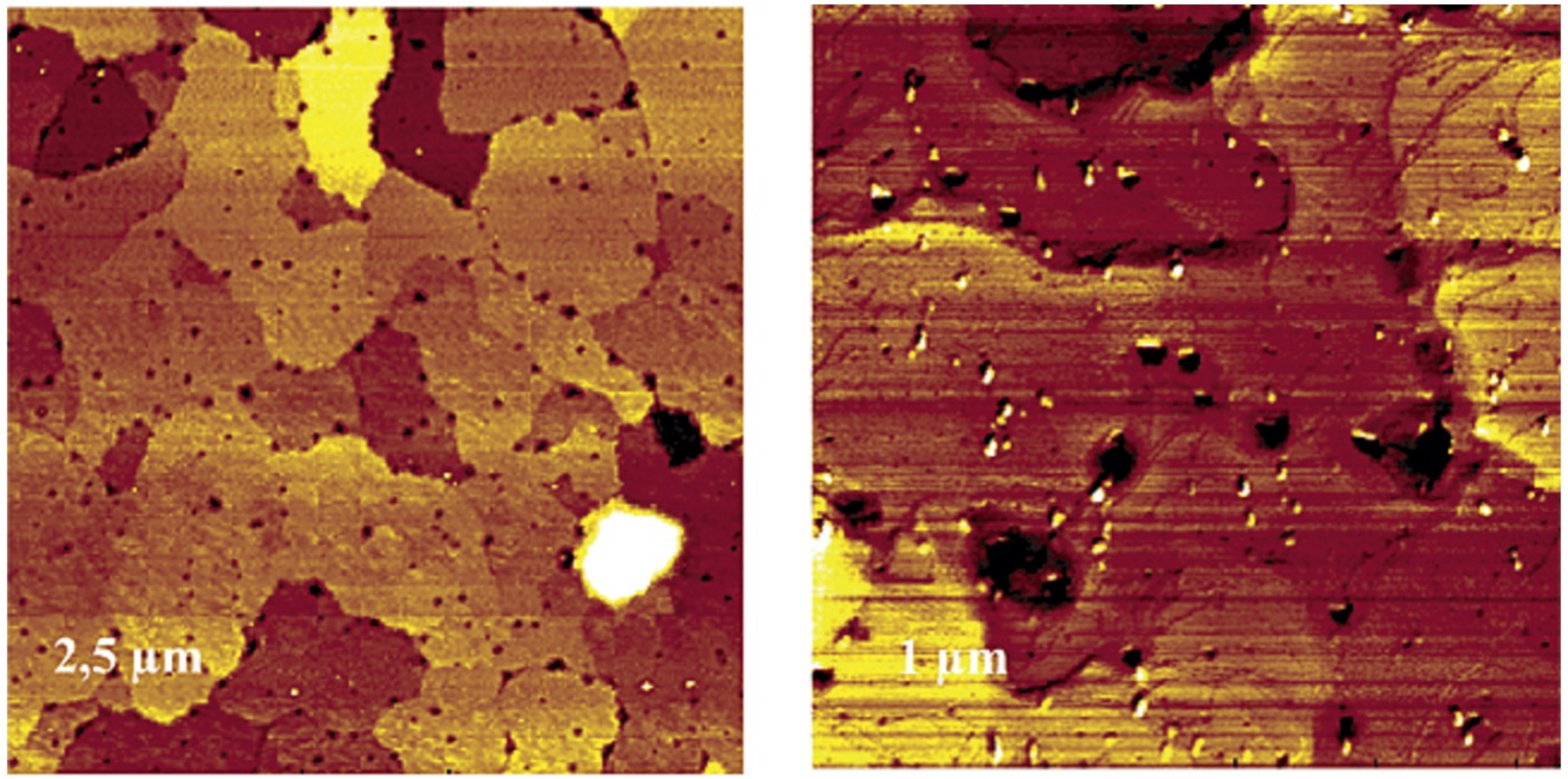
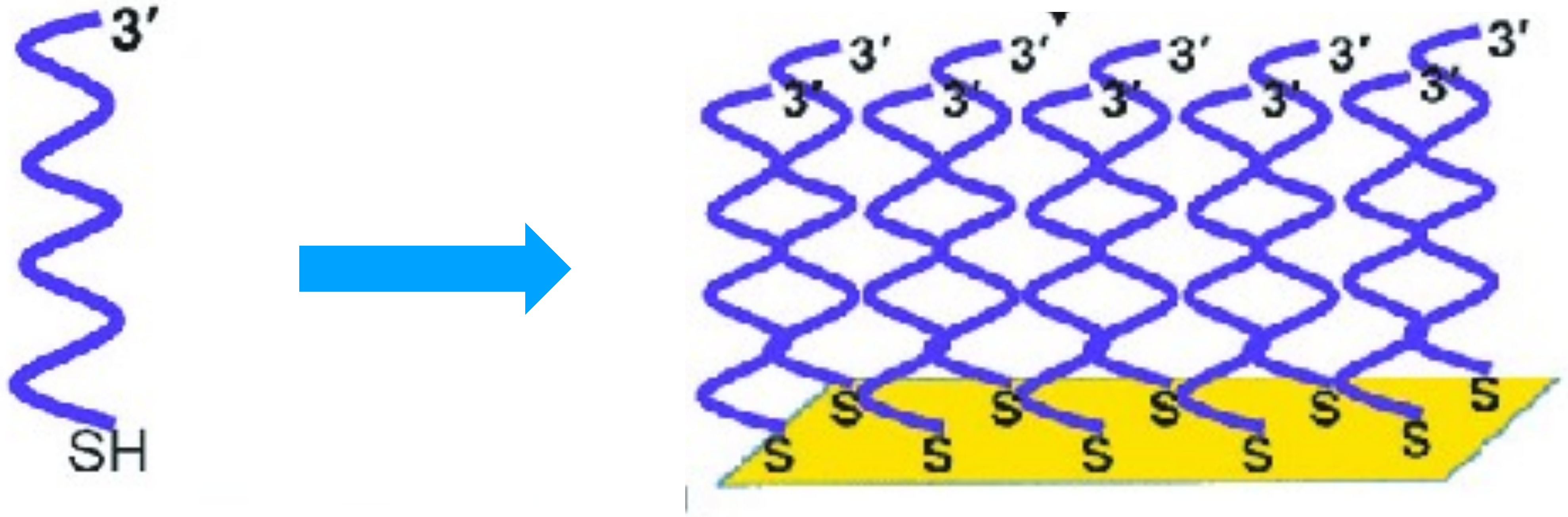
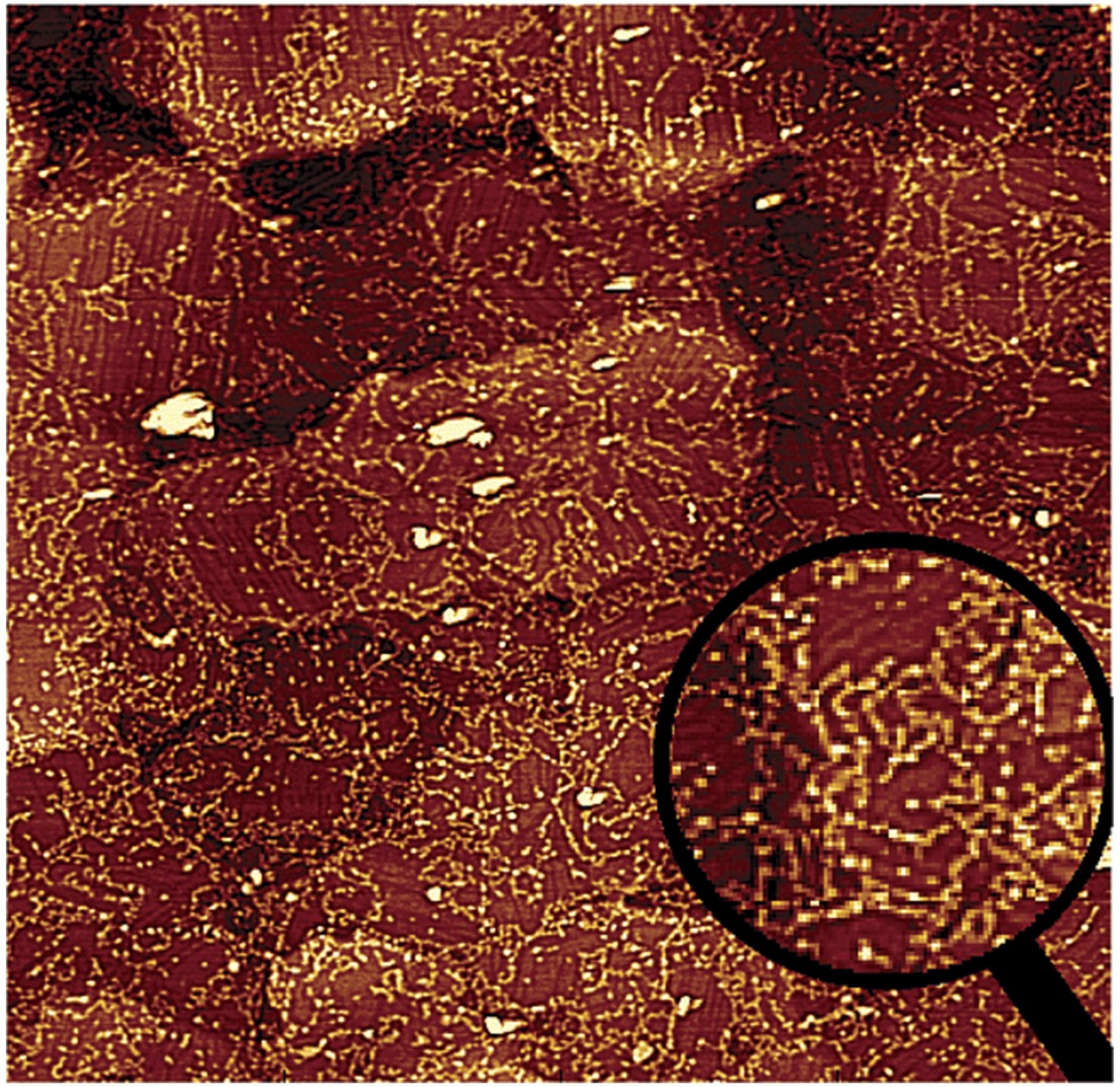
Atomic Force Microscopy to Visualize Surfaces



AFM image of Au (111) surface (terraces observed)



Surface exposed to a solution of oligonucleotides (25-base thiolated DNA)



2 µm

Mourougou-Candoni, *et al.*, *Langmuir*, 19, 3, **2003**

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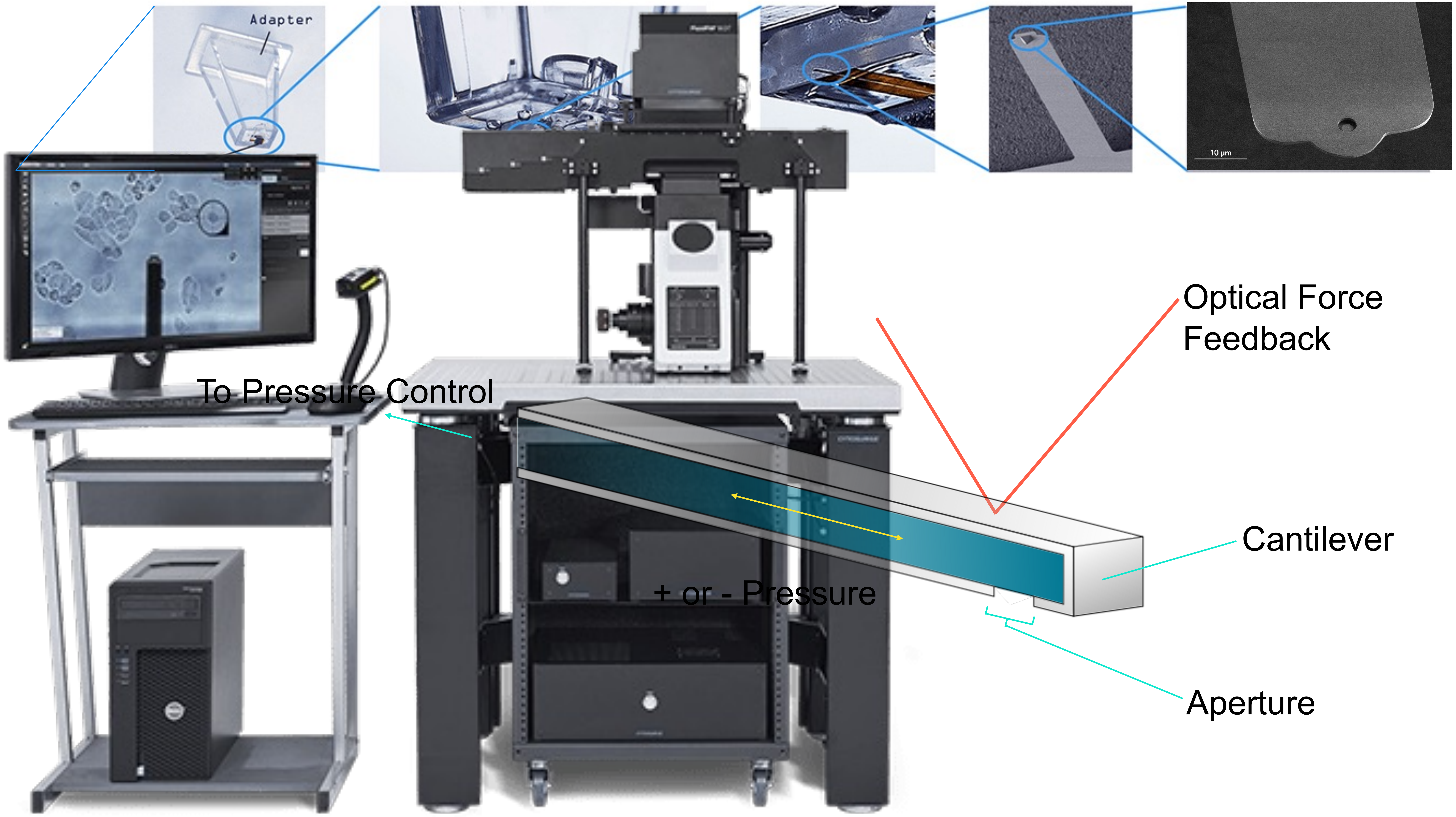
Advances in AFM – the Fluid Force Microscope (FluidFM)



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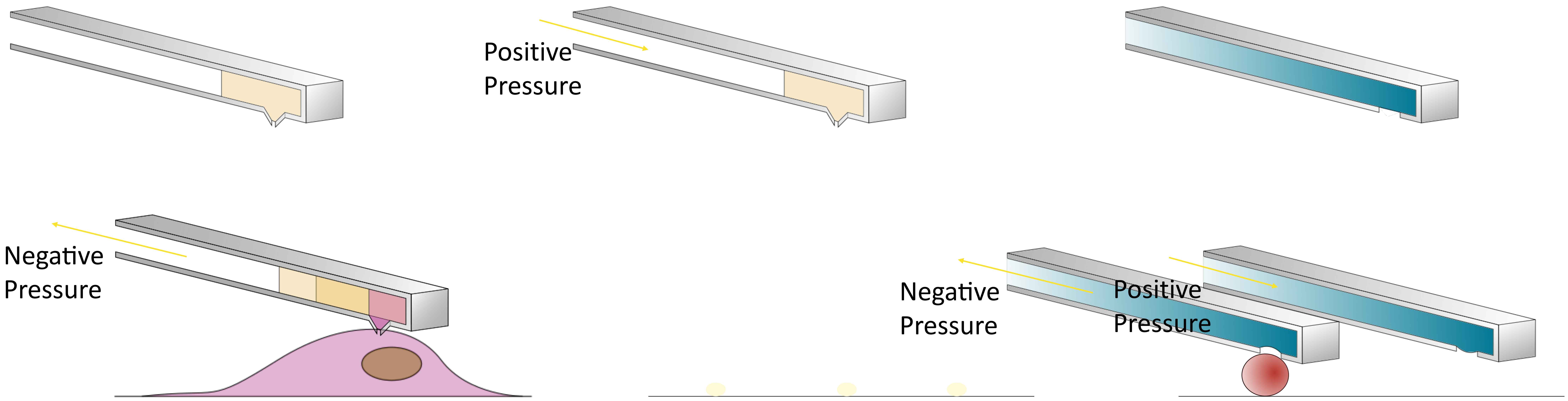
Advances in AFM – the Fluid Force Microscope (FluidFM)

Injection and Sampling | **Dispensing and Nanoprinting** | **Pick and Place**



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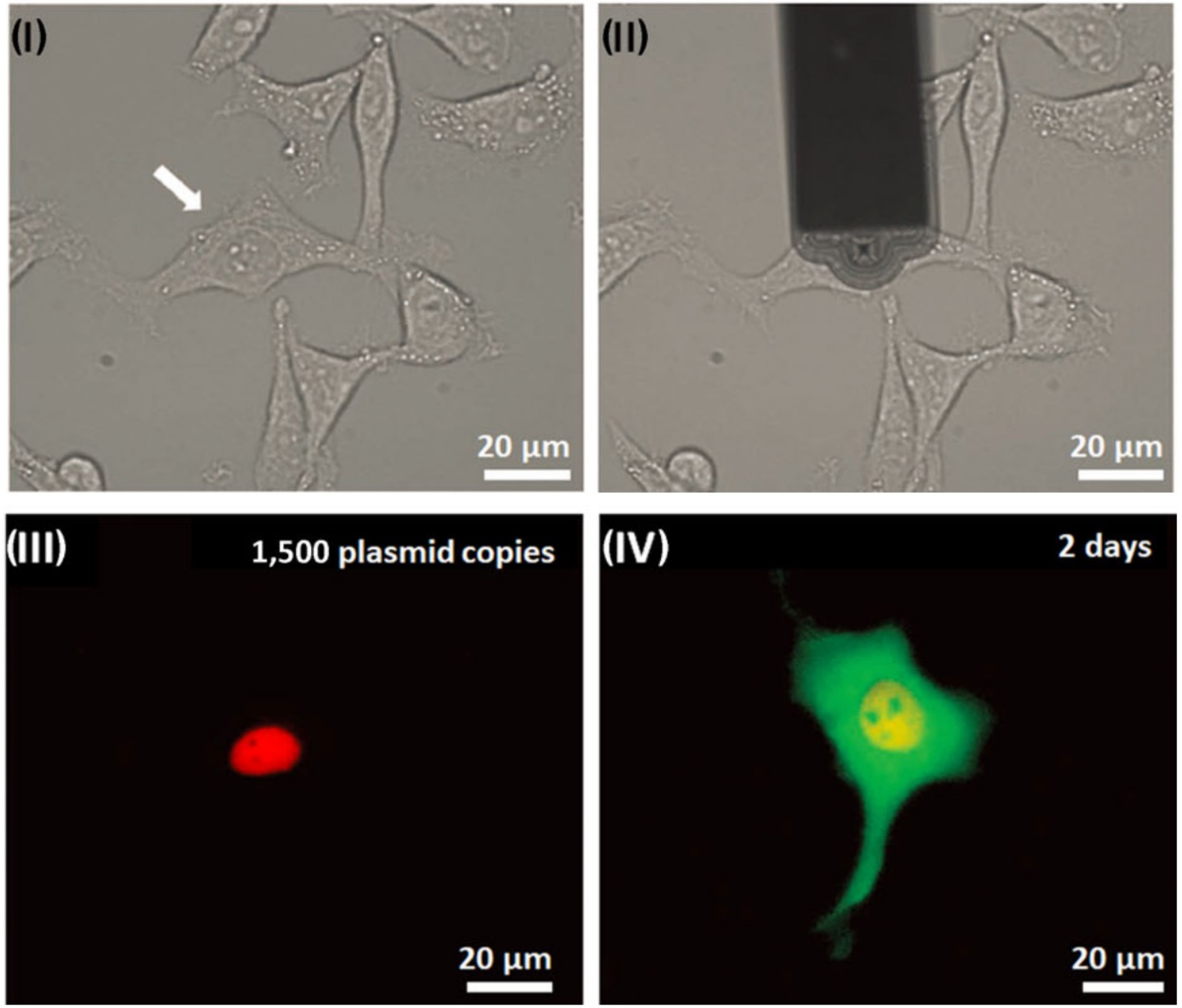
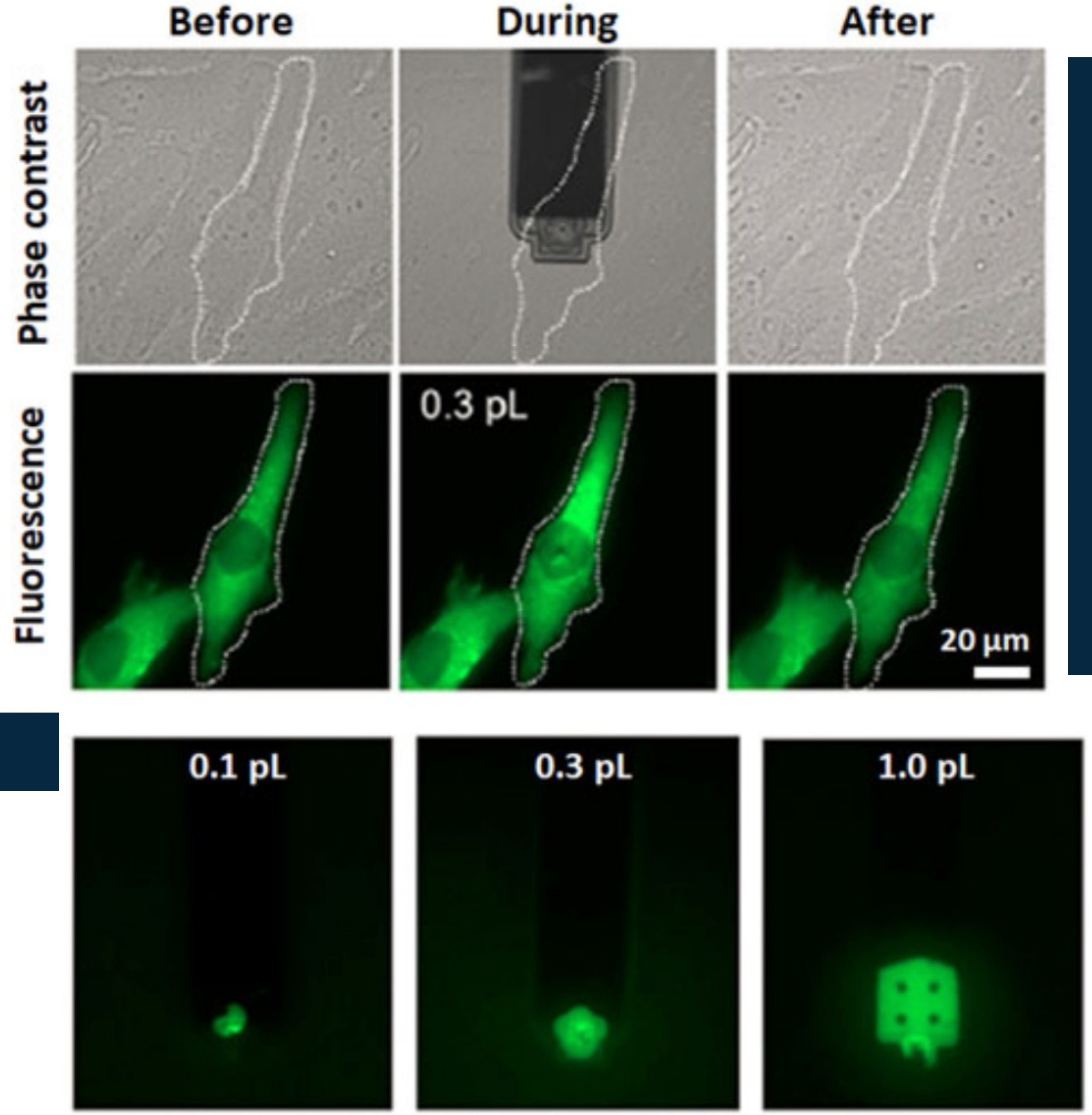
Applications of Using FluidFM and Interfacing with Cells

Delivering plasmid DNA to cell nucleus



Extract from nucleus (82% viability for 4.0 pL)



Li, *et al. Nano Res.*, 15, 773, **2022**

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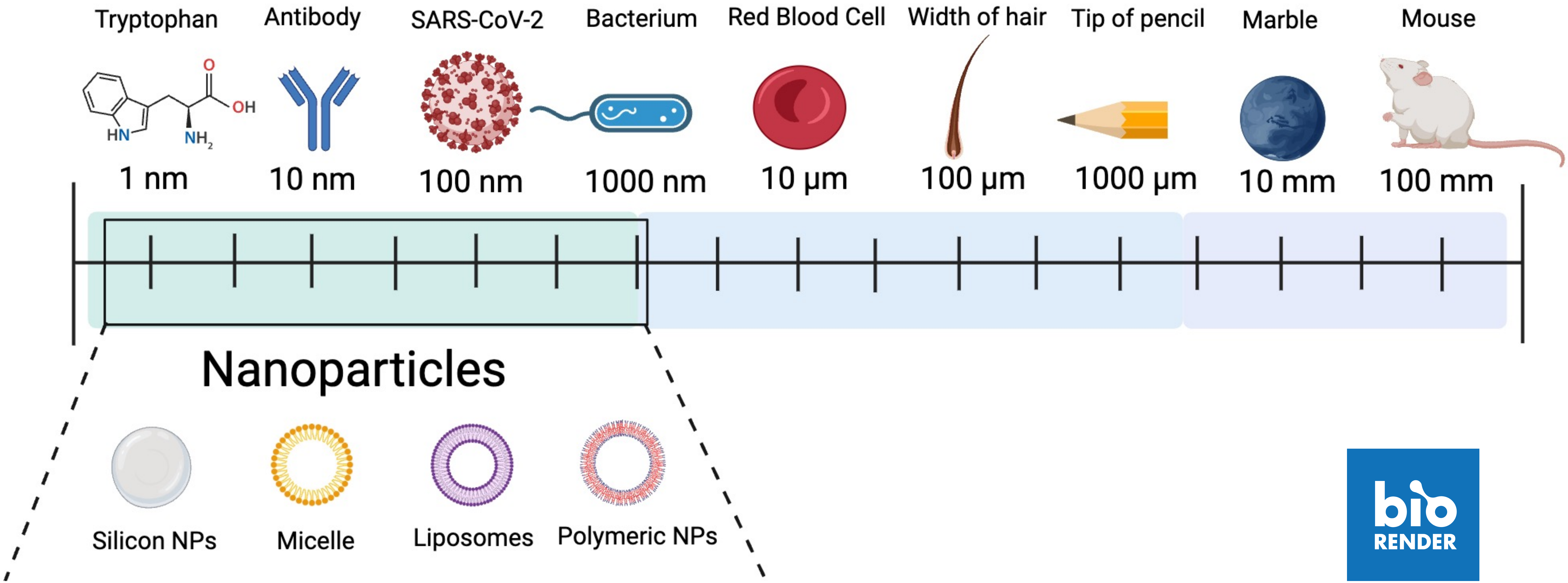
What is Nanoscience?

Study of objects and systems in which at least one dimension is 1-100 nm



Unique Properties at the Nanoscale

Increased surface-to-volume ratio ➔ dominance of surface effects over bulk properties

Bulk gold

Gold nanoparticles

Optical properties of metal nanoparticles are dependent on their sizes and geometries

Why?

H!Q

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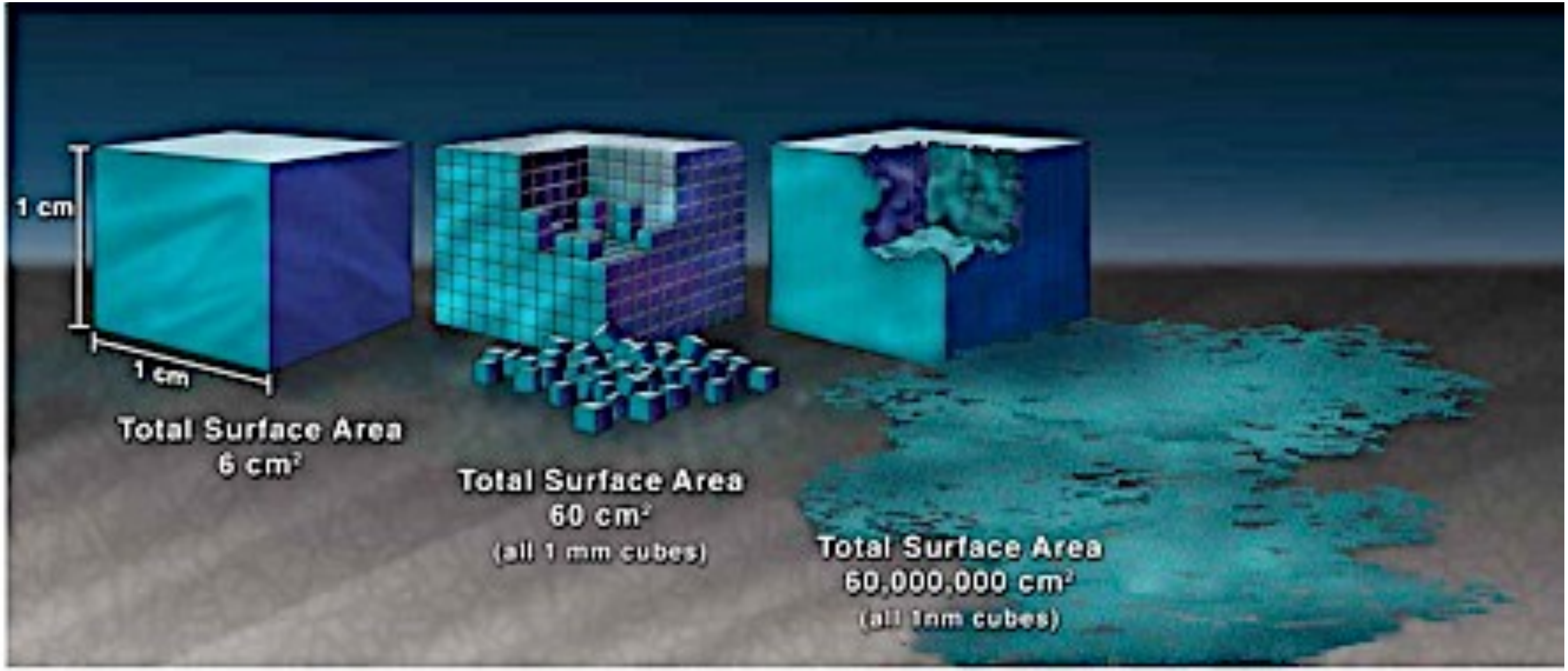
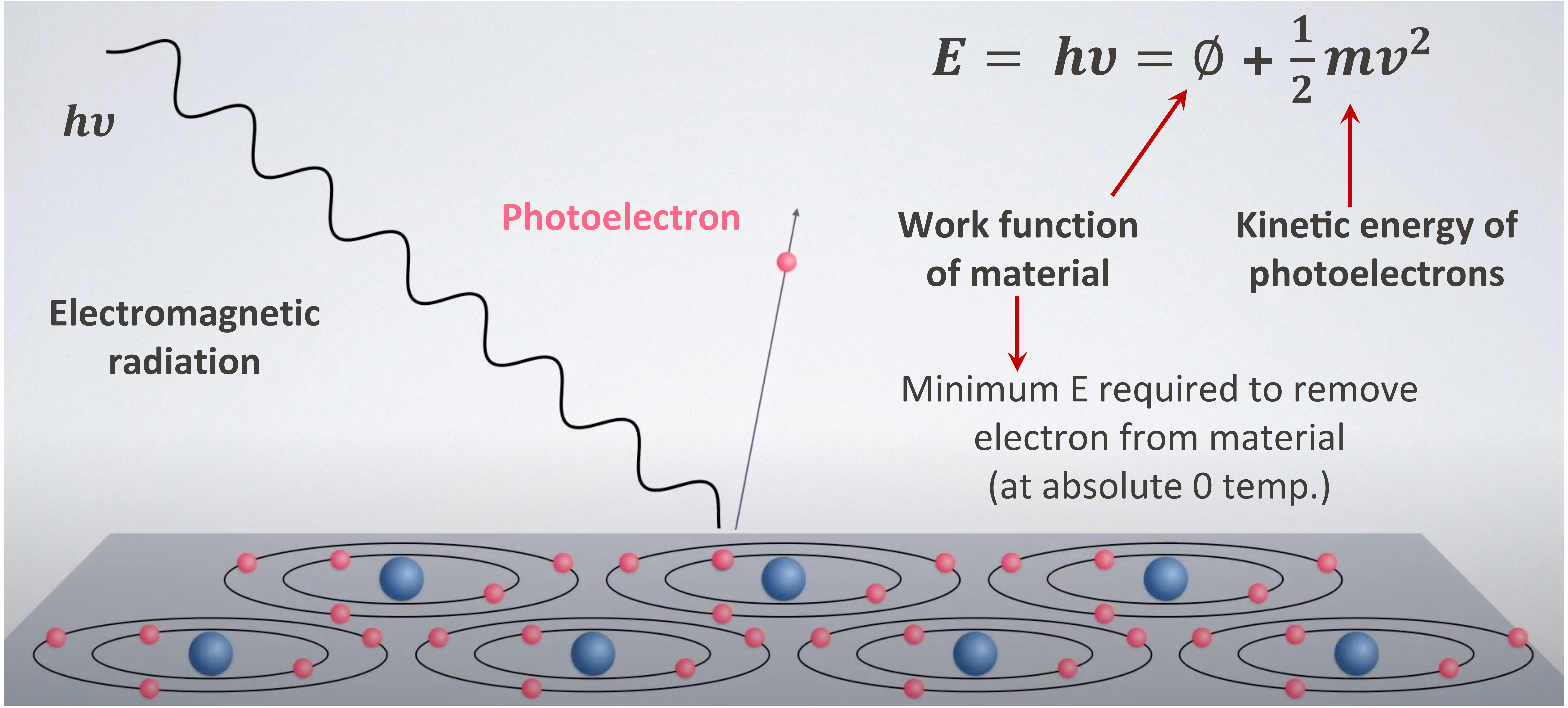
Why Nanoscale Matters for Electronic Properties at Surfaces

Increased surface-to-volume ratio ➔ significant number of electrons are at or near the surface, leading toe enhanced surface effects



Recap: Photoelectric Effect – Work Function of Material

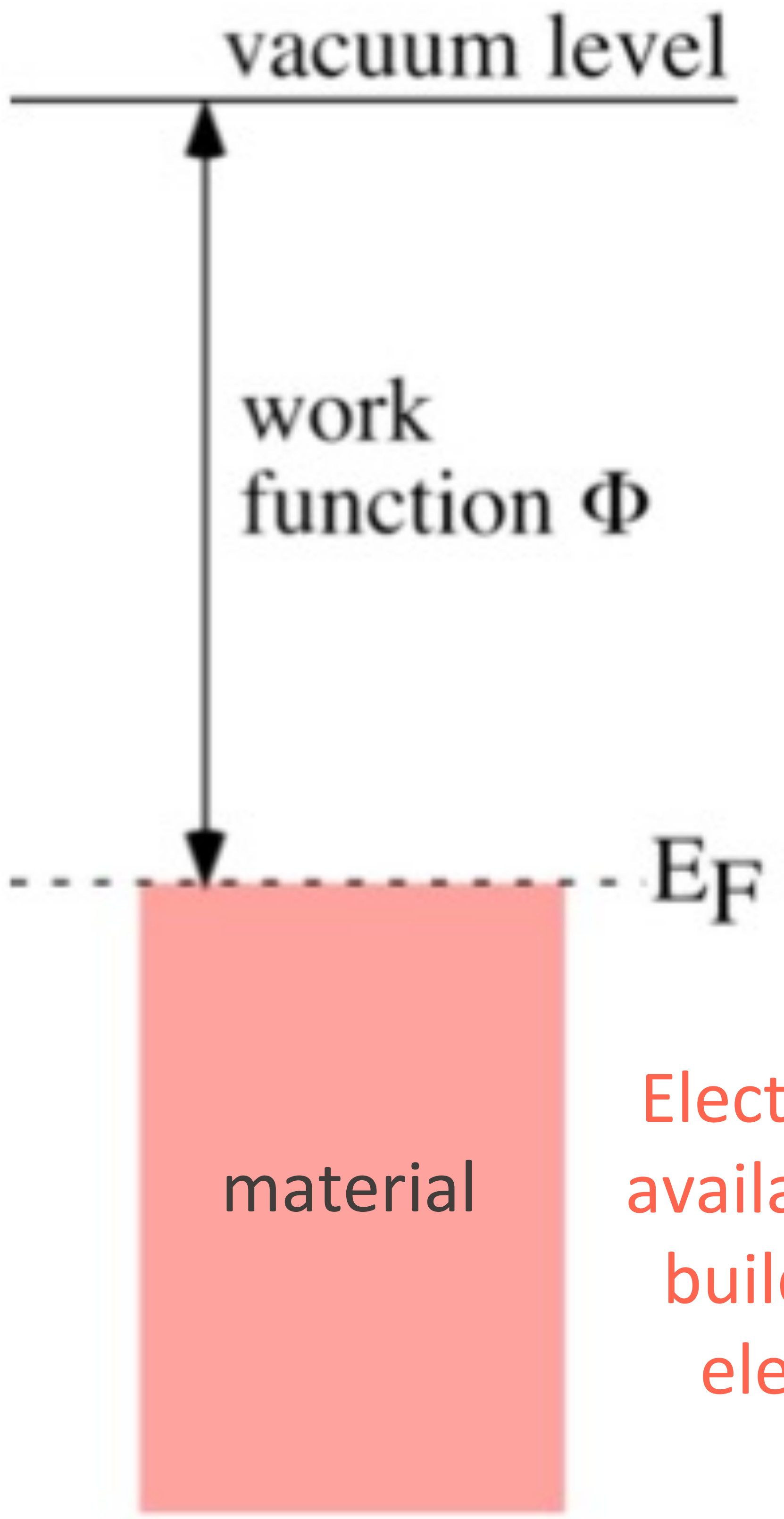


Surface of sample

Work Function of Different Materials

Work function (Φ) of = electron at = surface of a metal: difference between = potential energy of the electron at the vacuum level (about 100 Å from the surface) and the **Fermi level (E_F).** Represents the minimum energy required to eject an electron from the highest occupied level into vacuum

$$\Phi = E_{vac} - E_F$$

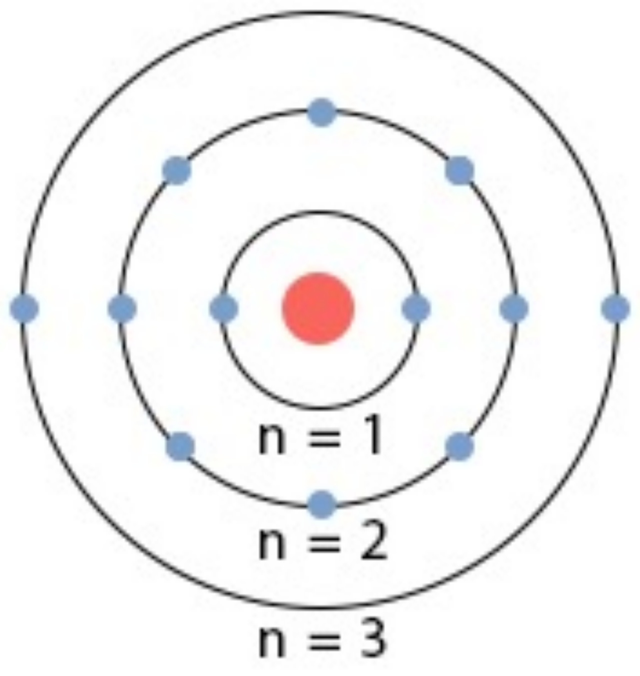


Electrons pack into lowest available energy states and build up a "Fermi sea" of electron energy states

Electrons are Fermions (subatomic particle that follows Fermi-Dirac statistics)

Pauli Exclusion Principle: electrons cannot exist in identical energy states (no two electrons can have identical quantum numbers)

Principal (n)

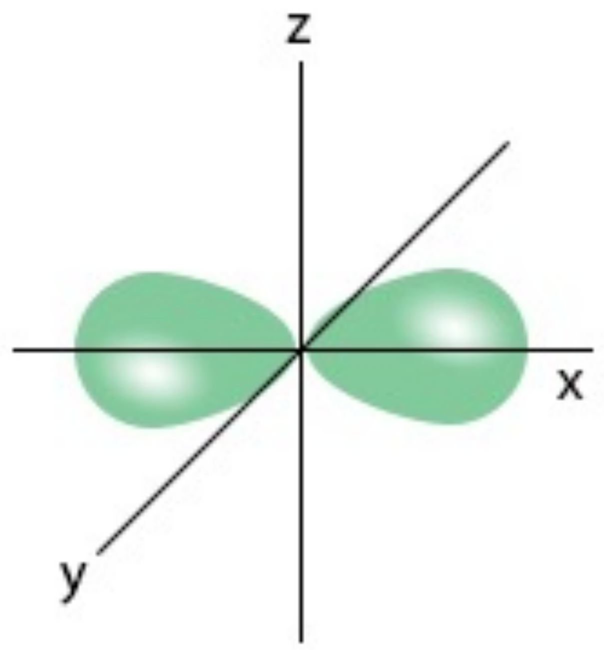


Distance of electron from nucleus

Orbital (l)

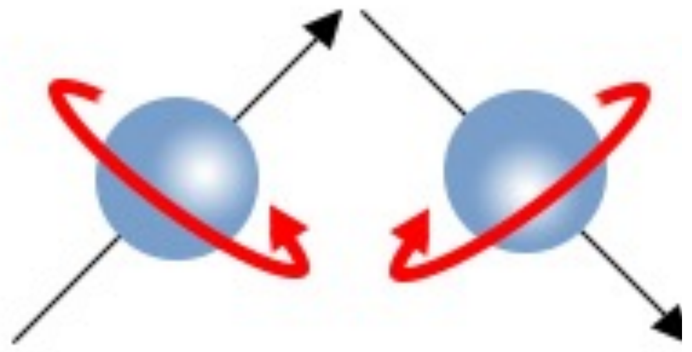
Shape of orbital

Magnetic (m_l)



Orientation of orbital

Spin (m_s)



Orientation of electron spin

Work Function of Different Materials

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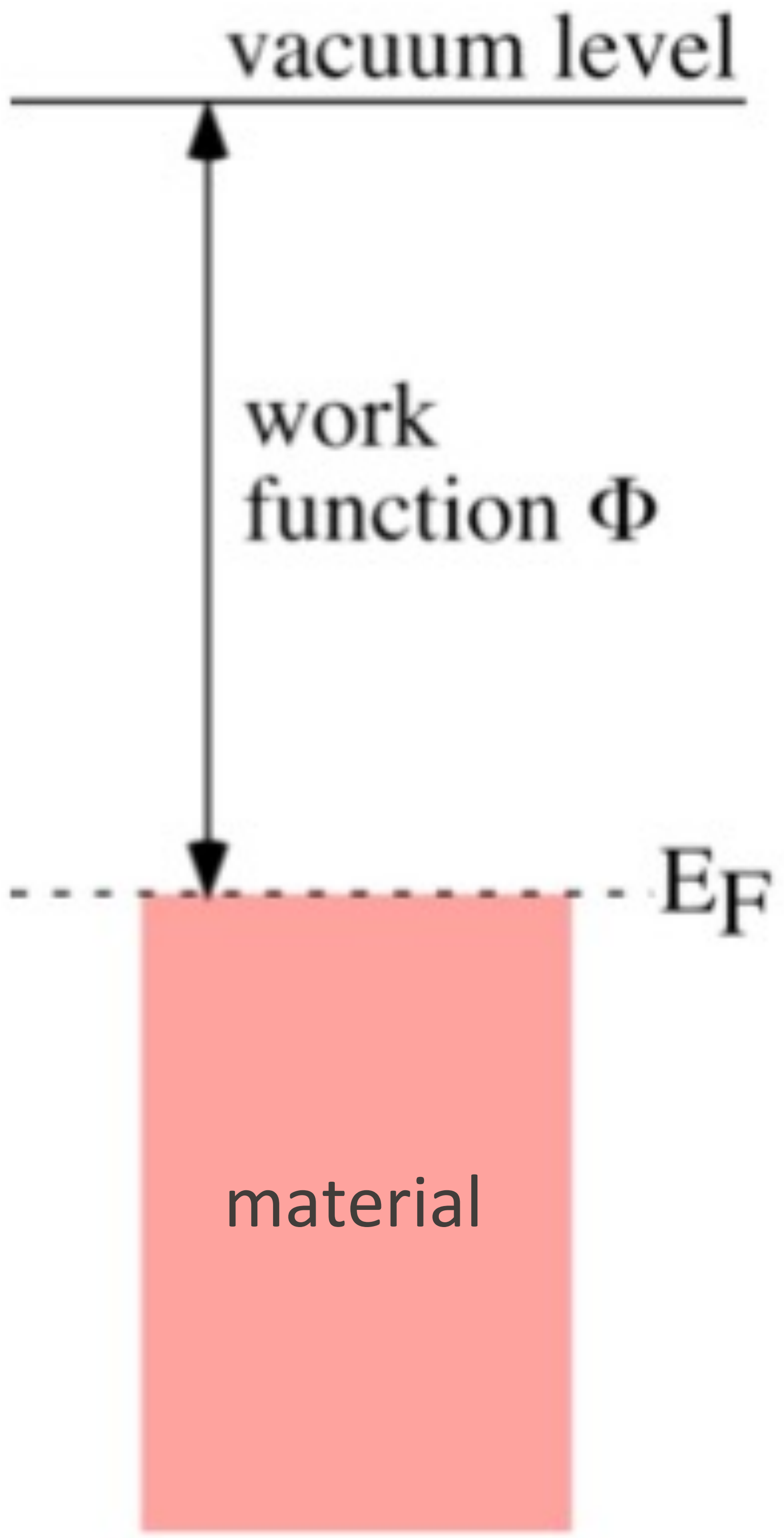


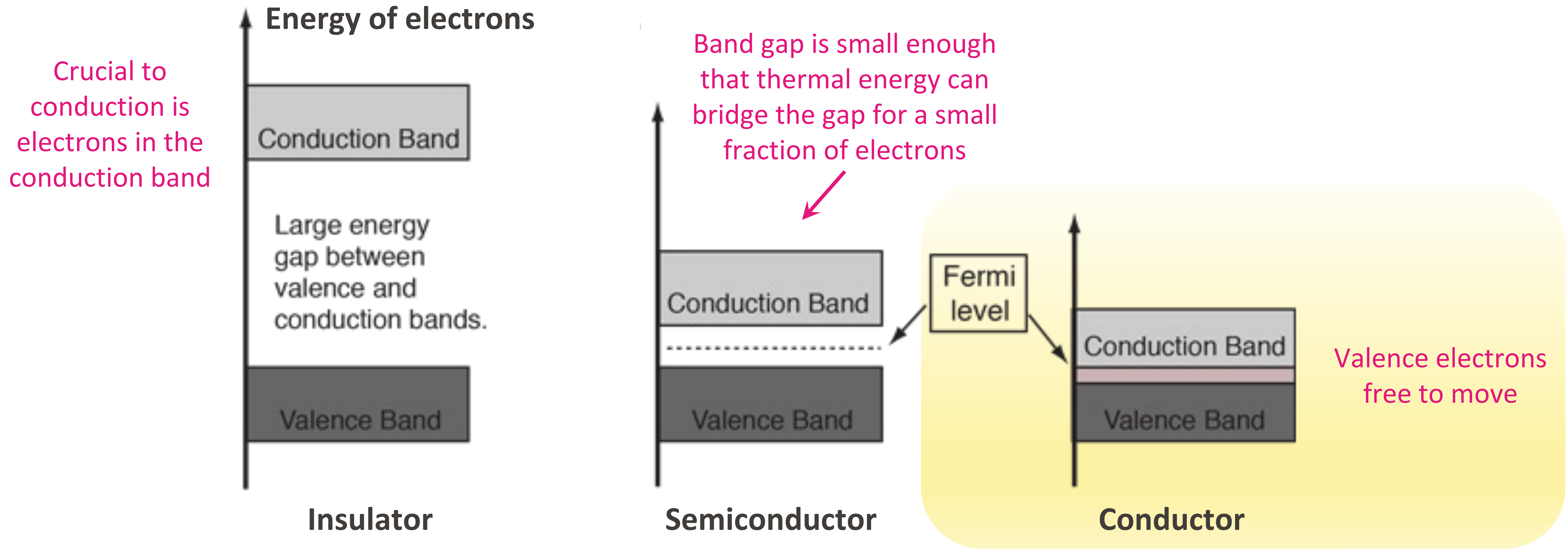
Element	Surface plane	Work Function in eV
Ag	(110)	4.52
Ag	(100)	4.64
Ag	(111)	4.74
Cs	polycrystalline	2.14
Cu	(110)	4.48
Cu	(100)	4.59
Cu	(111)	4.98
Ge	(111)	4.80
Ni	(110)	5.04
Ni	(100)	5.22
Ni	(111)	5.35
W	(111)	4.47
W	(100)	4.63
W	(110)	5.25

Φ depends on the surface property of the material (crystallographic orientation/contamination)

Rough surfaces have a lower work function

Fermi Level Plays Important Role in Band Theory of Solids

To visualize the differences between insulators, semiconductors, and conductors, we can plot the available energies for electrons in the materials



Position of the Fermi level relative to the conduction band is a crucial factor in determining electrical properties

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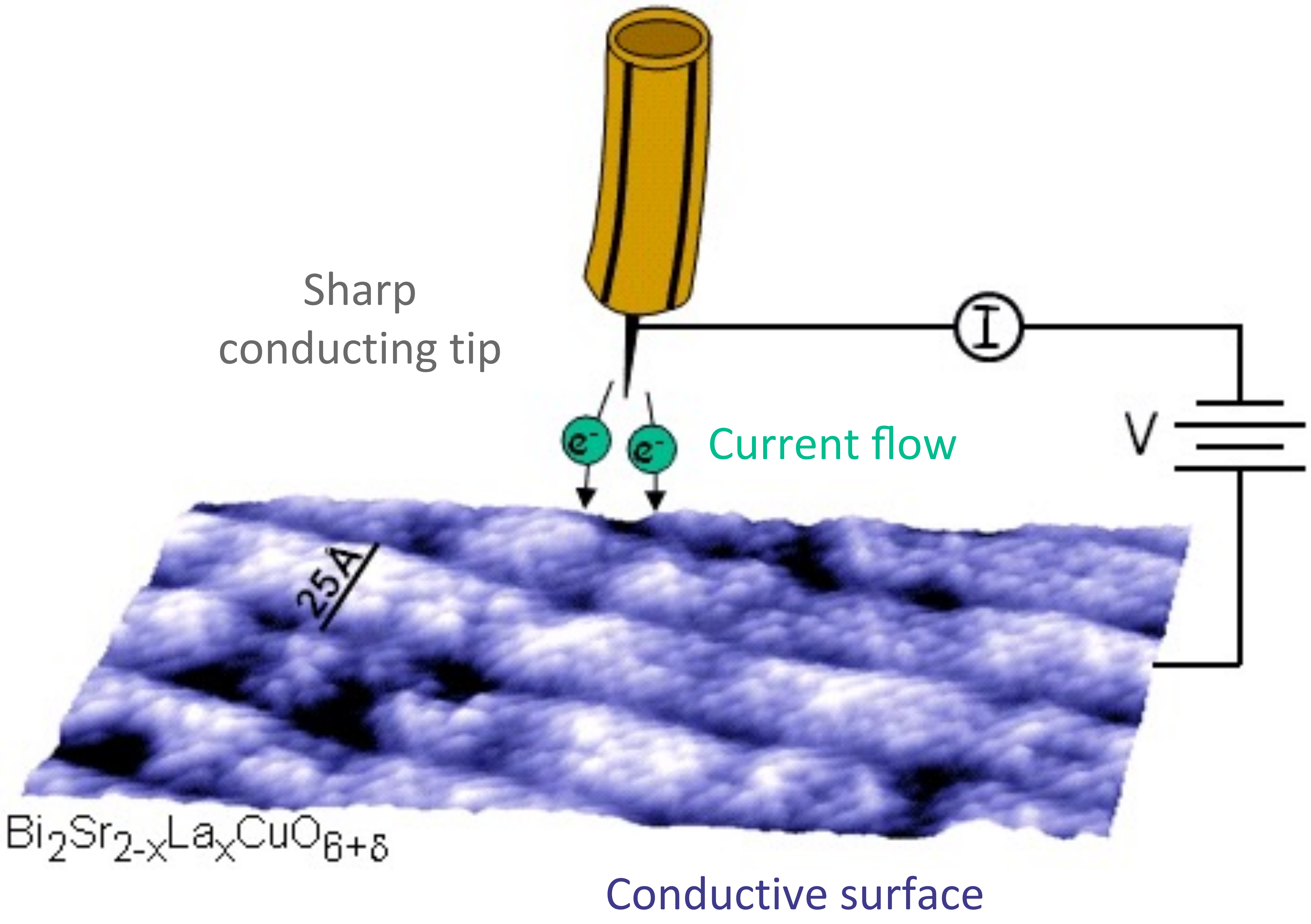
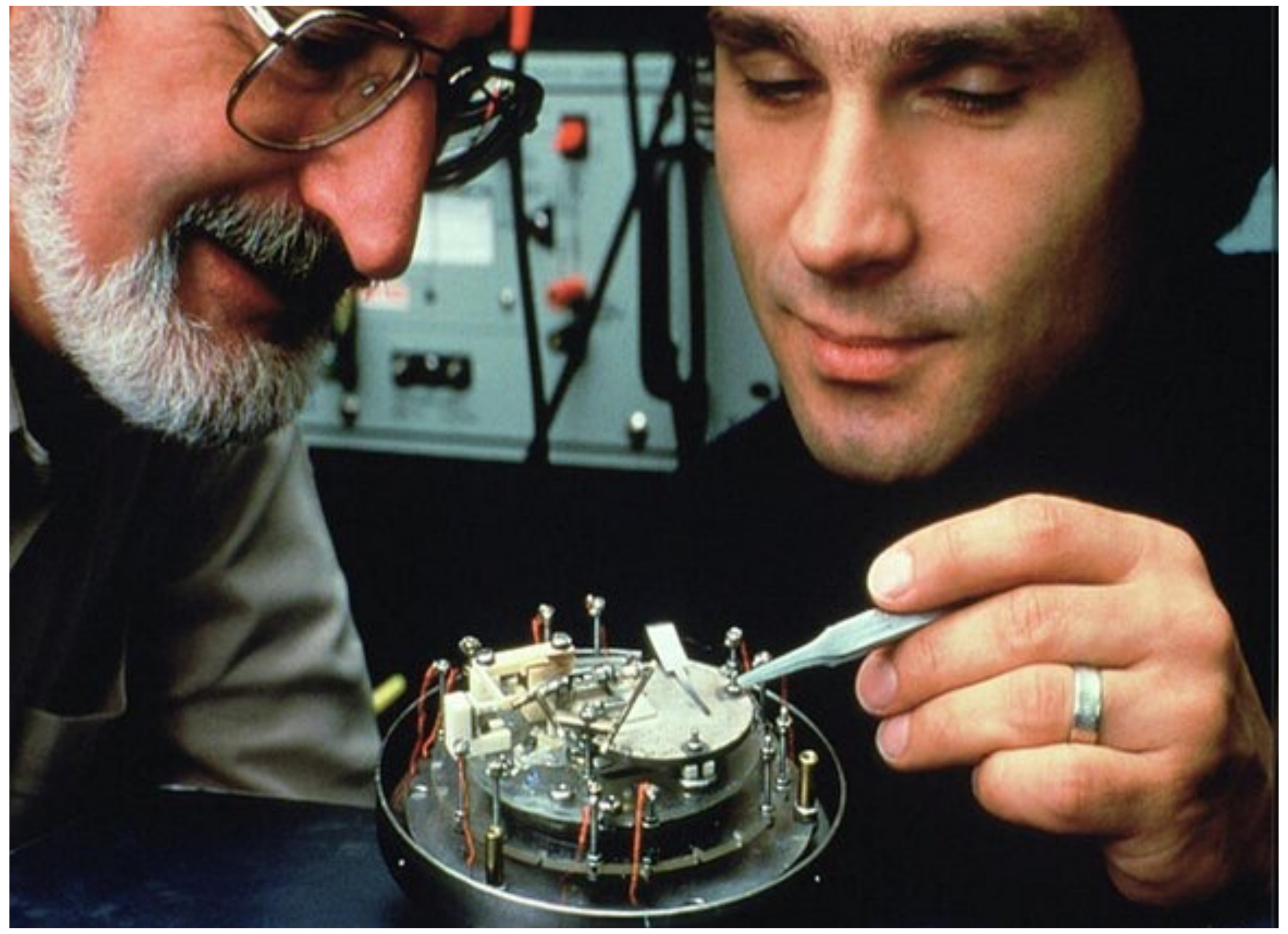
How Can We "See" Surfaces with Higher Resolution?

Scanning Tunneling Microscopy (STM)





Heinrich Rohrer & Gerd Binnig

Nobel Prize in Physics for invention of STM (1986)

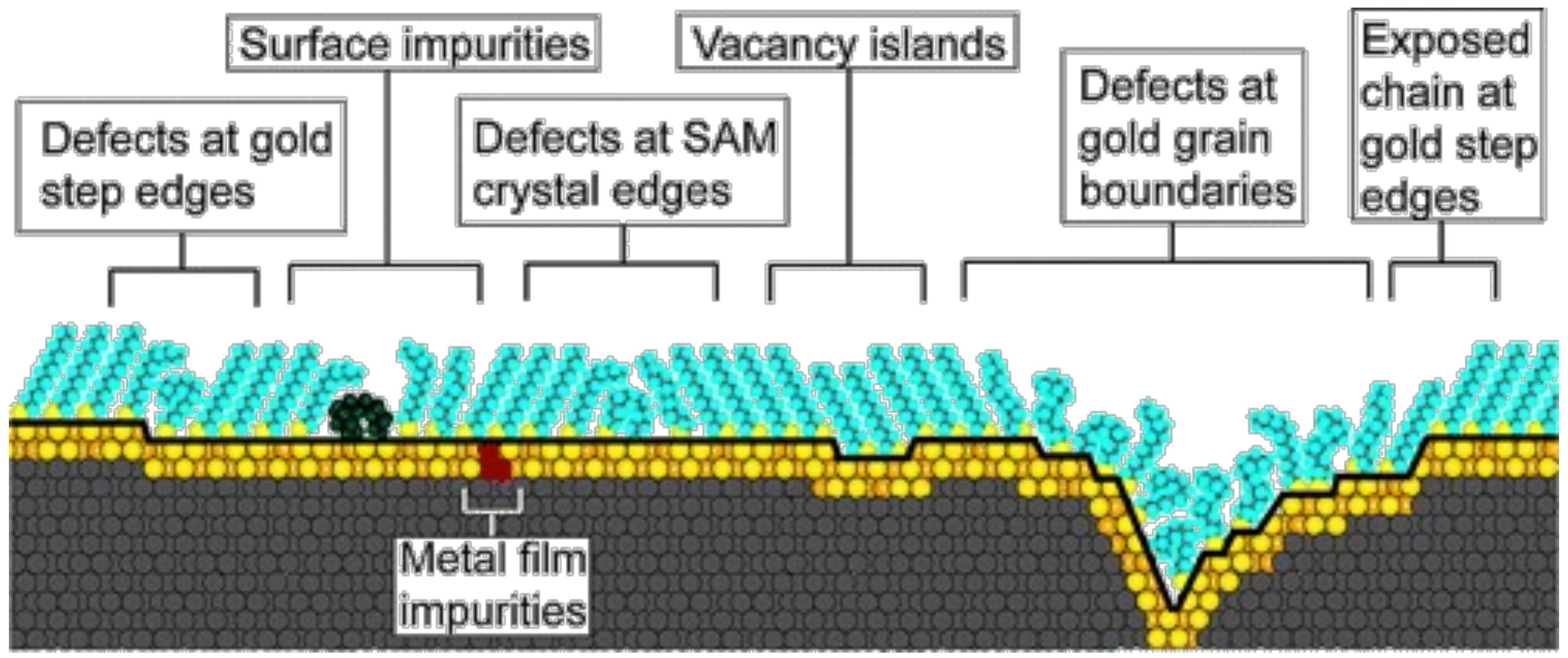
Atomic Resolution – Defect Sites can be Observed

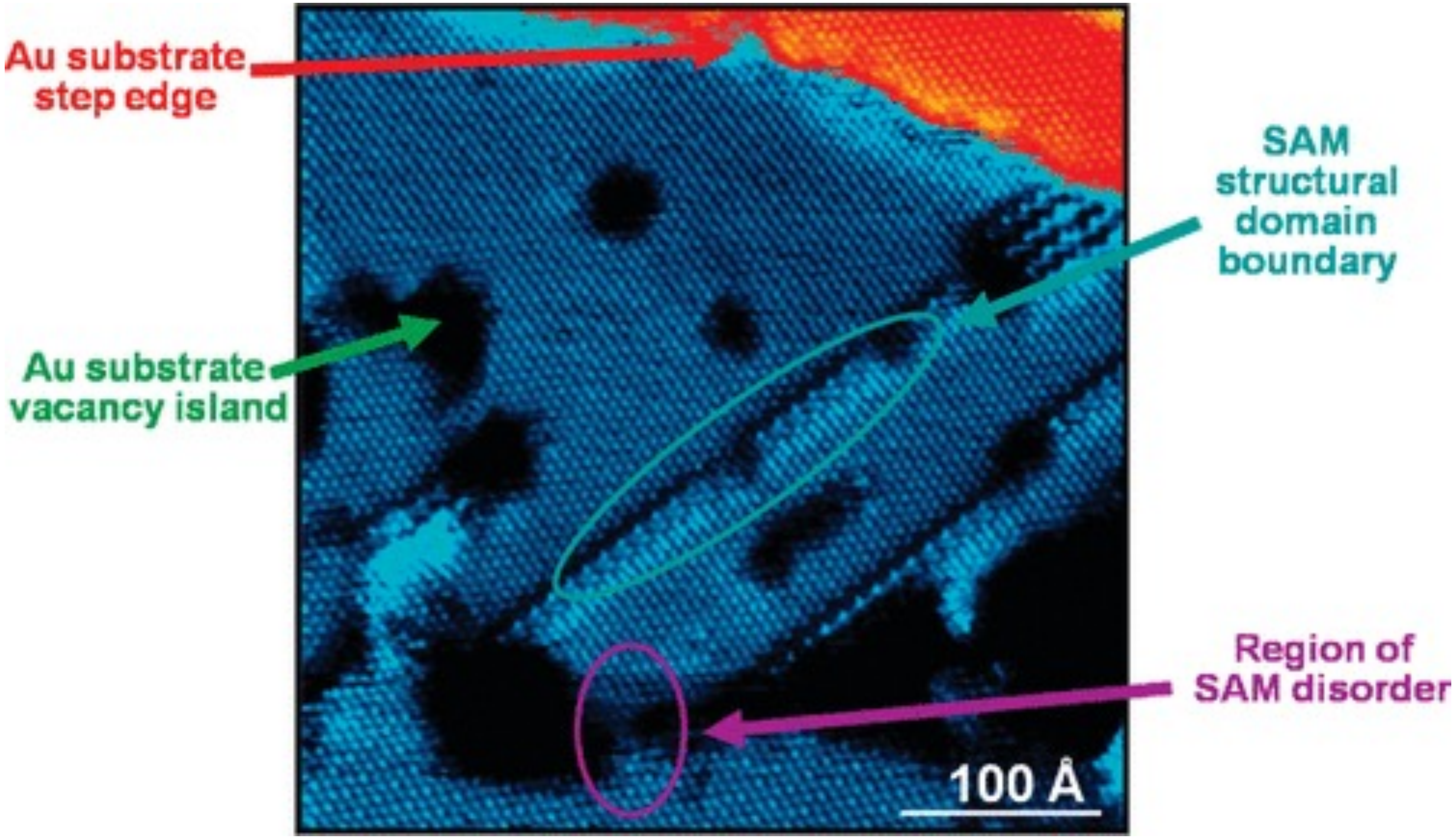
Chem. Rev. **2005,** *105,* 1103–1169 **1103**

Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology

J. Christopher Love,† Lara A. Estroff,† Jennah K. Kriebel,† Ralph G. Nuzzo,*,‡ and George M. Whitesides*,†

Department of Chemistry and the Fredrick Seitz Materials Research Laboratory, University of Illinois–Urbana–Champaign, Urbana, Illinois 61801 and Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138





STM image of decanethiol SAM on Au (111) indicating defect types

Weiss, *Acc. Chem. Res.*, *41*, 12, **2008**

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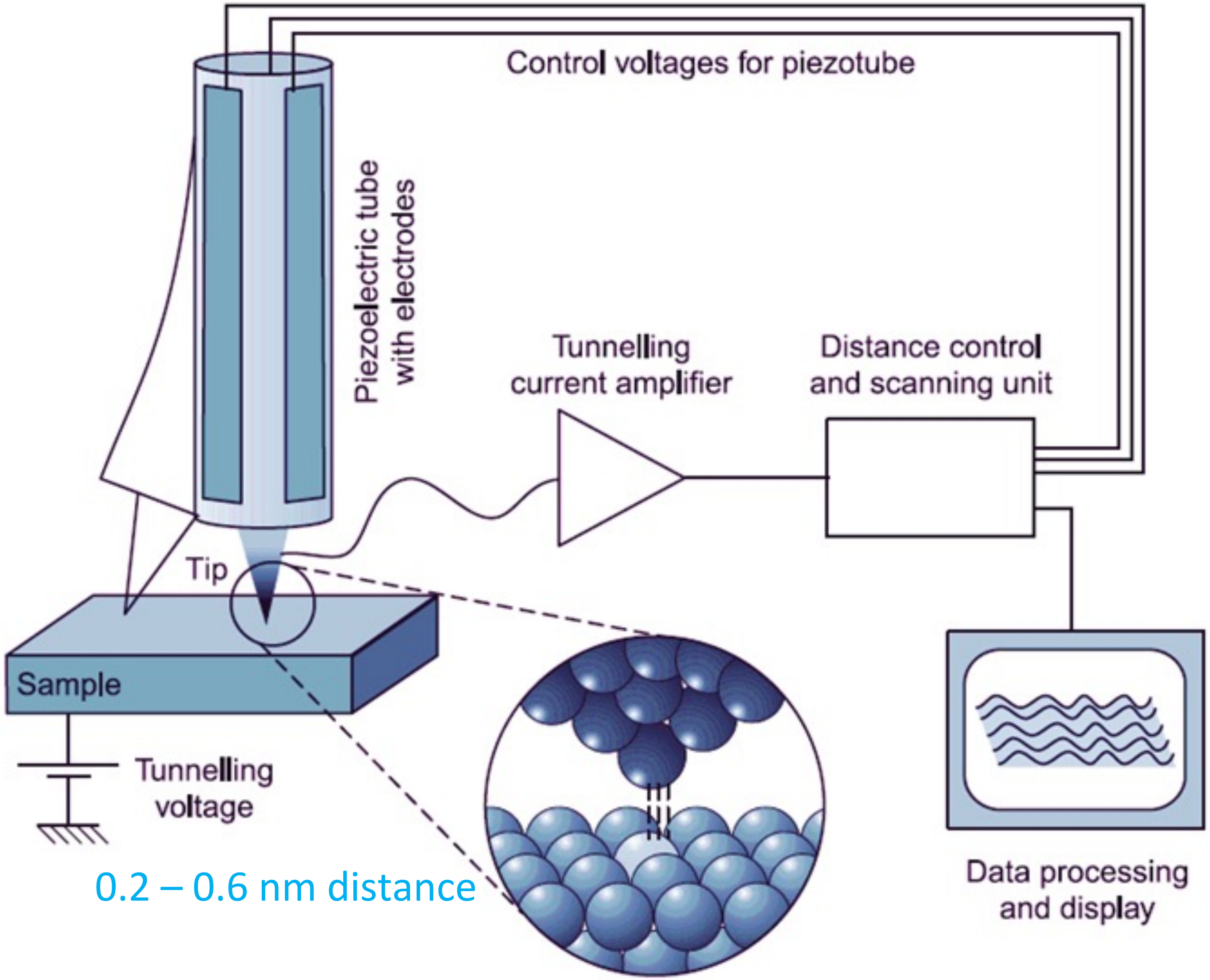
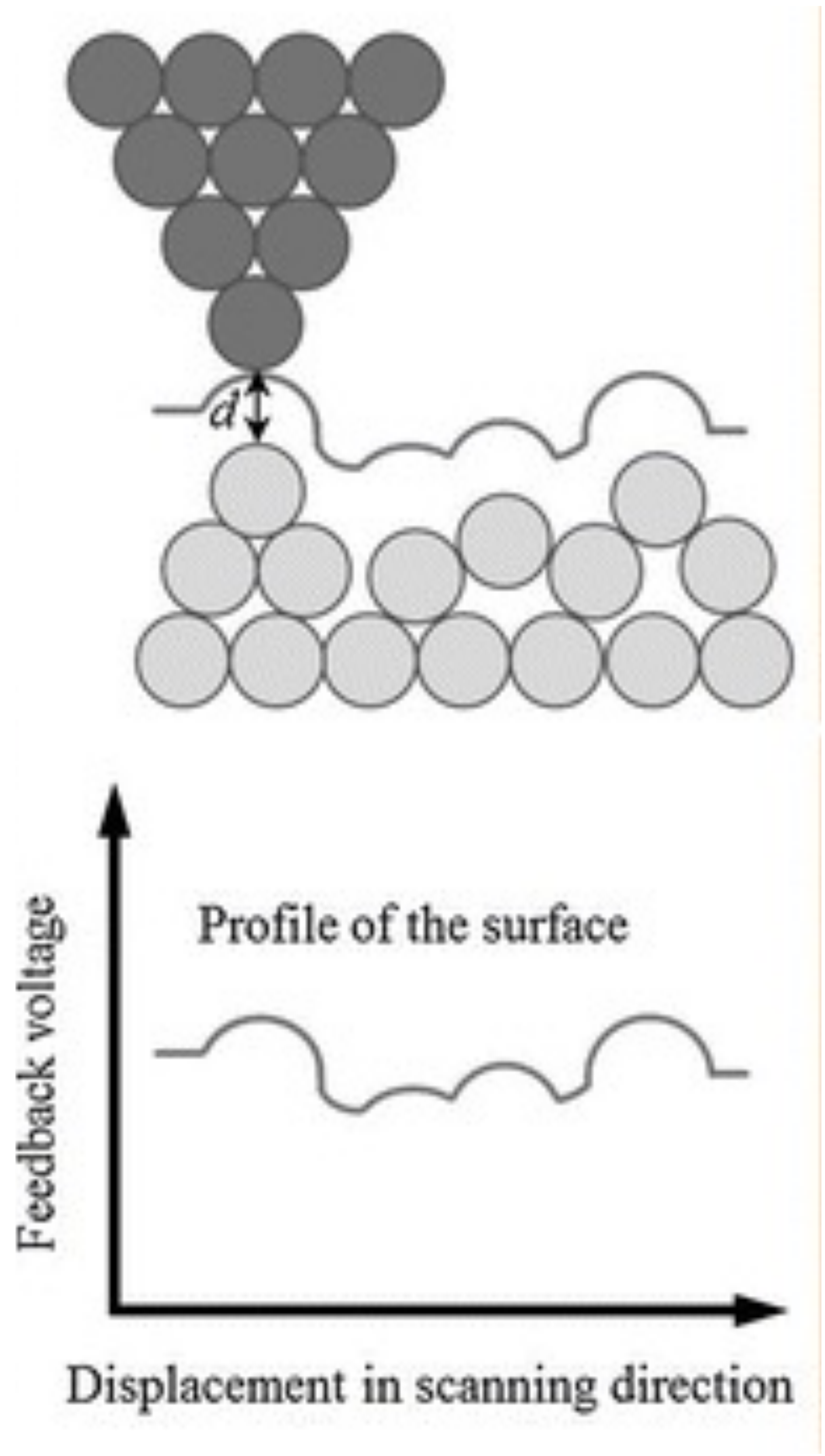
STM Uses a Tunneling Current to Map Atoms on Surfaces

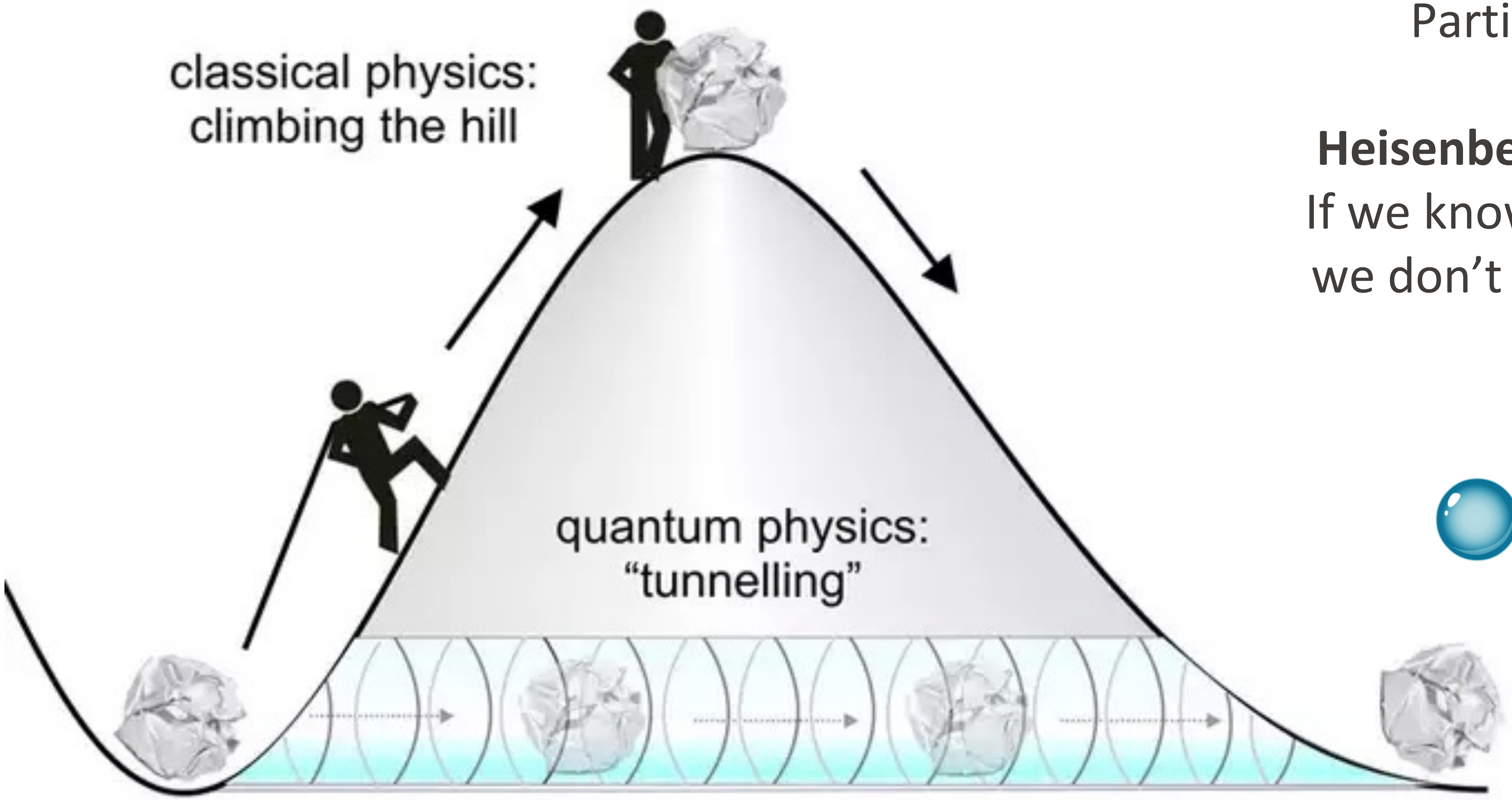


0.2 – 0.6 nm distance



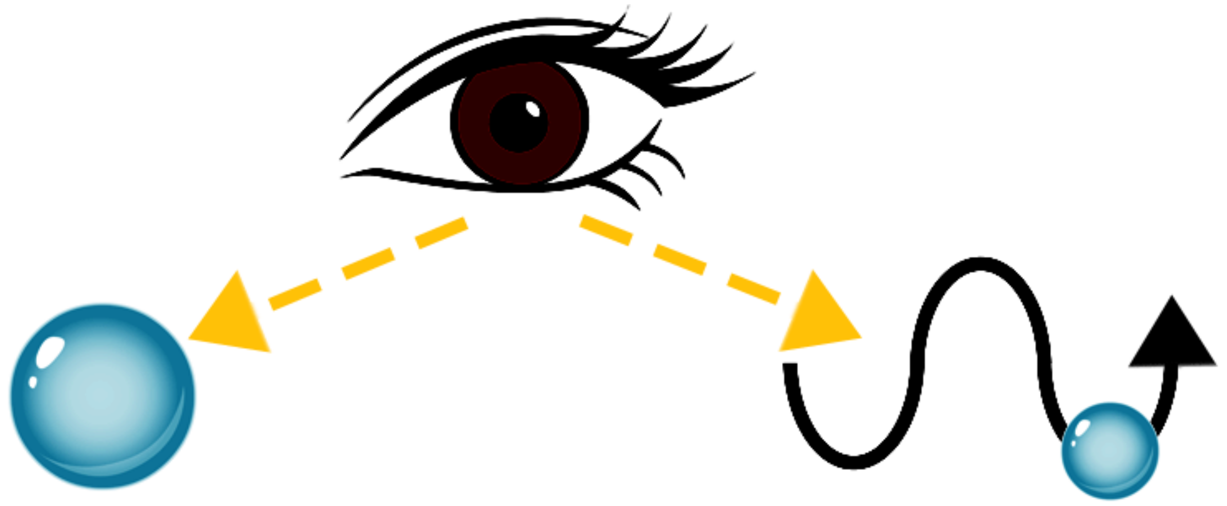
Wikipedia

What is Quantum Tunneling?



Particles can act as waves

Heisenberg Uncertainty Principle:
If we know a particle's momentum,
we don't know it's precise position



MAX-PLANCK-GESELLSCHAFT

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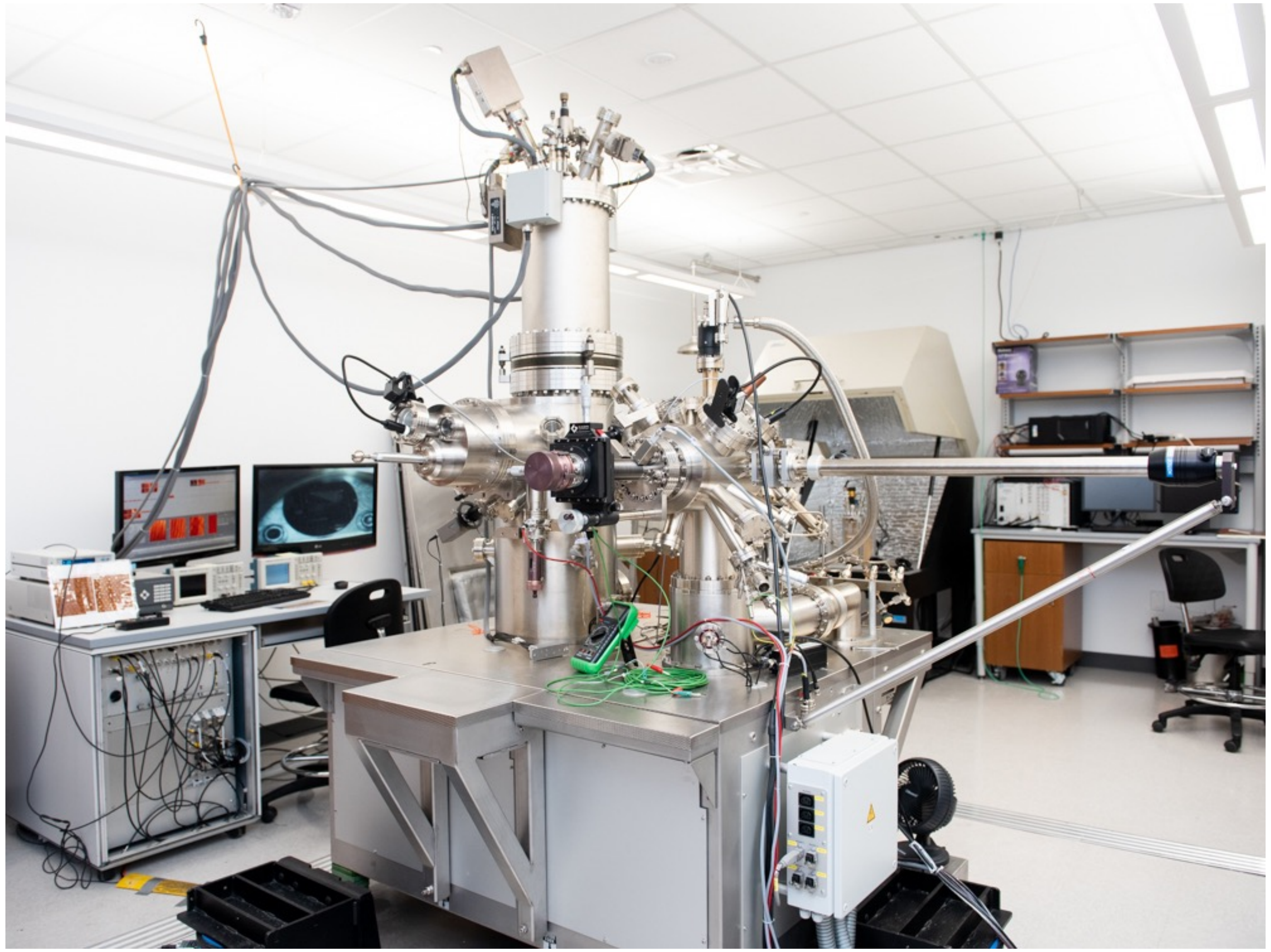
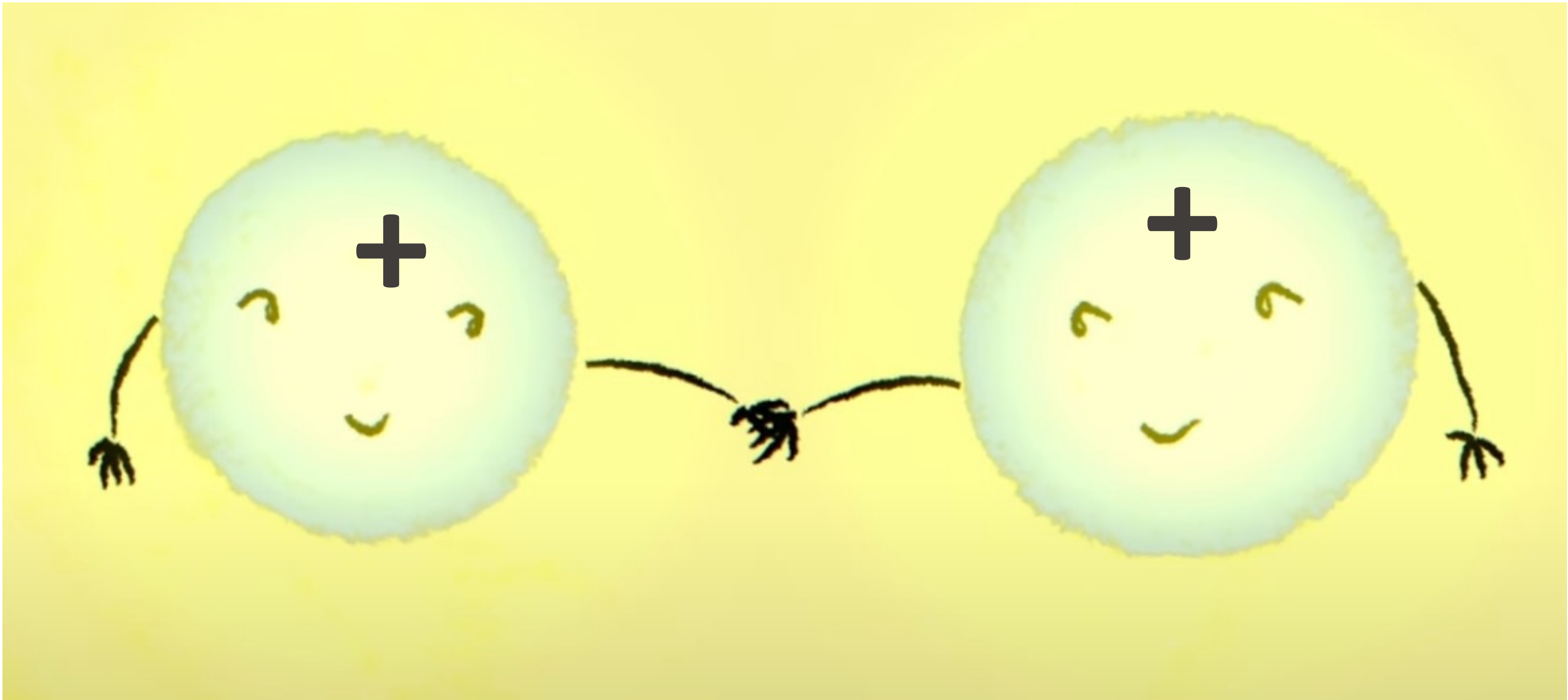
How is Quantum Tunneling Relevant in Our Lives?



Nuclear fusion of hydrogen atoms to form helium

Overcoming repulsion shouldn't be possible



Quantum tunneling
1 in a trillion encounters

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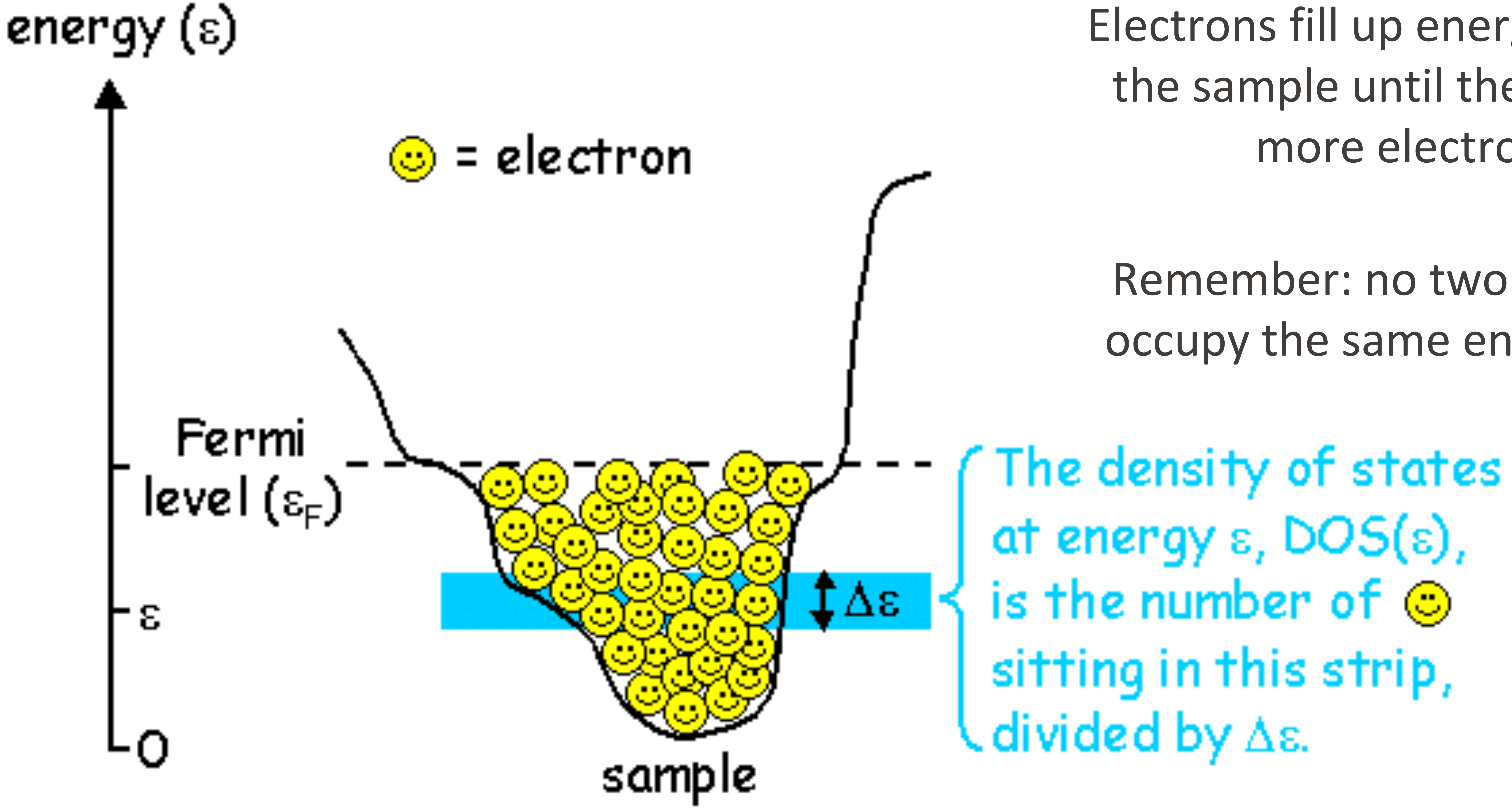
What is a Tunneling Current that Enables STM?



Electrons fill up energy valley in the sample until there are no more electrons

Remember: no two electrons occupy the same energy state

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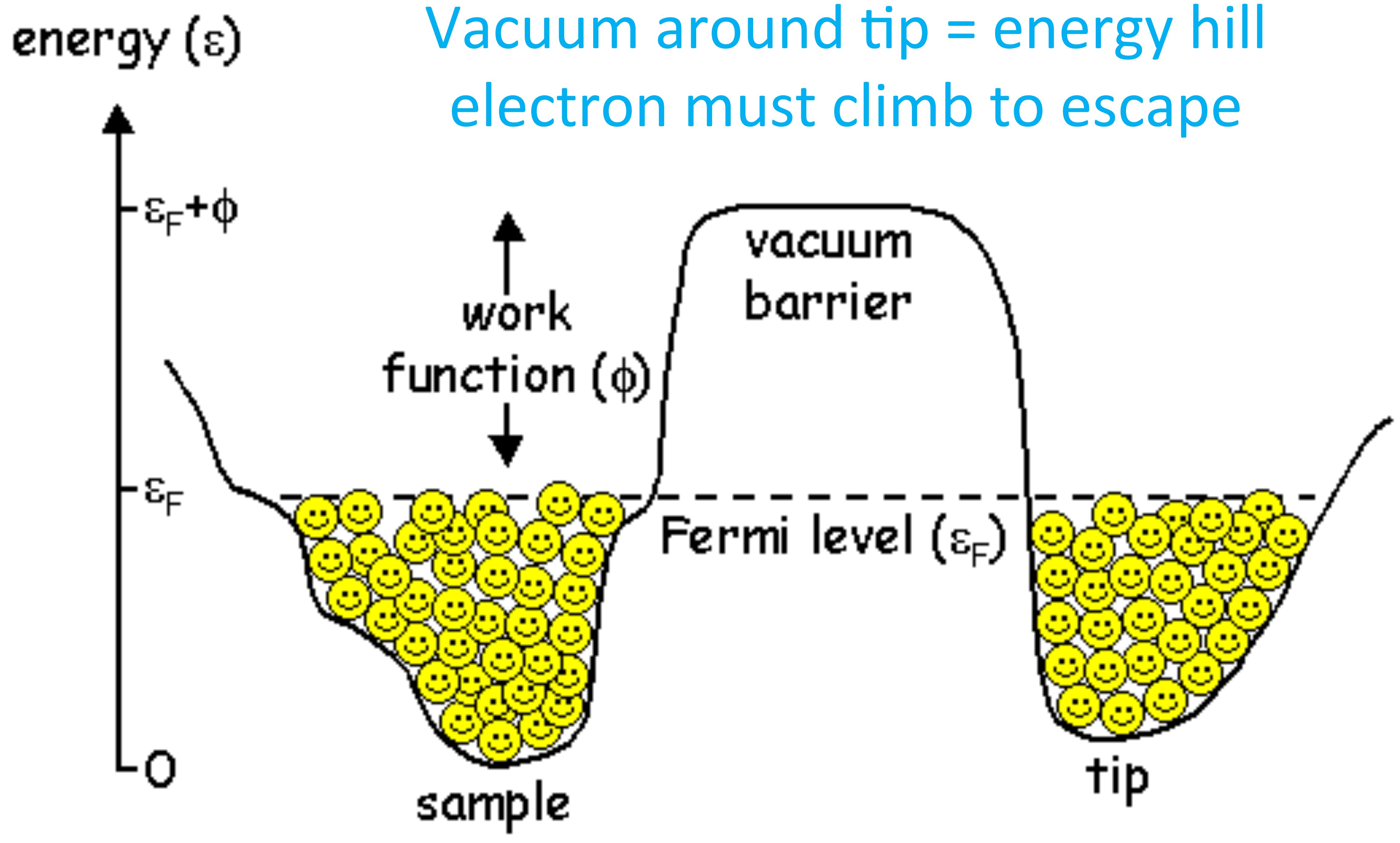
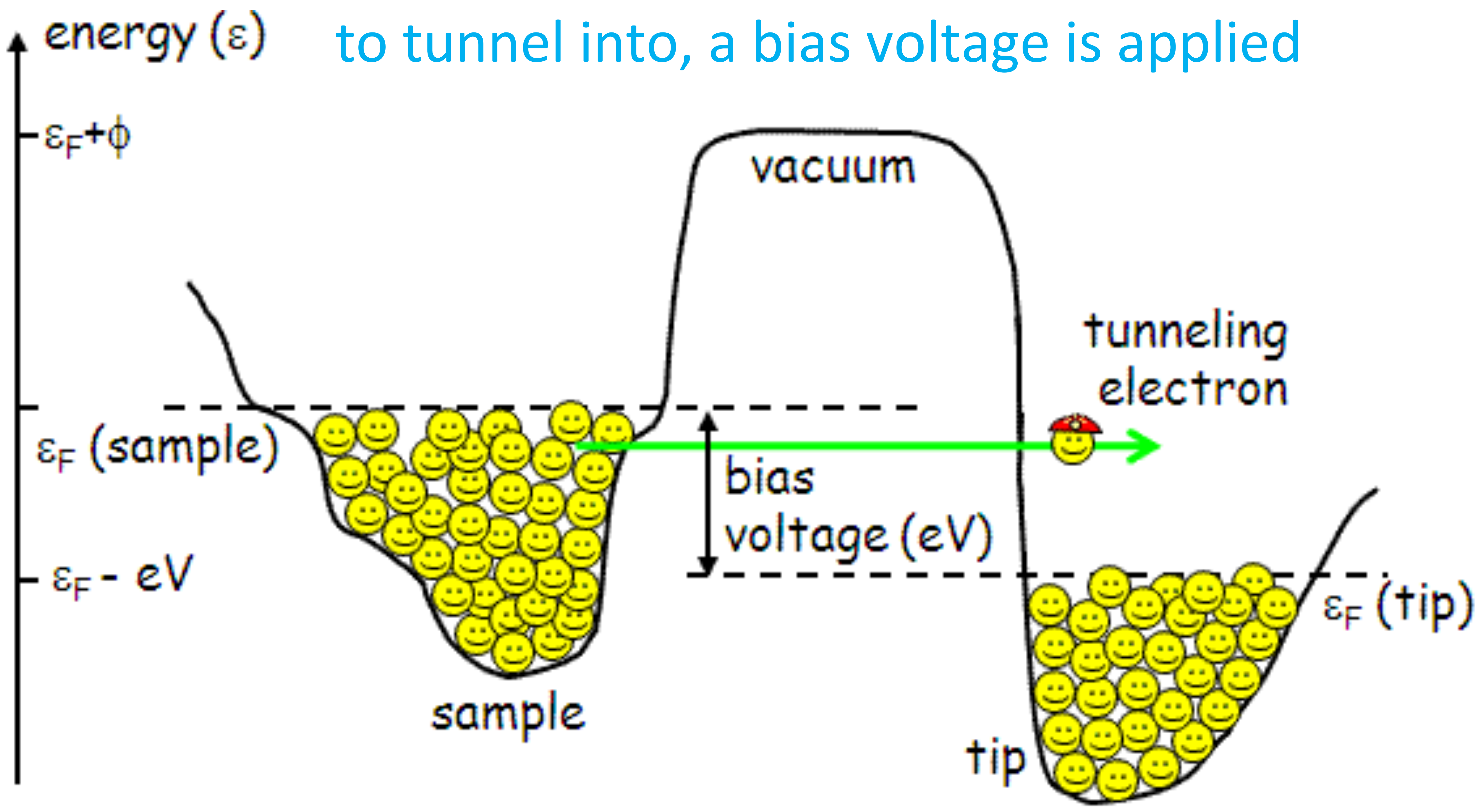
What is a Tunneling Current that Enables STM?

Vacuum around tip = energy hill electron must climb to escape



Electrons are happy sitting in either the tip or the sample (energy valleys)

To create empty states for electrons to tunnel into, a bias voltage is applied



Tunneling current proportional to density of states in sample

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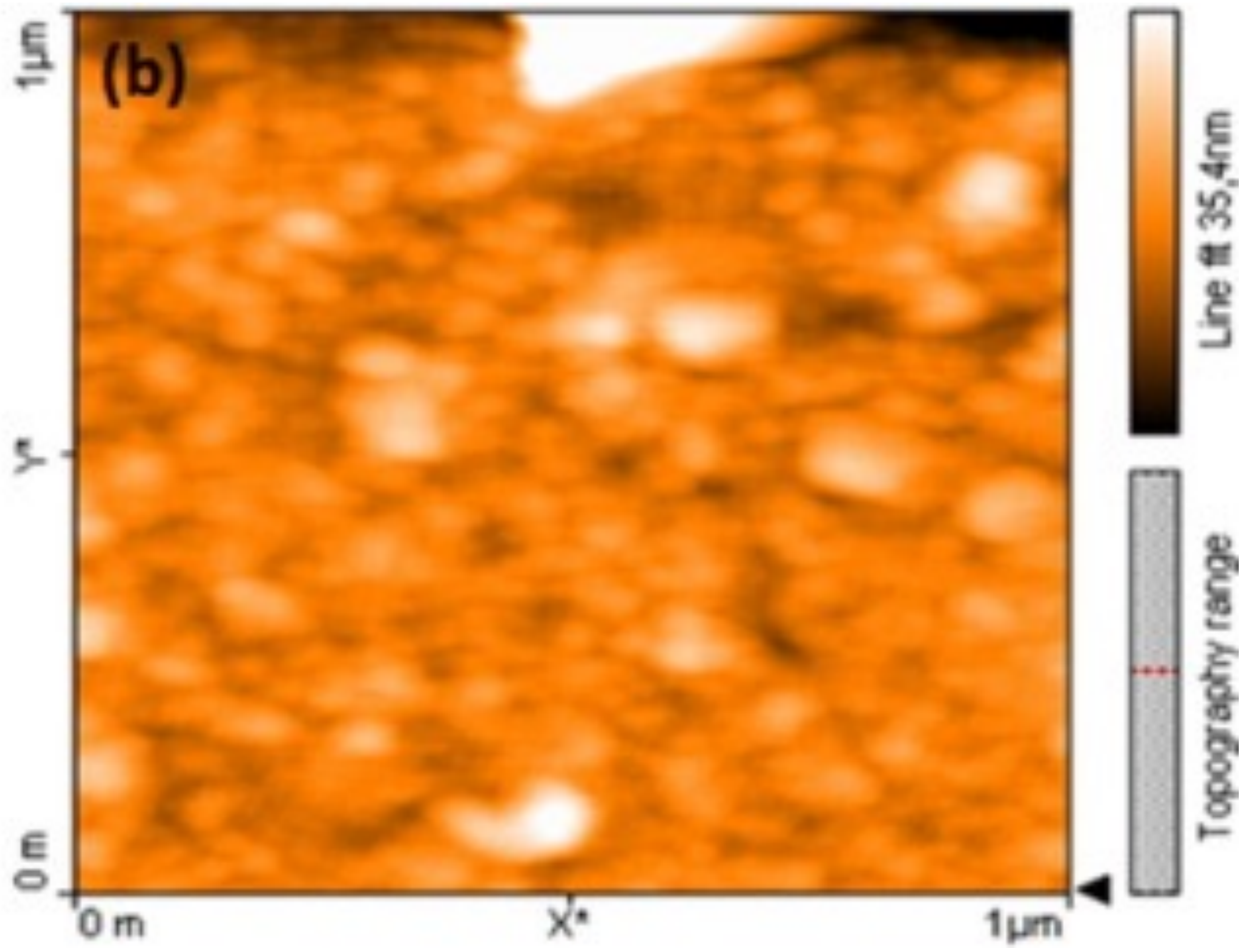
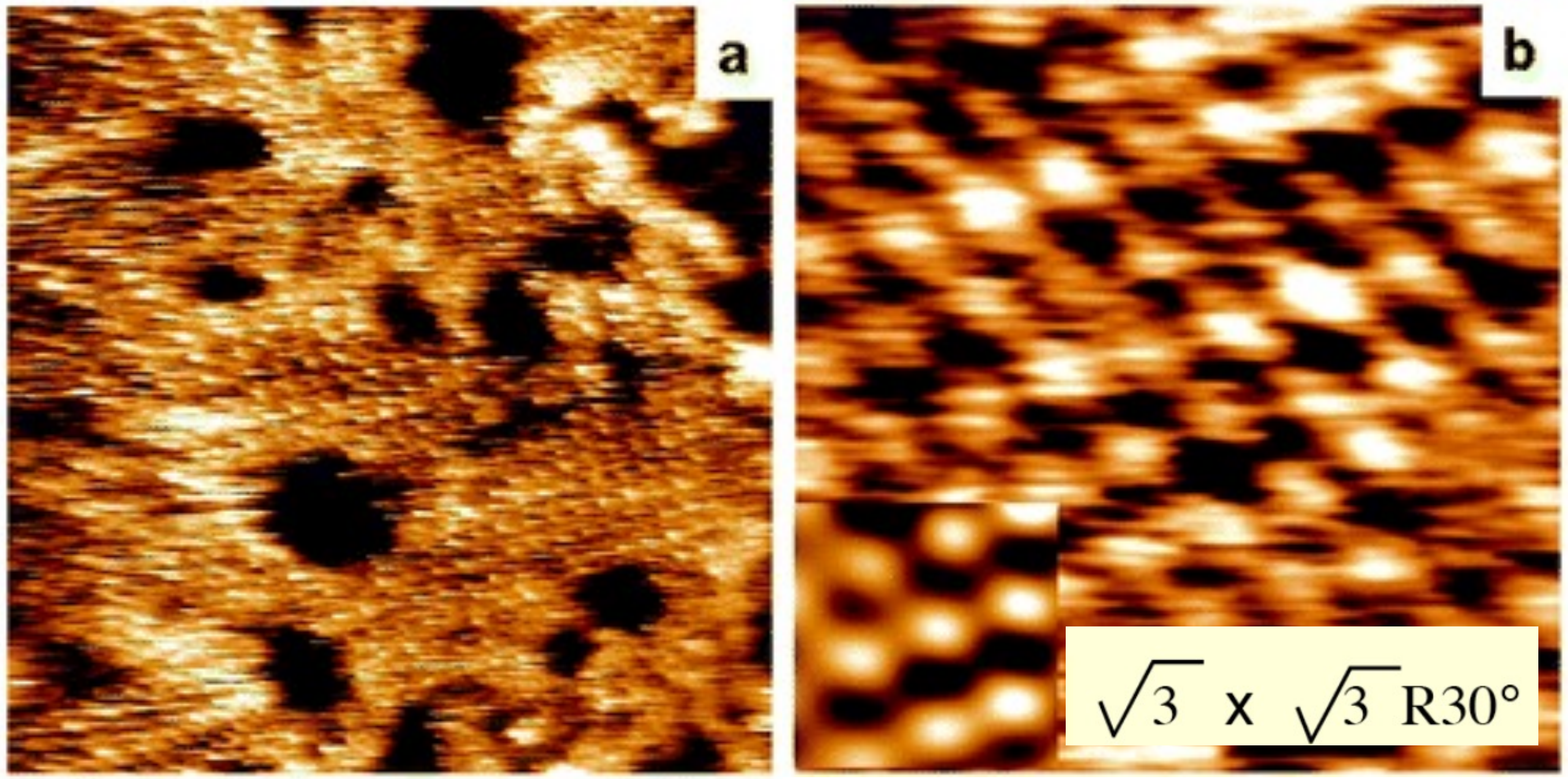
Resolution of AFM *vs.* STM – Hexadecanethiol (C16) on Au (111)





30 nm

4 nm

Simpler – works in air and liquids	More complex (requires UHV and low temp.)
Conducting/non-conducting surfaces	Only conducting surfaces
0.1-10 nm (0.1 is ultimate best equipment)	0.1 nm (0.01 nm in vertical direction)
Topography, force measurements, mechanical properties	Topography, electronic properties
Uddin, *Res. Phys.*, *7*, 2289, **2017**	Mendoza, *Langmuir*, *23*, 2, **2006**

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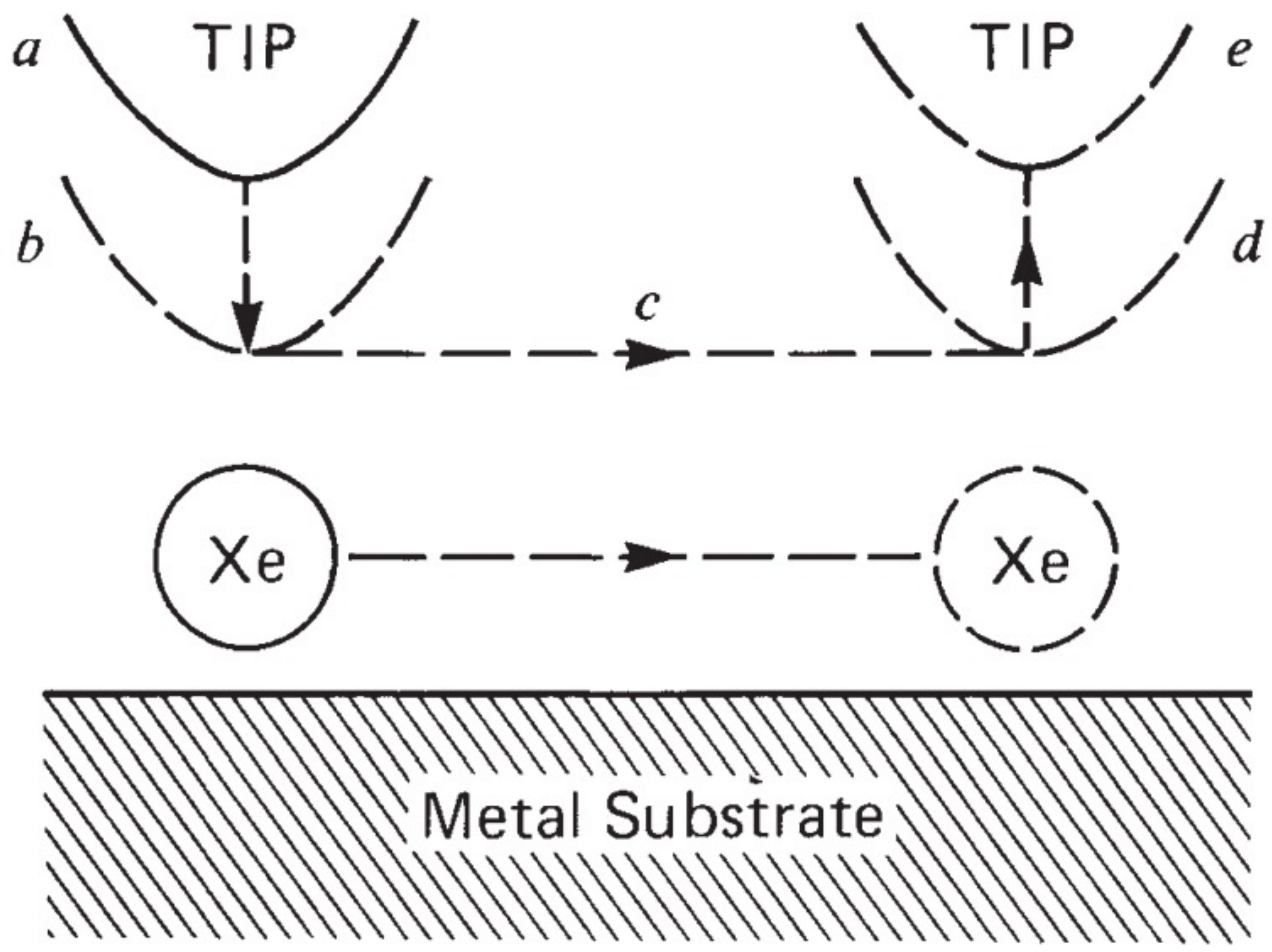
The Potential to Manipulate the Nanoscale

Positioning single atoms with a scanning tunnelling microscope

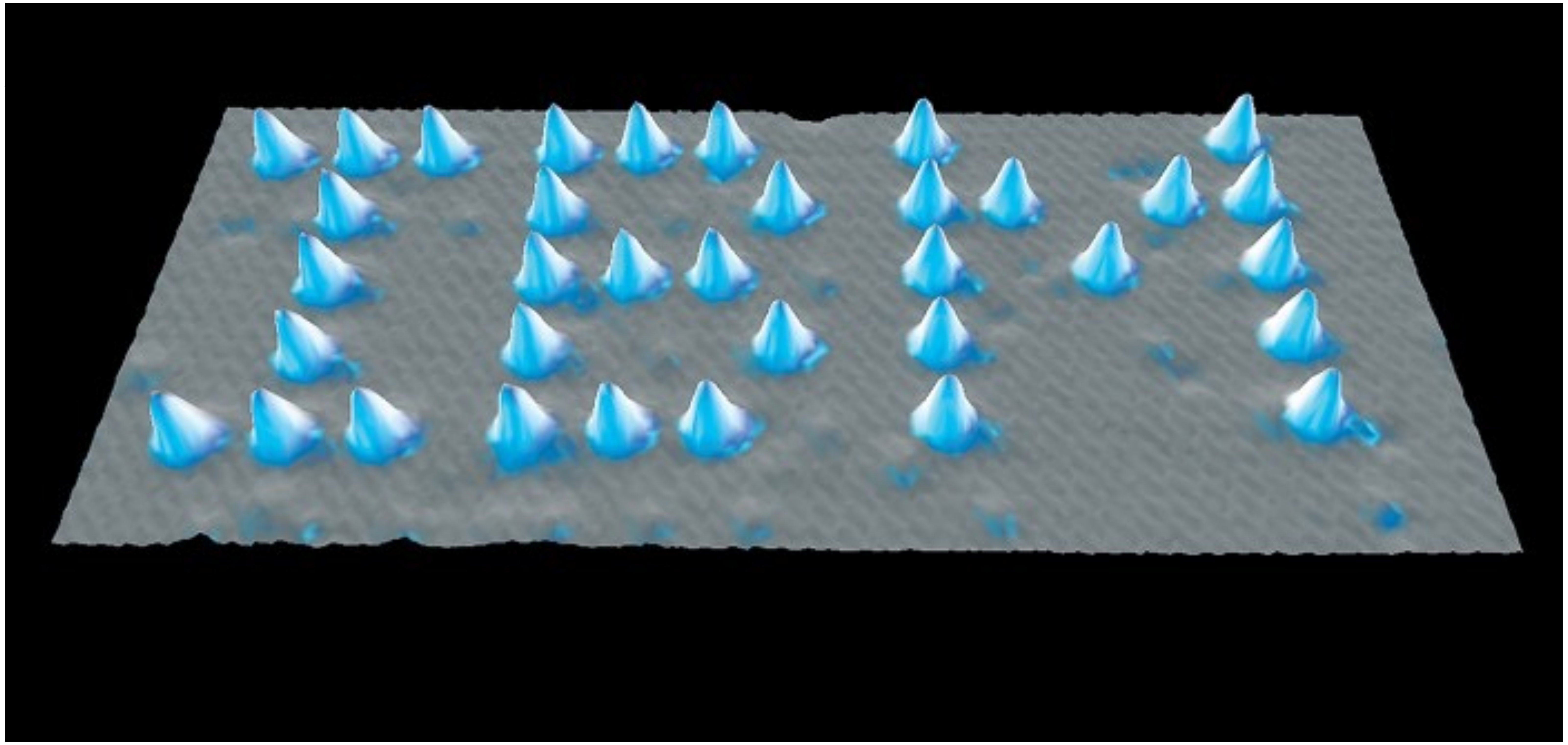
NATURE · VOL 344 · 5 APRIL 1990

D. M. Eigler & E. K. Schweizer*

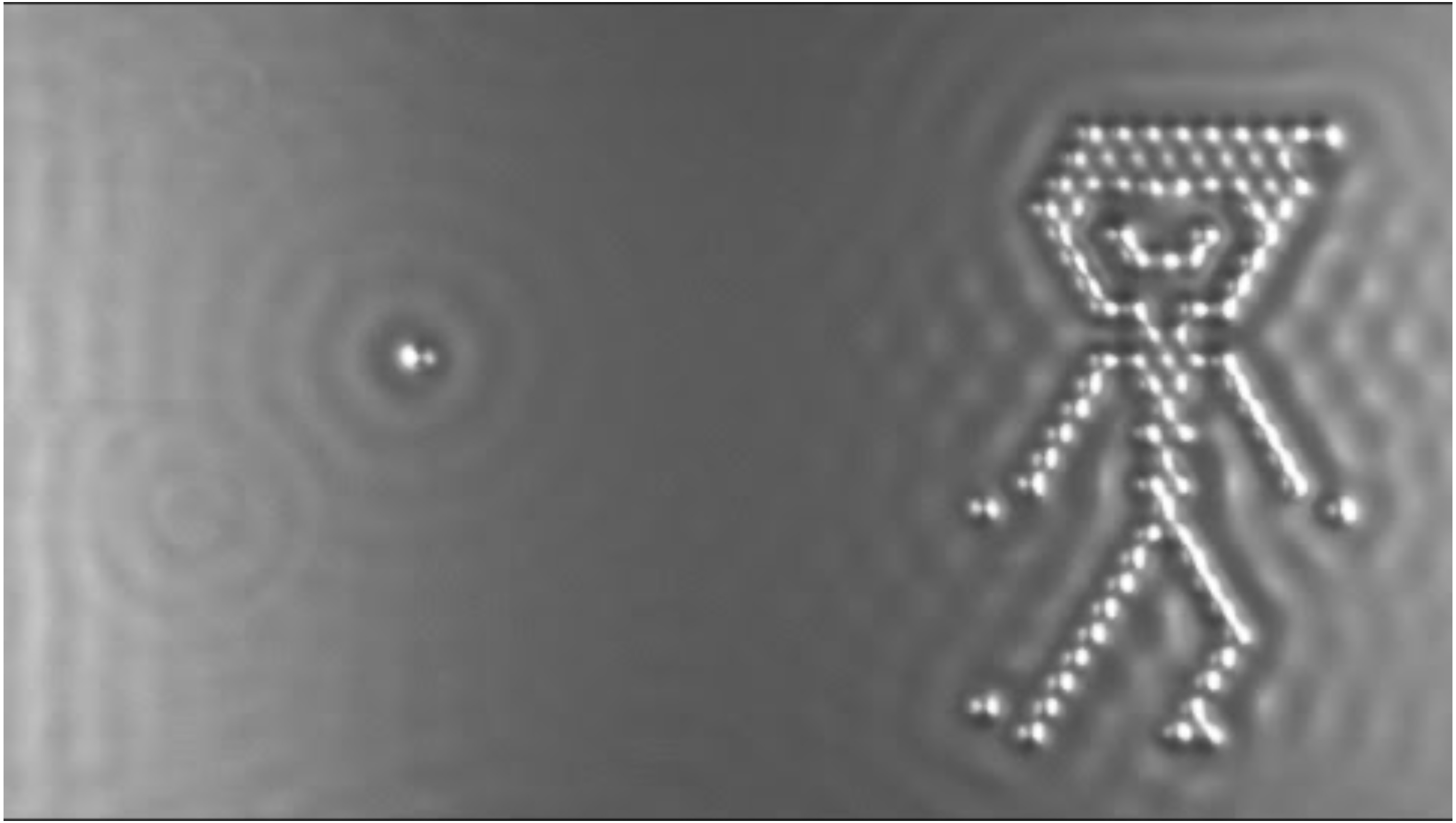
IBM Research Division, Almaden Research Center, 650 Harry Rd, San Jose, California 95120, USA



Nickel (110)



The World's Smallest Movie by IBM



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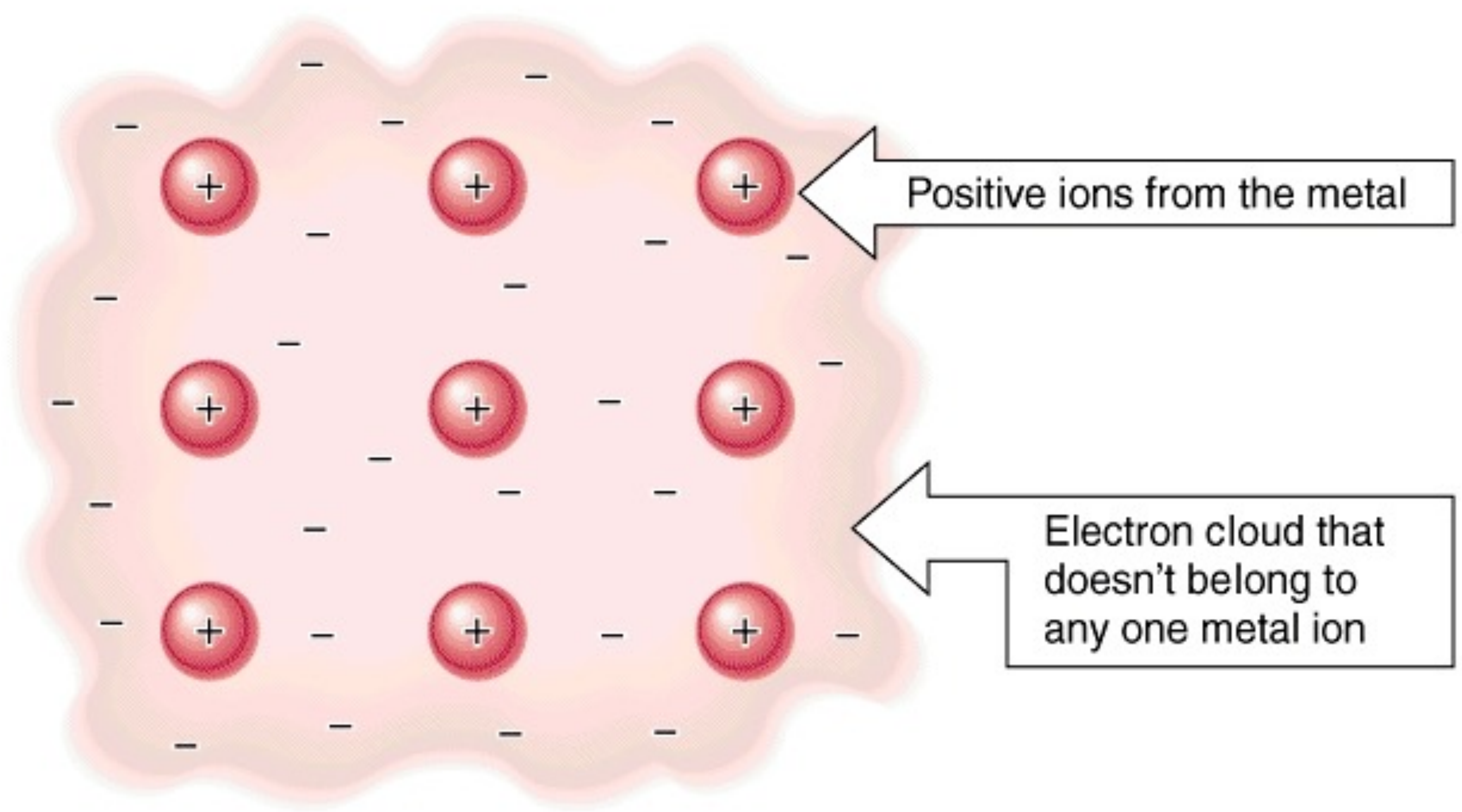
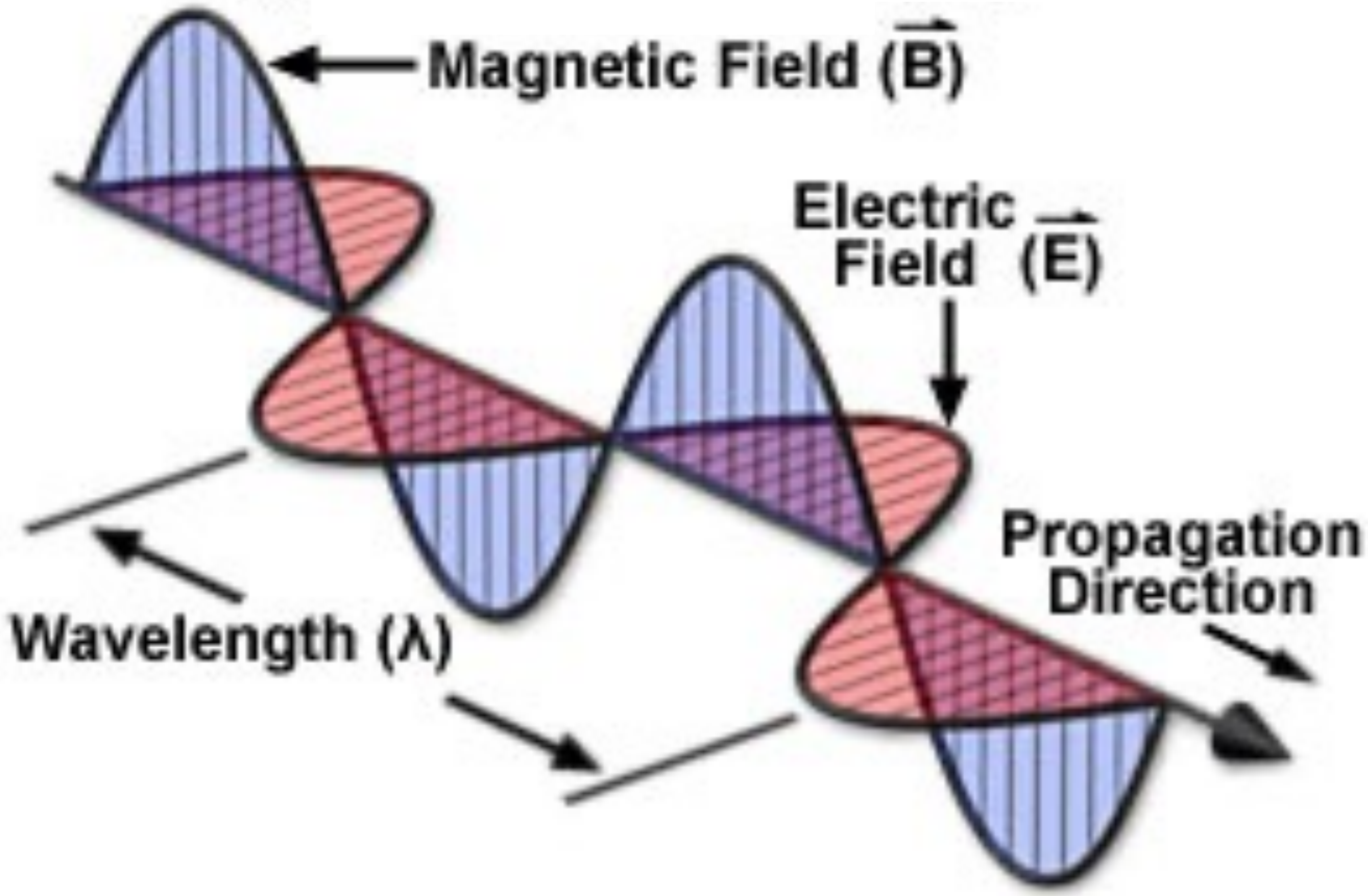
Influencing the Sea of Electrons on Surfaces Using Light

The Free Electron Sea

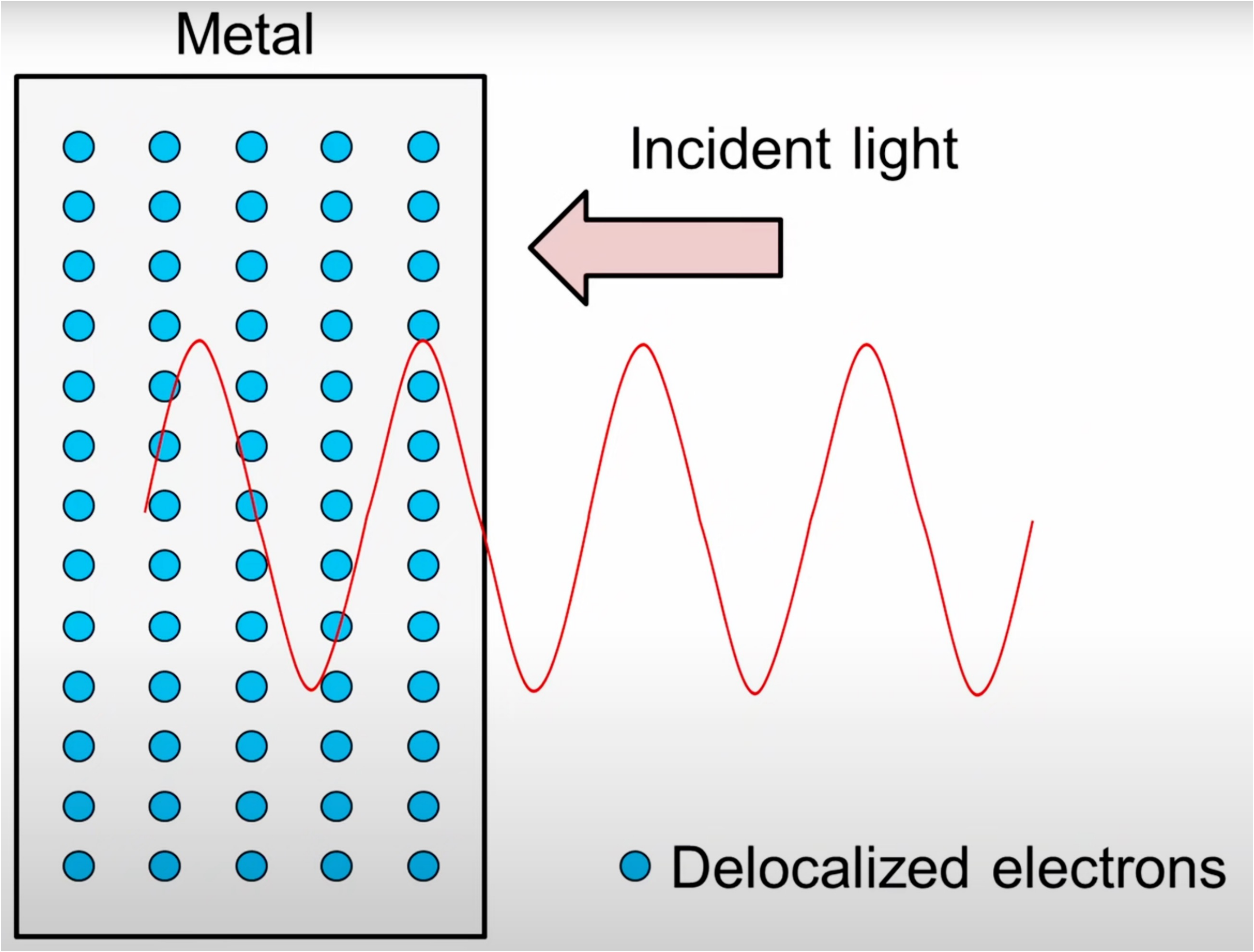


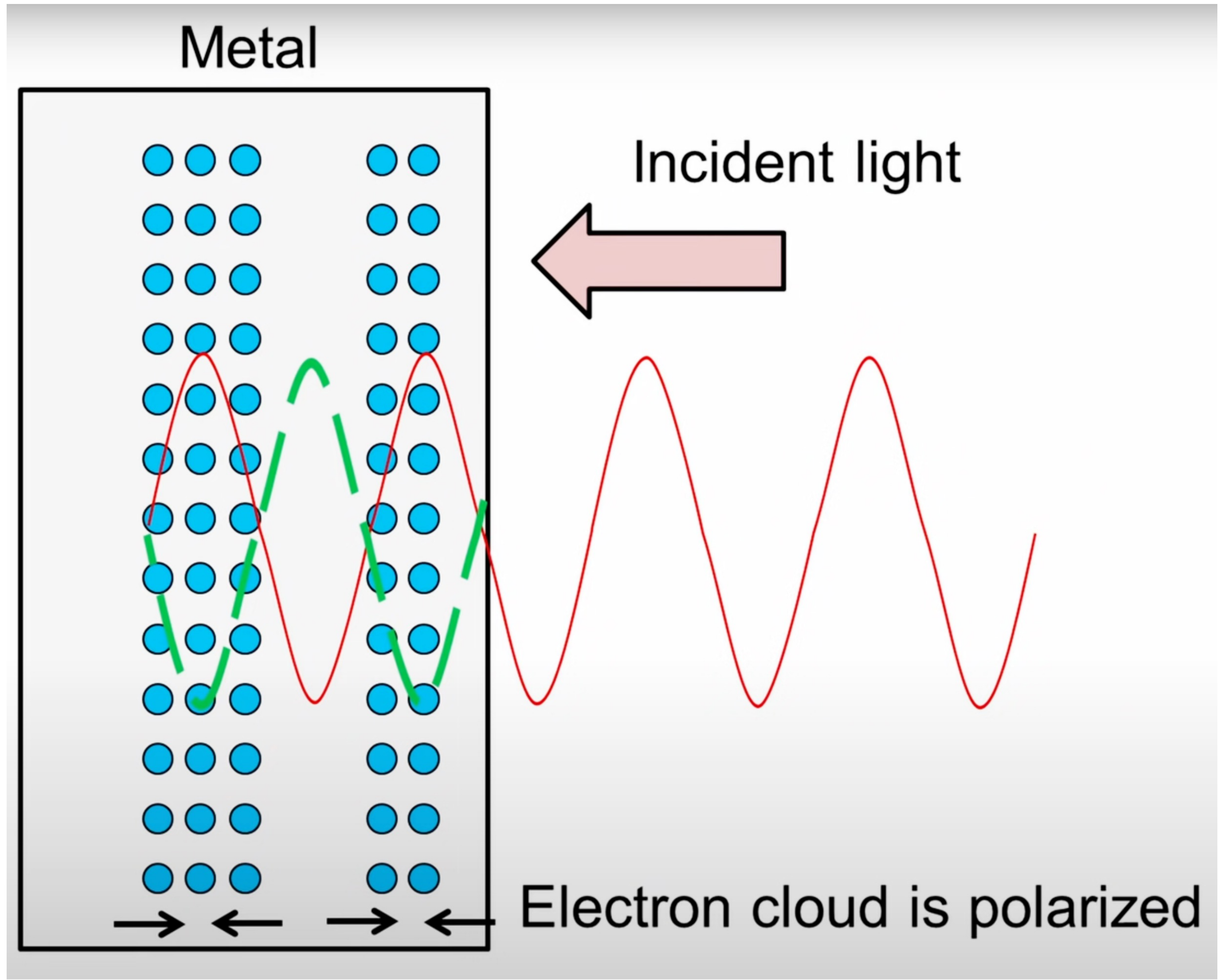
Light as an oscillating electromagnetic field



Electrons in metal are affected by the electromagnetic field from light incident to surface

Effect of Plasmon Resonance





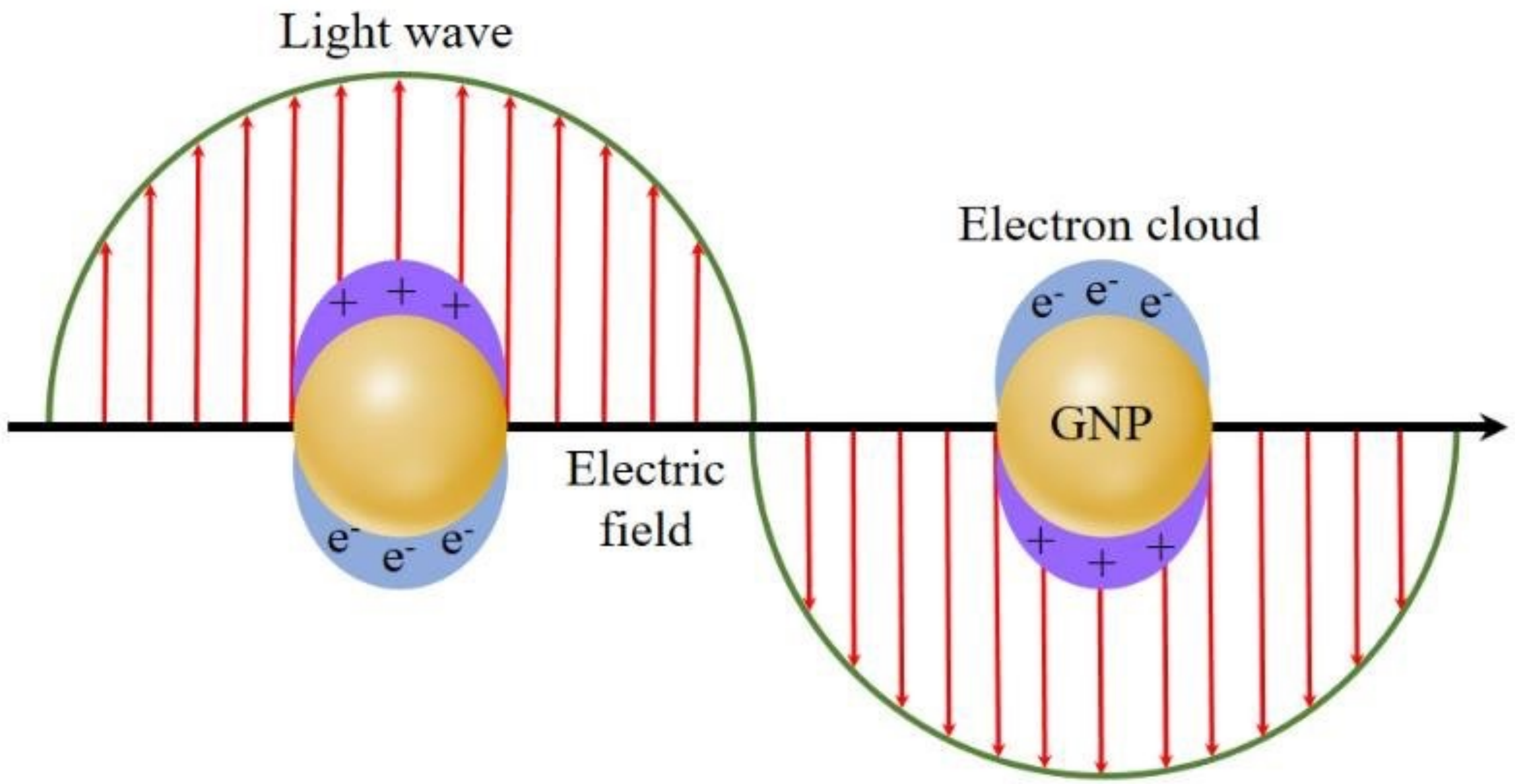
Incident light excites electrons on metal surface

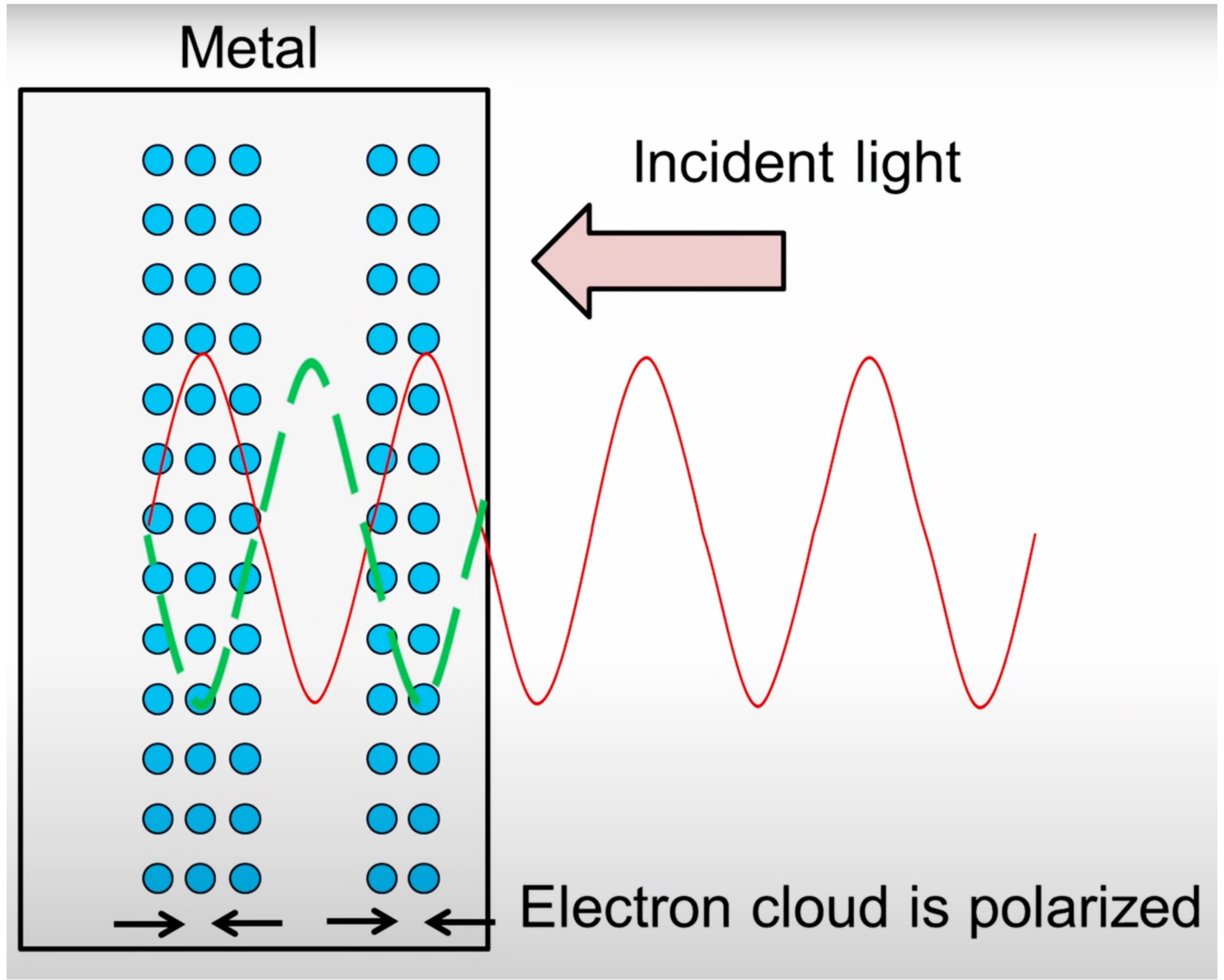
Oscillating field of light interacts with free electrons

Electron cloud is perturbed

Electrons begin to oscillate collectively as a polarized cloud (plasmon)

Effect of Plasmon Resonance





Electron cloud is perturbed

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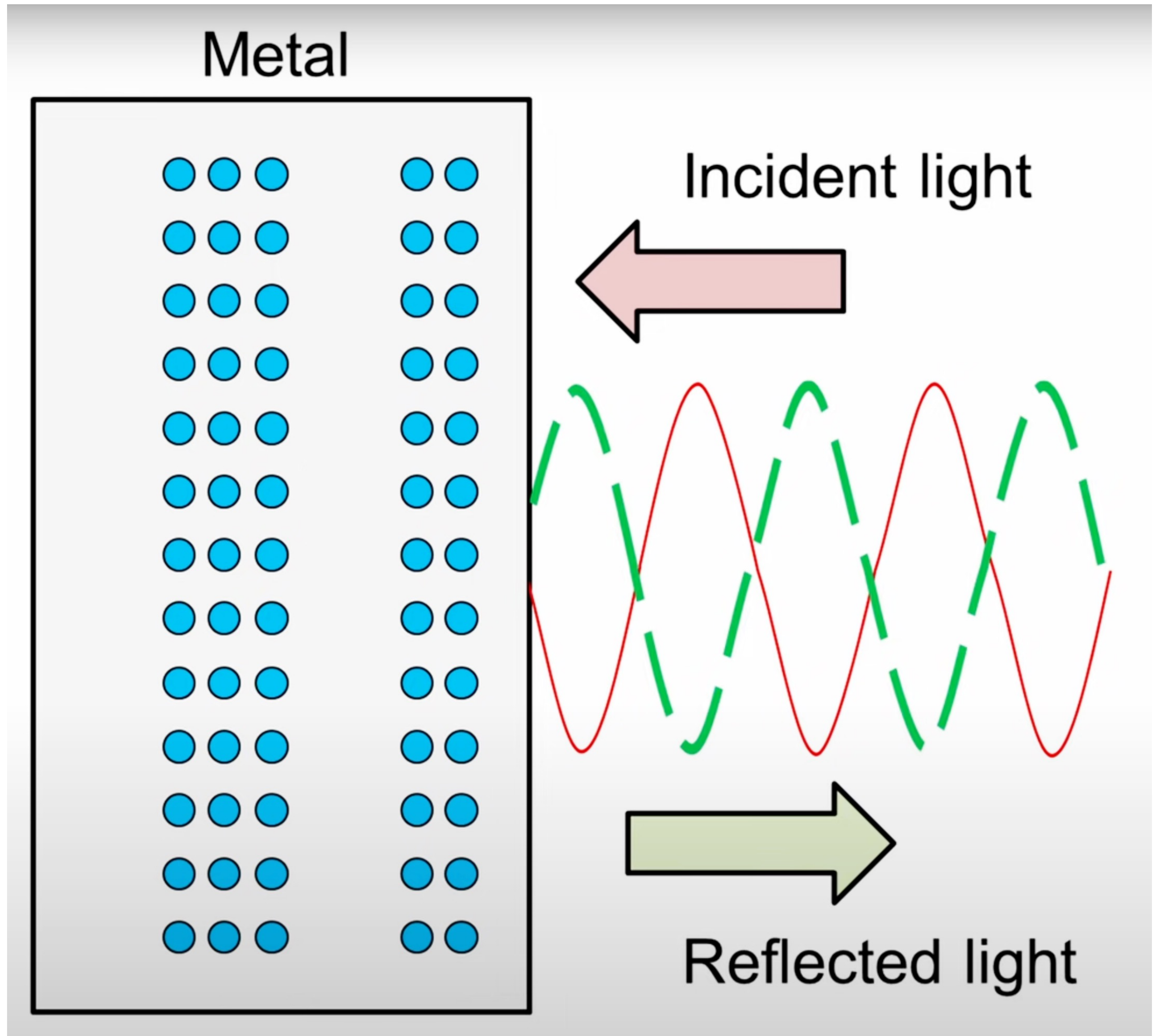
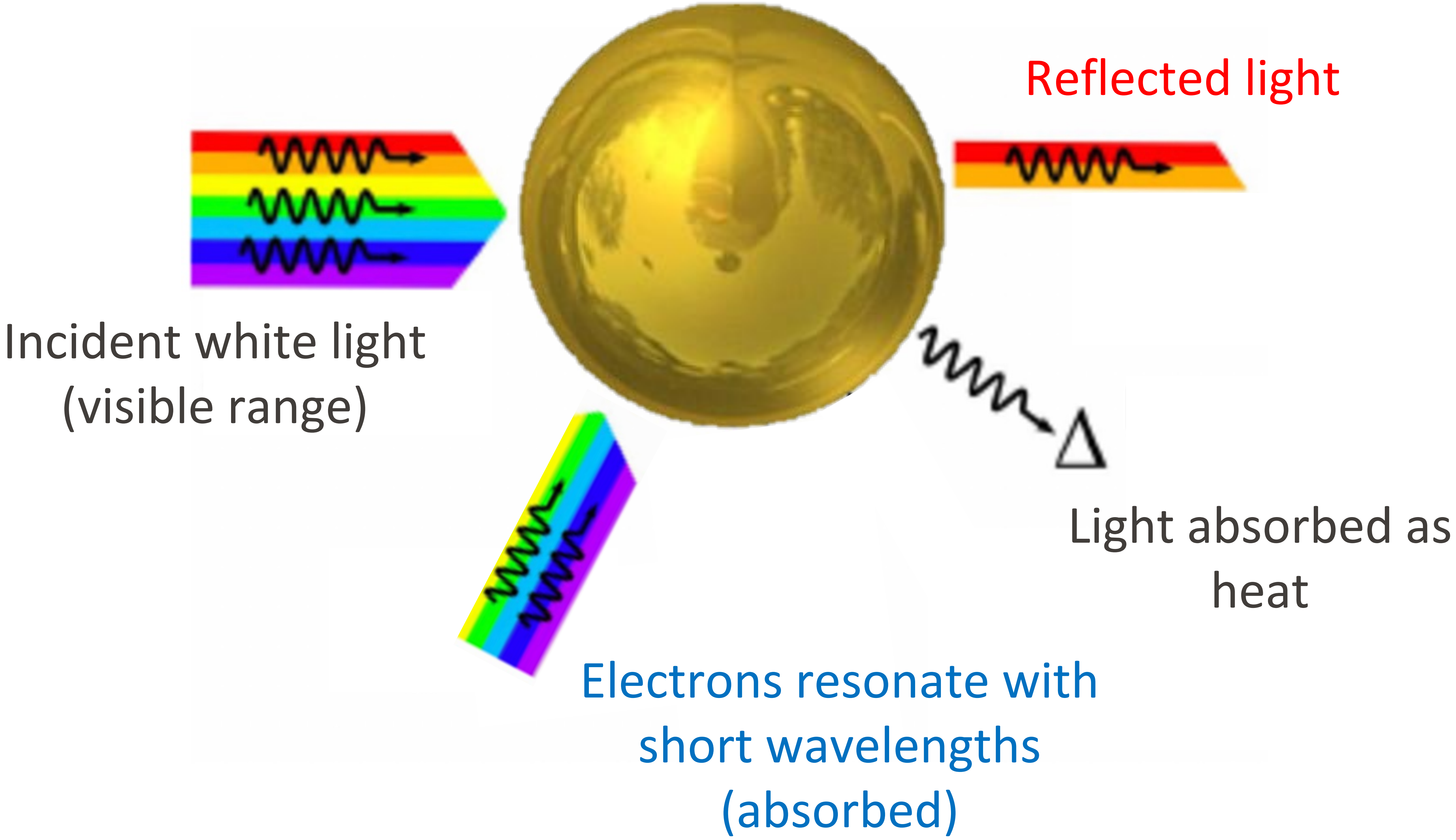
Effect of Plasmon Resonance





At resonance frequency, incident light energy transferred to oscillating electron cloud (plasmon excitation)

Only specific wavelengths of light are reflected back while others are absorbed or scattered

Relative contributions of absorption and scattering determined by size and shape of plasmonic particles

Going Back Many Centuries (4th Century): Lycurgus Cup

The glass contains gold and silver nanoparticles 10–100 nm in size

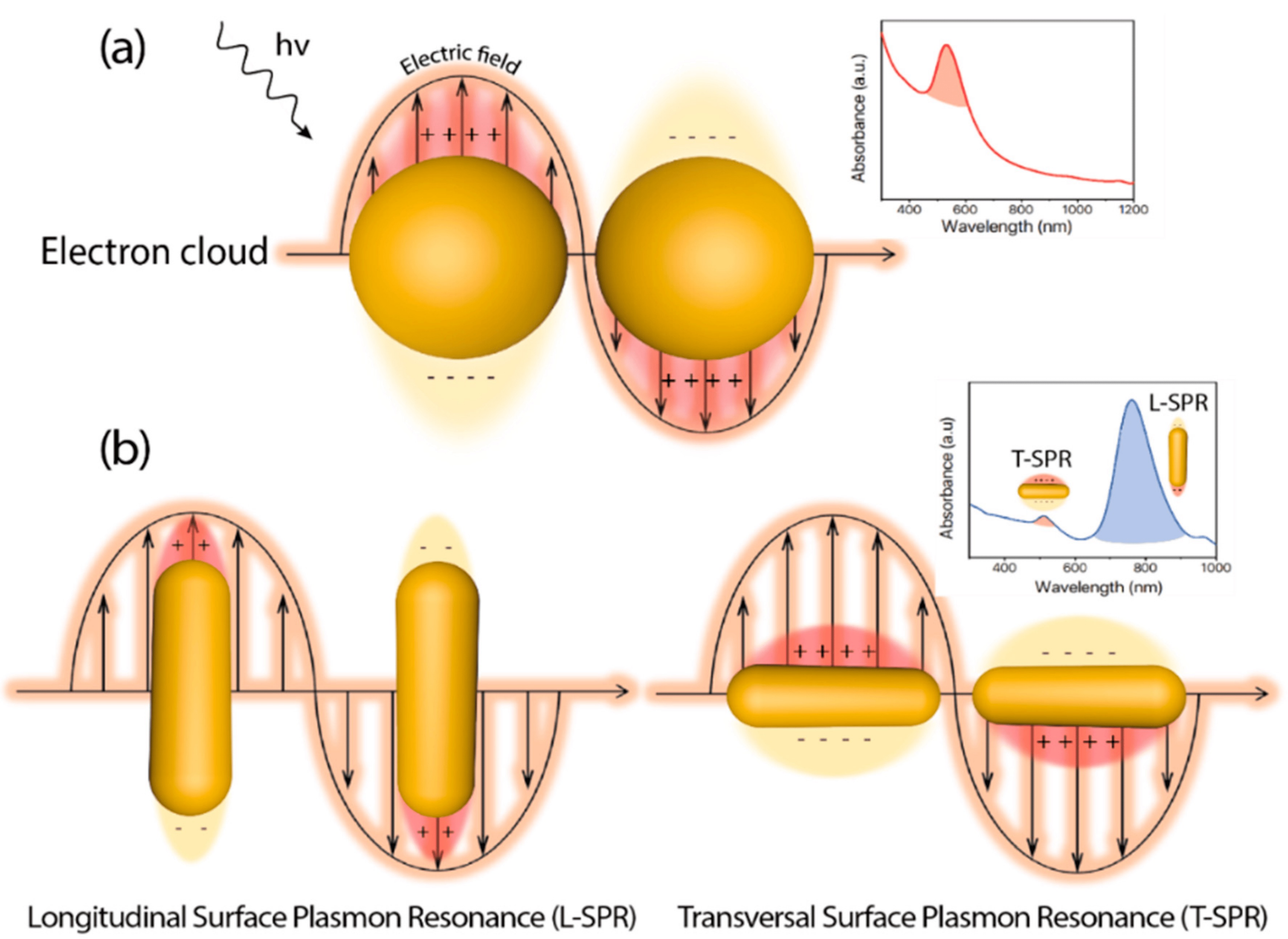
Resonance scatters green wavelengths

Lit from front (reflection)

Lit from behind (transmission)

Nanoparticles absorb shorter wavelengths (blue and green) and remaining wavelengths pass through and is transmitted

Broader Color Range with Asymmetric Nanostructures



While nanoparticles are symmetric, **nanorods** are anisotropic (different resonant frequencies depending on aspect ratio leading to multiple plasmon resonances

Garcia-Peiro *et al., Catalysts, 10, 12,* **2020**

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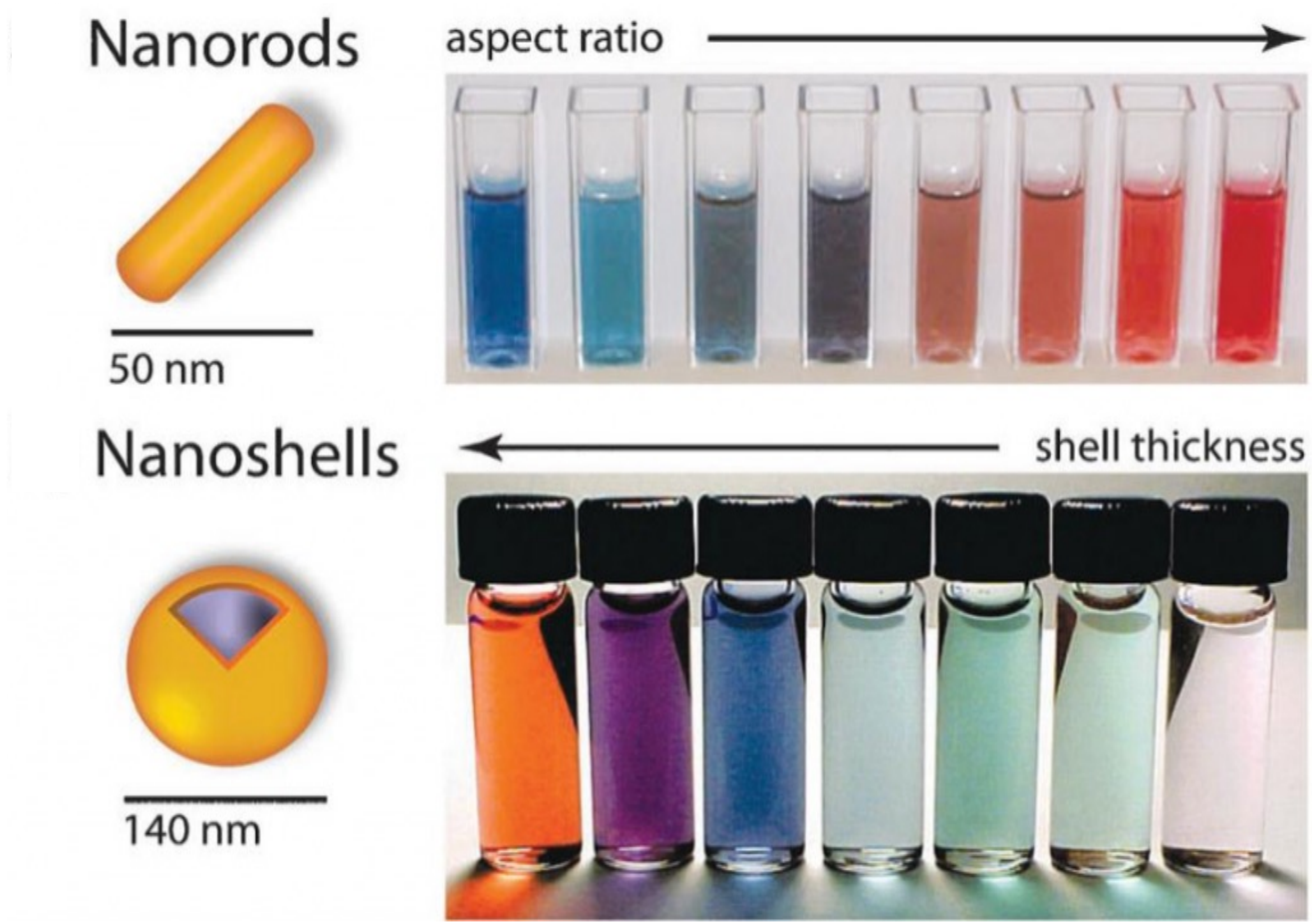
Broader Color Range with Asymmetric Nanostructures



While nanoparticles are symmetric, **nanorods** are anisotropic (different resonant frequencies depending on aspect ratio leading to multiple plasmon resonances

Nanoshells have inner and outer plamon modes with tunable optical properties based on shell thickness

Xiong *et al., Nanoscale, 6, 23,* **2014**

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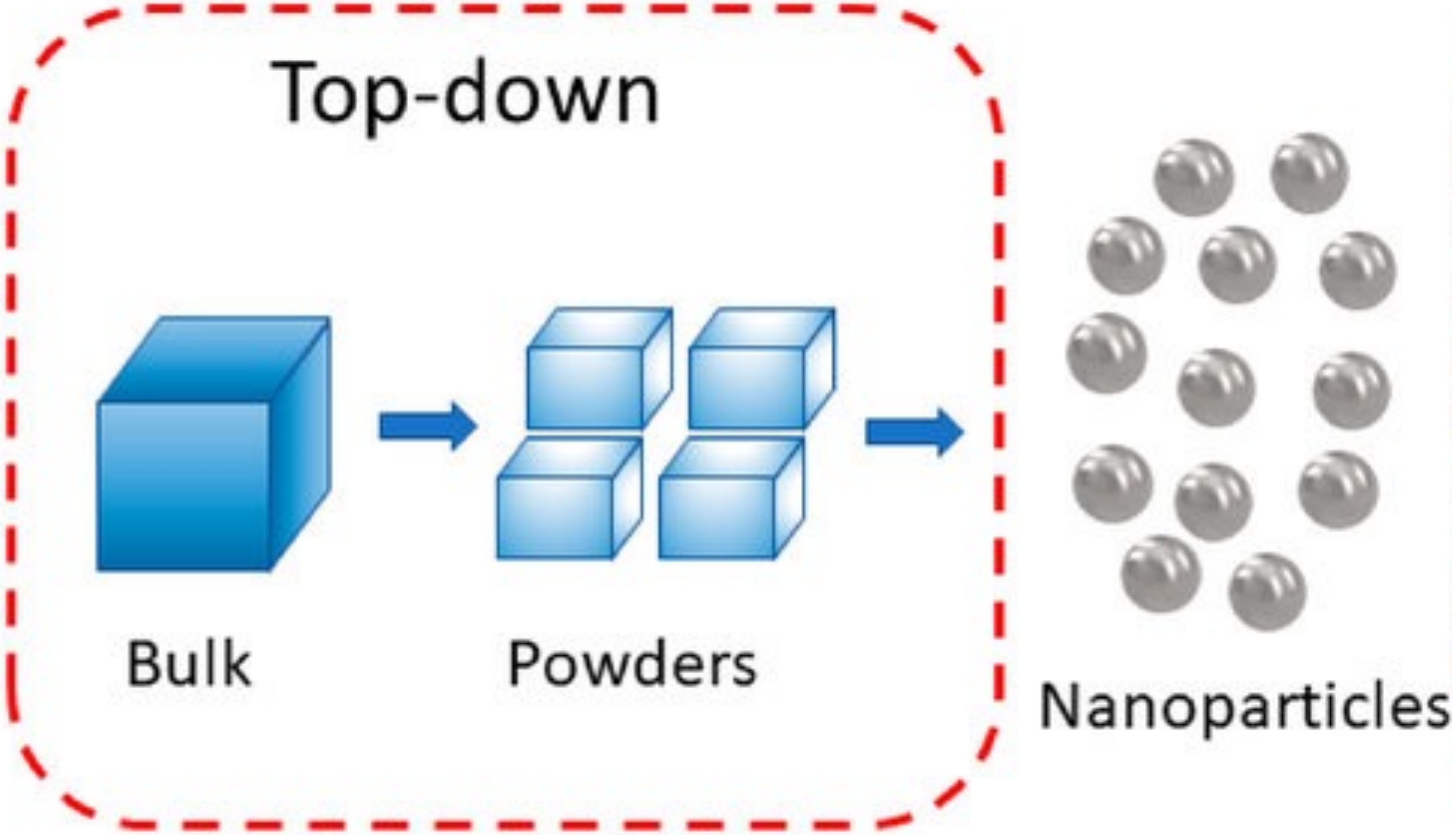
How to Synthesize Gold Nanoparticles?

Bottom-up *vs.* Top-down fabrication of materials like nanoparticles



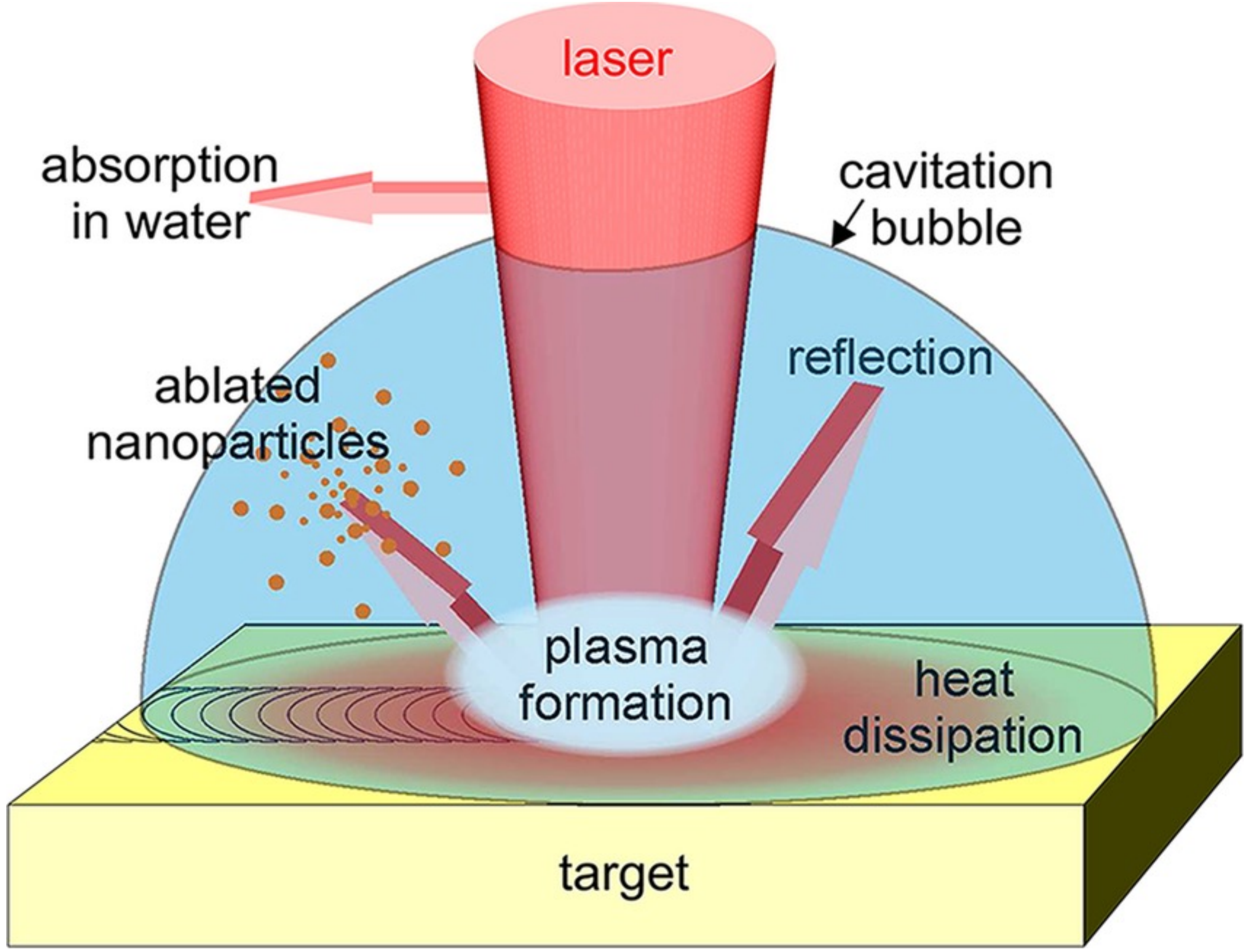
Physical methods

Source: Lu *et al.*, *Biosens.*, *10, 11*, **2020**

CHEMINA

How to Synthesize Gold Nanoparticles?

Bottom-up *vs.* Top-down fabrication of materials like nanoparticles



Physical methods

Laser ablation

Reich *et al., ChemPhysChem., 20, 8,* **2019**

How to Synthesize Gold Nanoparticles?

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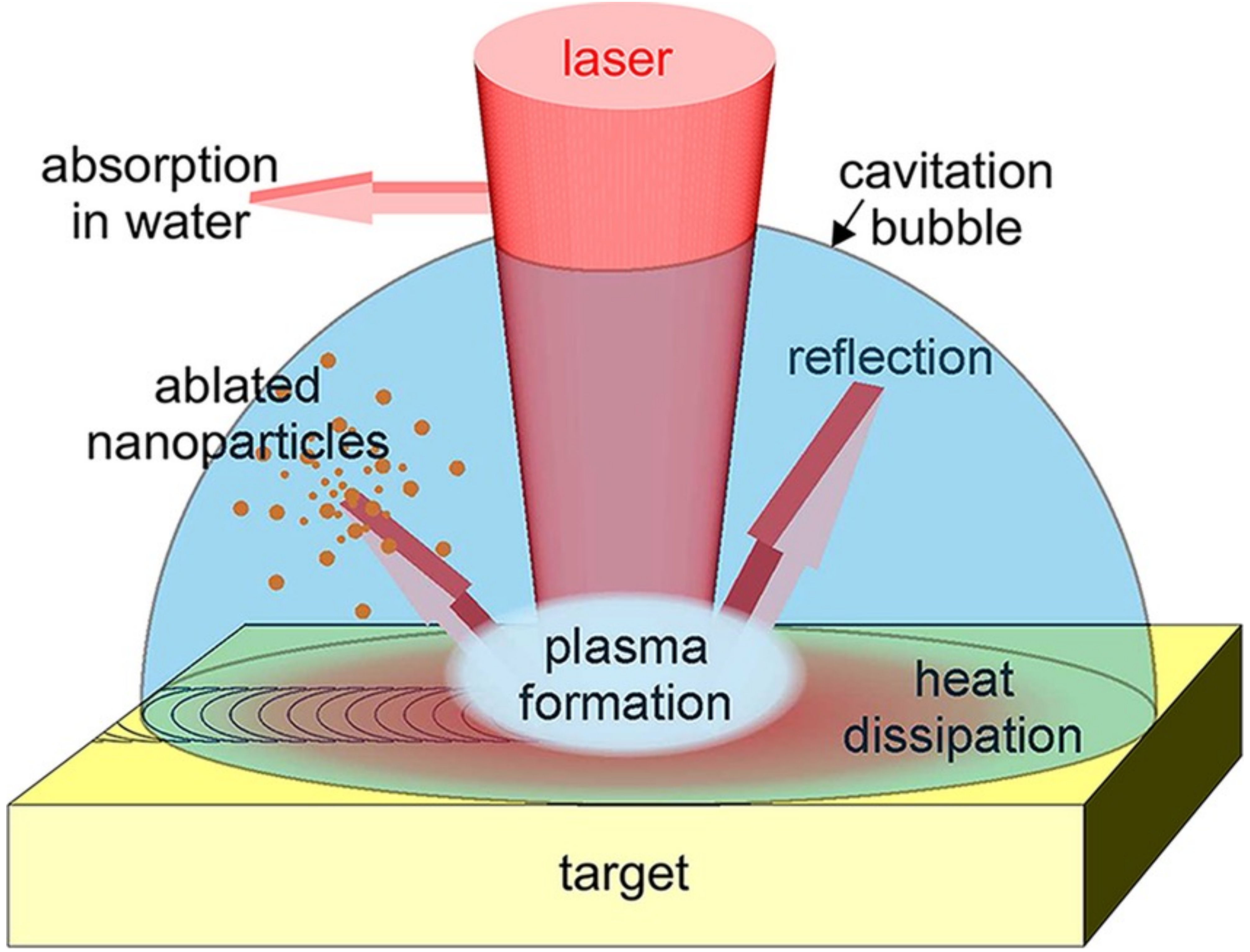

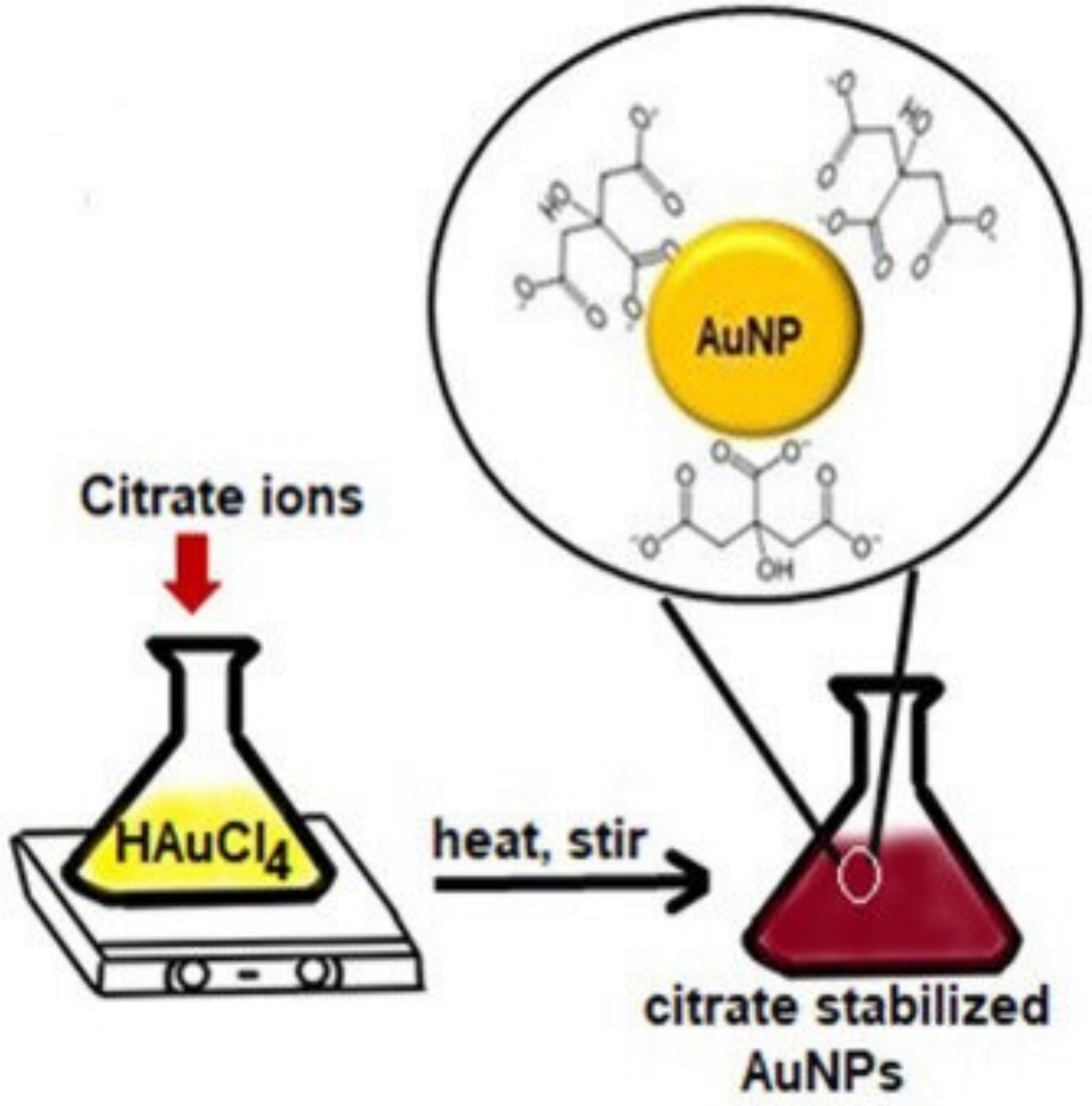

$$Au^{3+} + \underbrace{C_6H_8O_7}_{\text{Citric acid (reducing agent)}} \rightarrow Au$$

Citric acid
(reducing agent)

Physical methods

Laser ablation

Physical/chemical methods

Turkevich method (citrate reduction)

Amina *et al., Int. J. Nanomedicine., 15, 9823*, **2020**

Summary of Today's Class

- Surface Chemistry – recap and go more in-depth from the end of last class
- AFM to Visualize Surfaces – with unique advances like FluidFM
- Intro to Nanoscience – recap on work function and band theory
- STM for Higher Resolution Imaging of Surfaces – tunneling effect
- Nanoscale Interactions with Light – recap on plasmon resonance

Exercise Session: Packing of SAMs and Nanoparticle plasmon resonance