

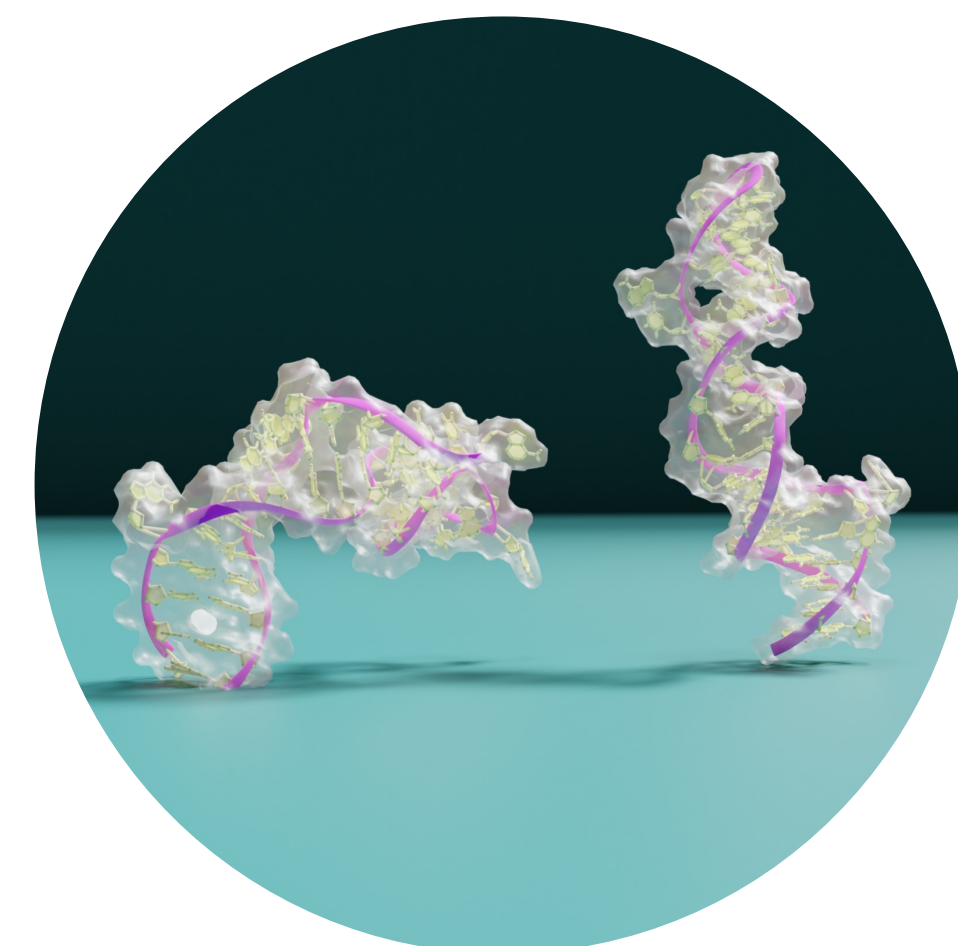
Applications Lesson 10

MSE 304

Nako Nakatsuka

Nako.Nakatsuka@epfl.ch

November 22nd 2024



My Academic Journey



Laboratory of Chemical Nanotechnology

Campus Biotech, Geneva

Swiss Center of Excellence in Biotechnology focused on:
Neuroscience & Neurotechnology
Digital Health
Global Health

The Campus functions as a giant incubator focused on translation of fundamental science into real solutions that have an impact on society

EPFL

Neuro **X** Institute

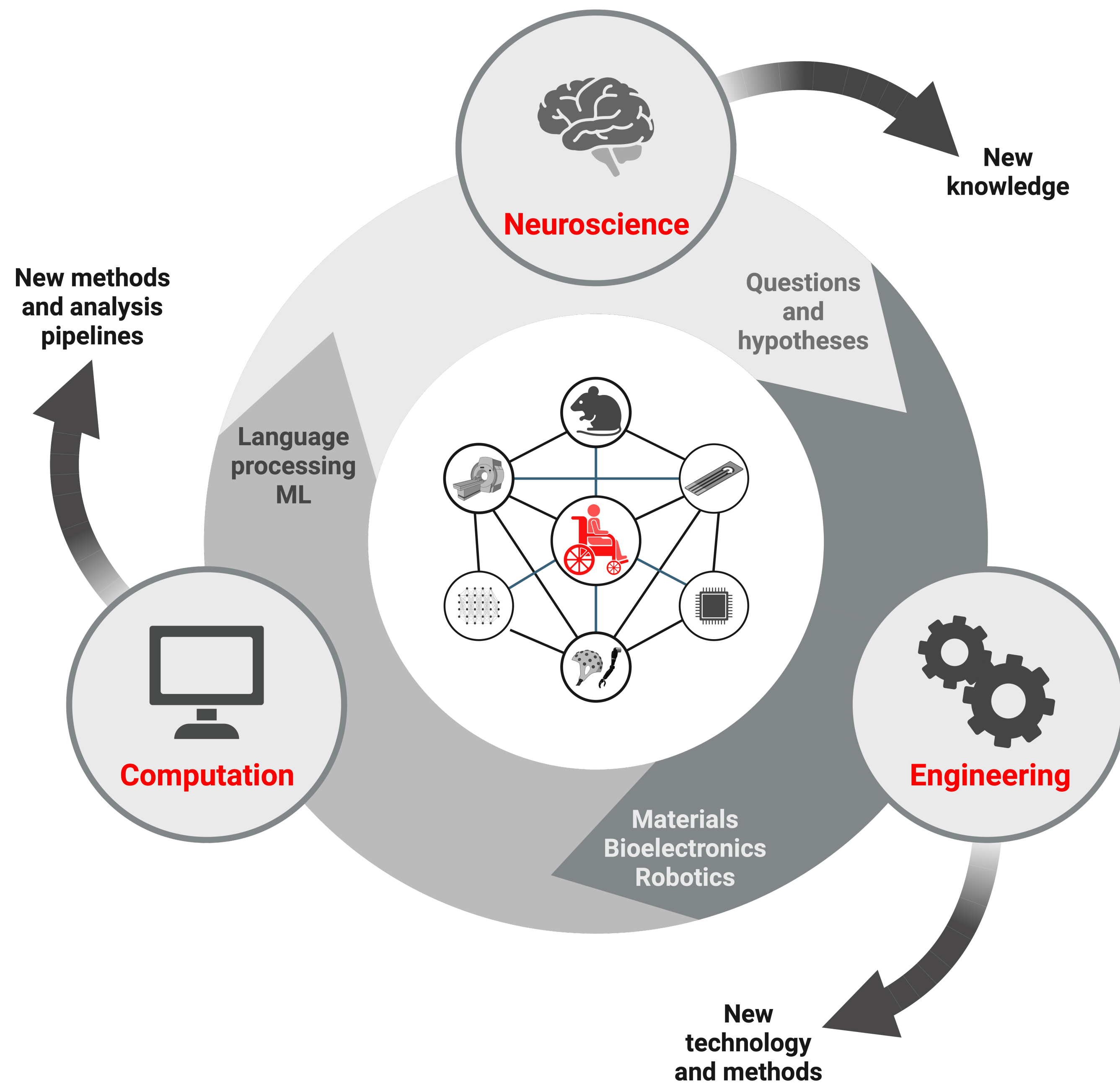


**UNIVERSITÉ
DE GENÈVE**

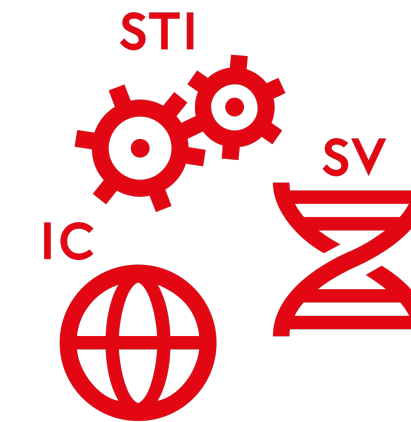
WYSS  CENTER



fondazione
bertarelli



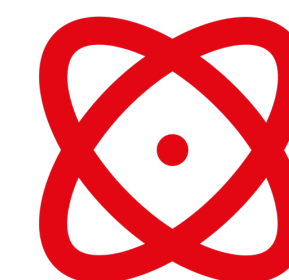
Neuro X Institute



Interschool
Institute



10
Professors



+150
Collaborators / PhD students

Laboratory of Chemical Nanotechnology

Harnessing nanoscale chemistry to design technologies to improve human health

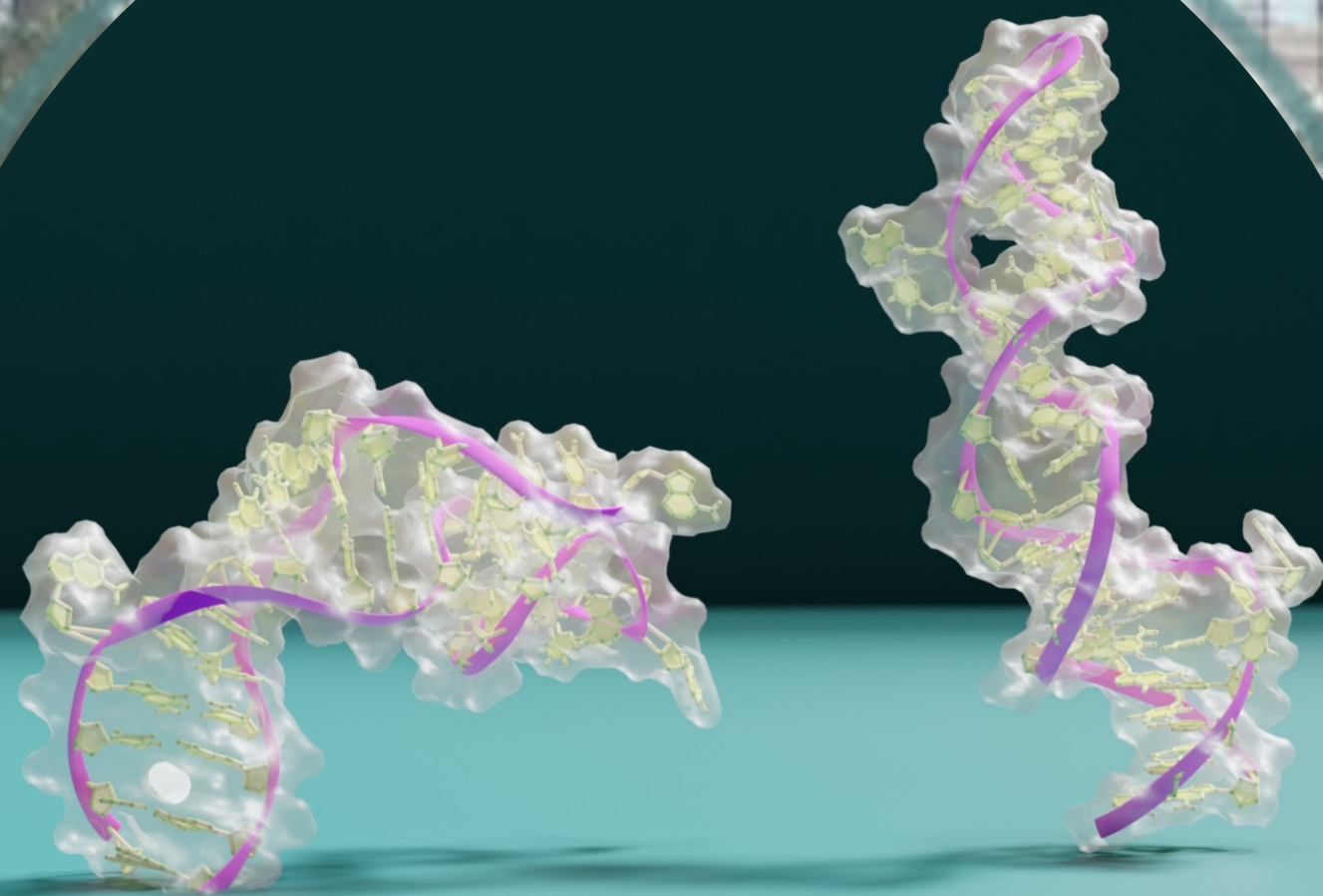
Chemistry



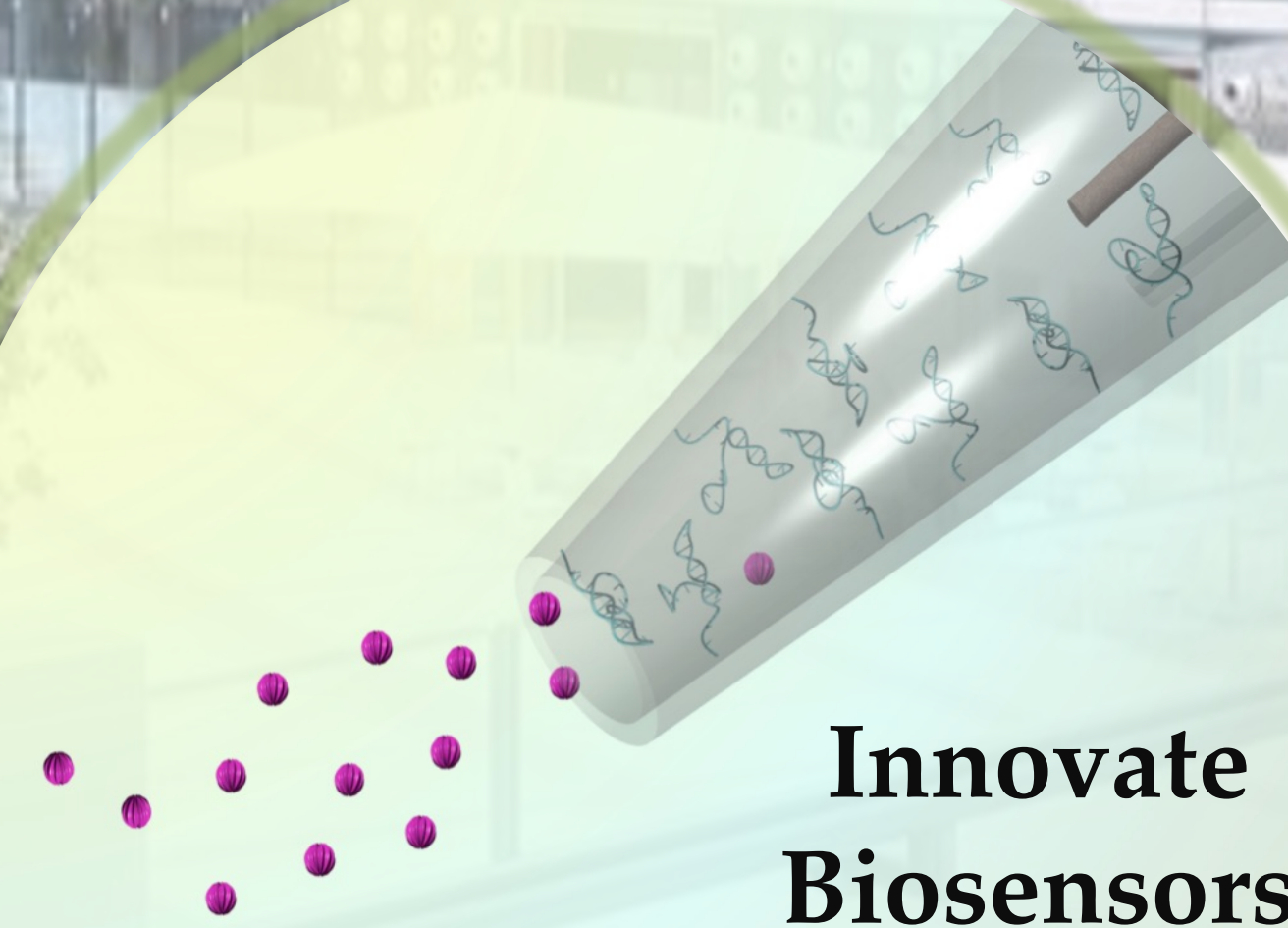
Engineering



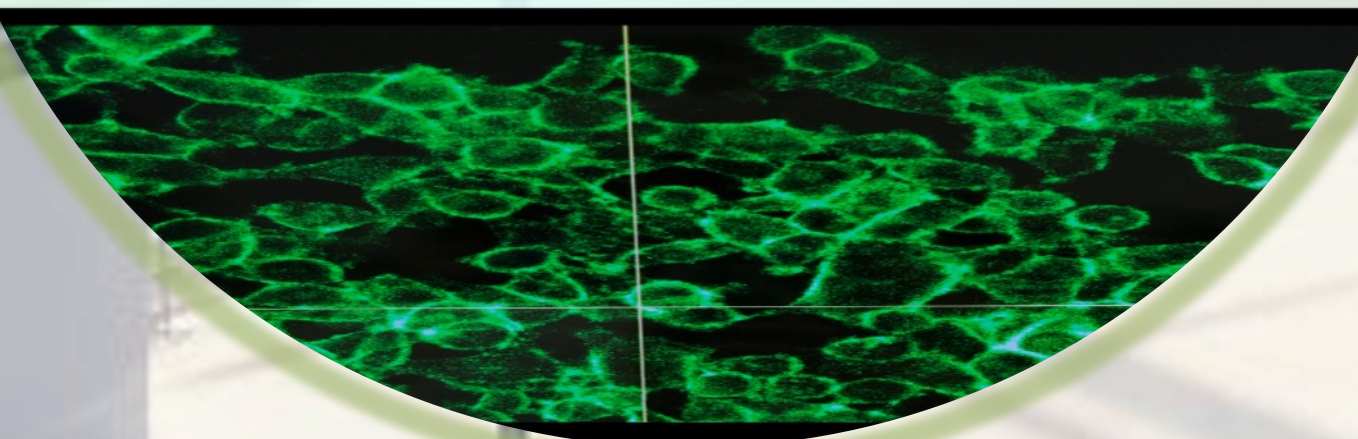
Neuroscience



Characterize Molecular Interactions



Innovate Biosensors



Tackle Brain Disorders

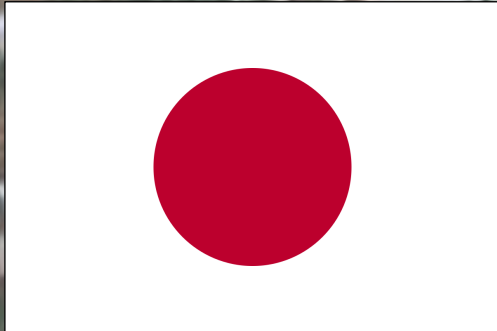


Laboratory of Chemical Nanotechnology

Driving innovation with a diverse multidisciplinary team



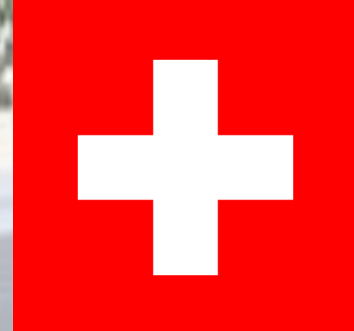
Nako
Nakatsuka



Jessica
Empain



Annina
Stuber



Nick
Mahtani



Lianxin
Xu



Emily
Schafer



Jacob
Surgailis



Sandra
Hernandez
Escobar



campus
biotech

Goal of the Next Few Weeks of Classes on Applications

- Be mesmerized by the diverse applications where surfaces & interfaces play a key role
- Observe how the fundamentals you learned in prior classes can be applied
- Recap on some basic chemistry concepts to understand surfaces & interfaces
- Learn techniques that enable characterization of surfaces & interfaces

What we cover in today's class:

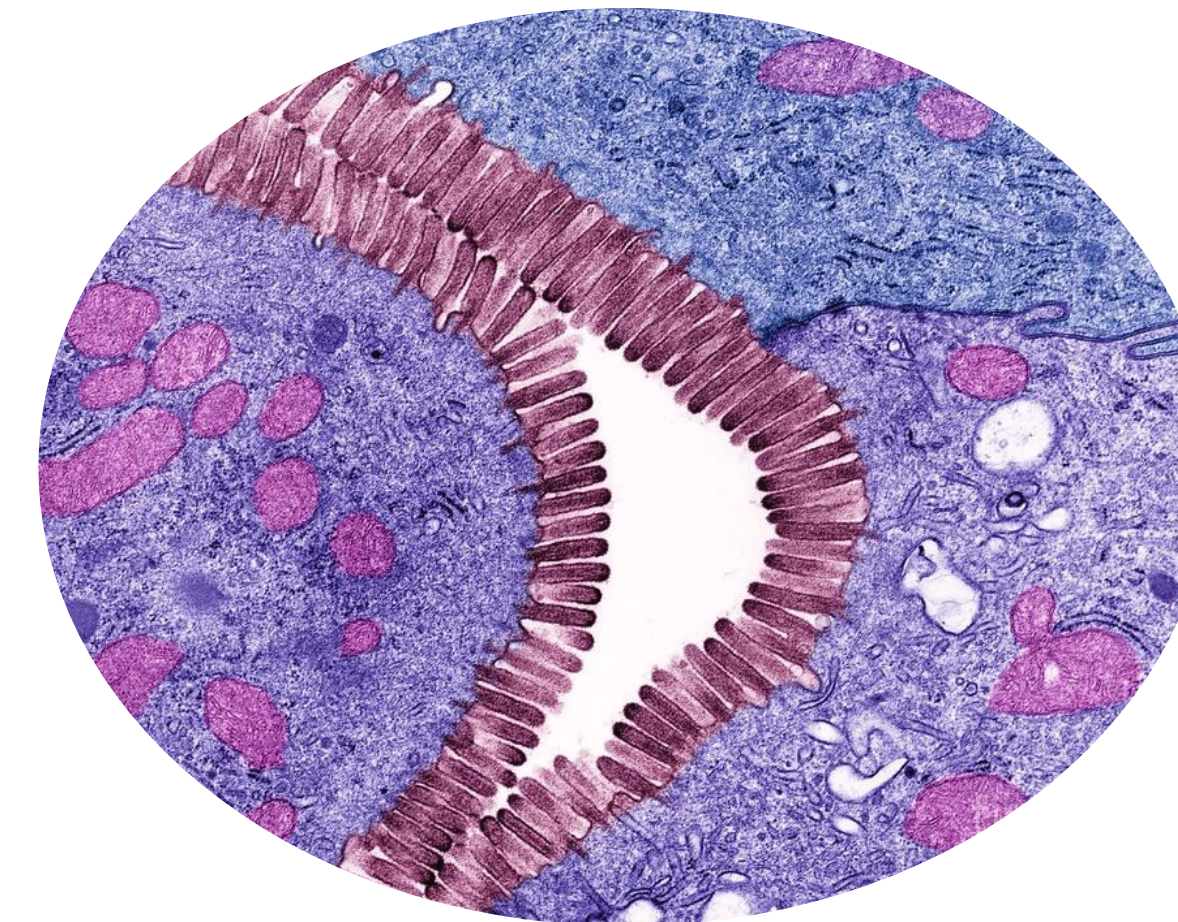
- **Surfaces and Interfaces in Nature** – a recap on intermolecular interactions
- **Artificial Surfaces** – the challenge of cleaning
- **Techniques to Monitor Surfaces** – contact angle and XPS

Surfaces & Interfaces in Nature

Specific surface area = ratio of area (A) to volume (V)
Nature harnesses high A/V materials

The Brain

- 86 billion neurons
- 100 trillion synapses
- Neural connectivity
- Efficient metabolism



Microvilli (small intestine)

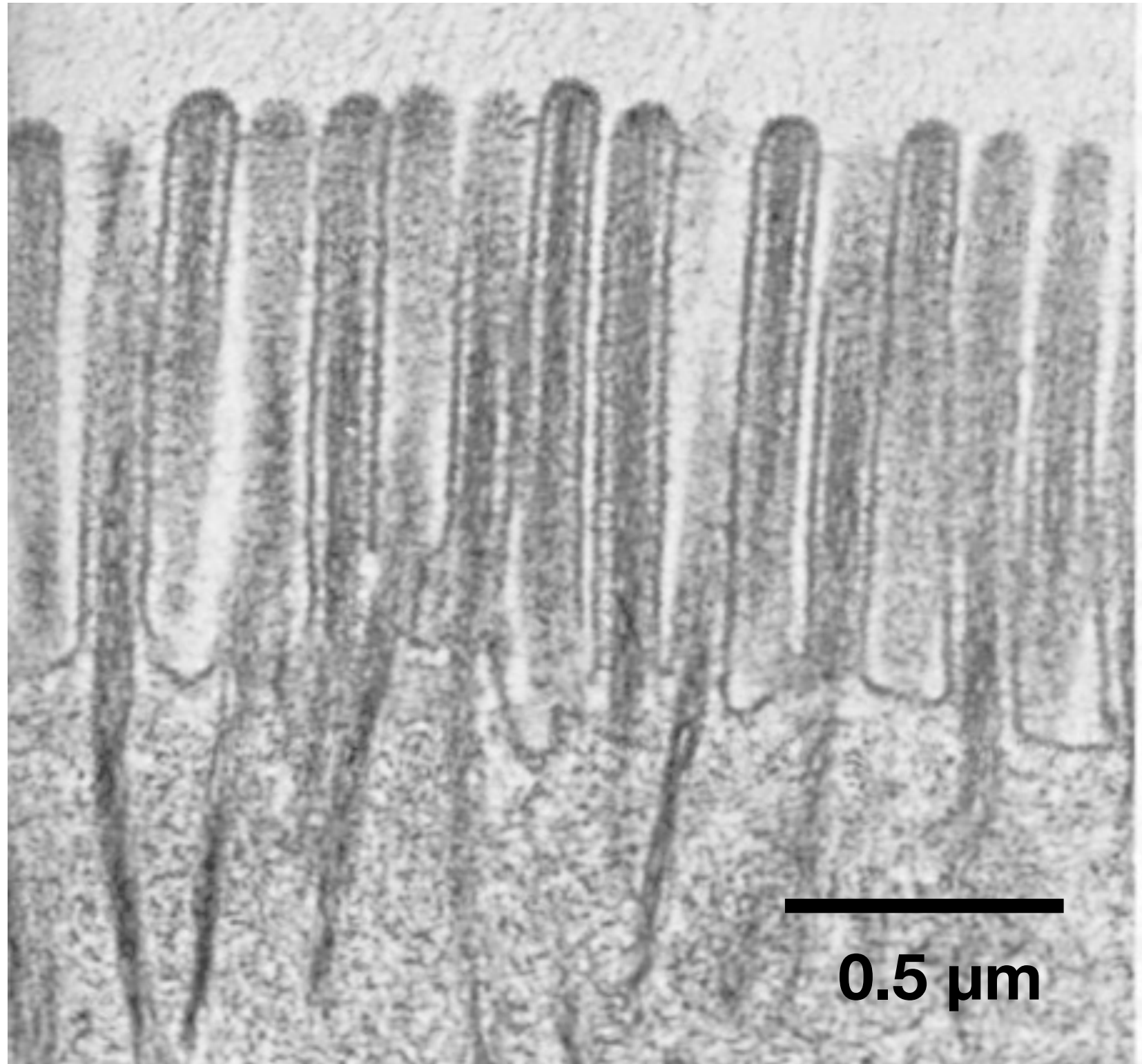
- Absorption & exchange
- Efficient interactions
- Cell-environment interfaces for biochemical reactions

Chemical reactions often take place at interfaces

Materials with high A/V play an important role in several artificial surfaces & interfaces
(e.g. catalysts)

High Area to Volume in Microvilli Enables Digestion

Question: How long would it take to digest a sandwich without microvilli?



$$A = \pi \cdot d \cdot h$$

Diameter (d) = $0.1 \mu\text{m} = 1 \times 10^{-7} \text{ m}$
Length (h) = $1 \mu\text{m} = 1 \times 10^{-6} \text{ m}$

$$A = \pi \cdot (1 \times 10^{-7} \text{ m}) \cdot (1 \times 10^{-6} \text{ m}) = 3.14 \times 10^{-13} \text{ m}^2$$

Assume microvilli covers most intestinal surface ~ 1000 microvilli/ μm^2

Total microvilli on 1 cm^2 surface:

$$1 \text{ cm}^2 = 10^8 \mu\text{m}^2 \Rightarrow 10^8 \times 1000 = 10^{11} \text{ microvilli}$$

$$\text{Total Surface Area} = 10^{11} \times 3.14 \times 10^{-13} \text{ m}^2 = 31.4 \text{ m}^2$$

So if on average, it takes someone 4 h to digest a sandwich WITH microvilli...
it would take **1,256,000 hours $\approx$ 143 years** WITHOUT microvilli!!!

$$\text{Ratio} = \frac{31.4 \text{ m}^2}{10^{-4} \text{ m}^2} = 314,000$$

With microvilli (points to numerator)
Without microvilli (flat surface) (points to denominator)

How Does a Gecko Stick on a Wall?



1. Their hands and feet excrete sticky materials (goo)
2. Their hands and feet have tiny hooks
3. Their hands and feet are like tiny suction cups
4. None of the above

How Does a Gecko Stick on a Wall?



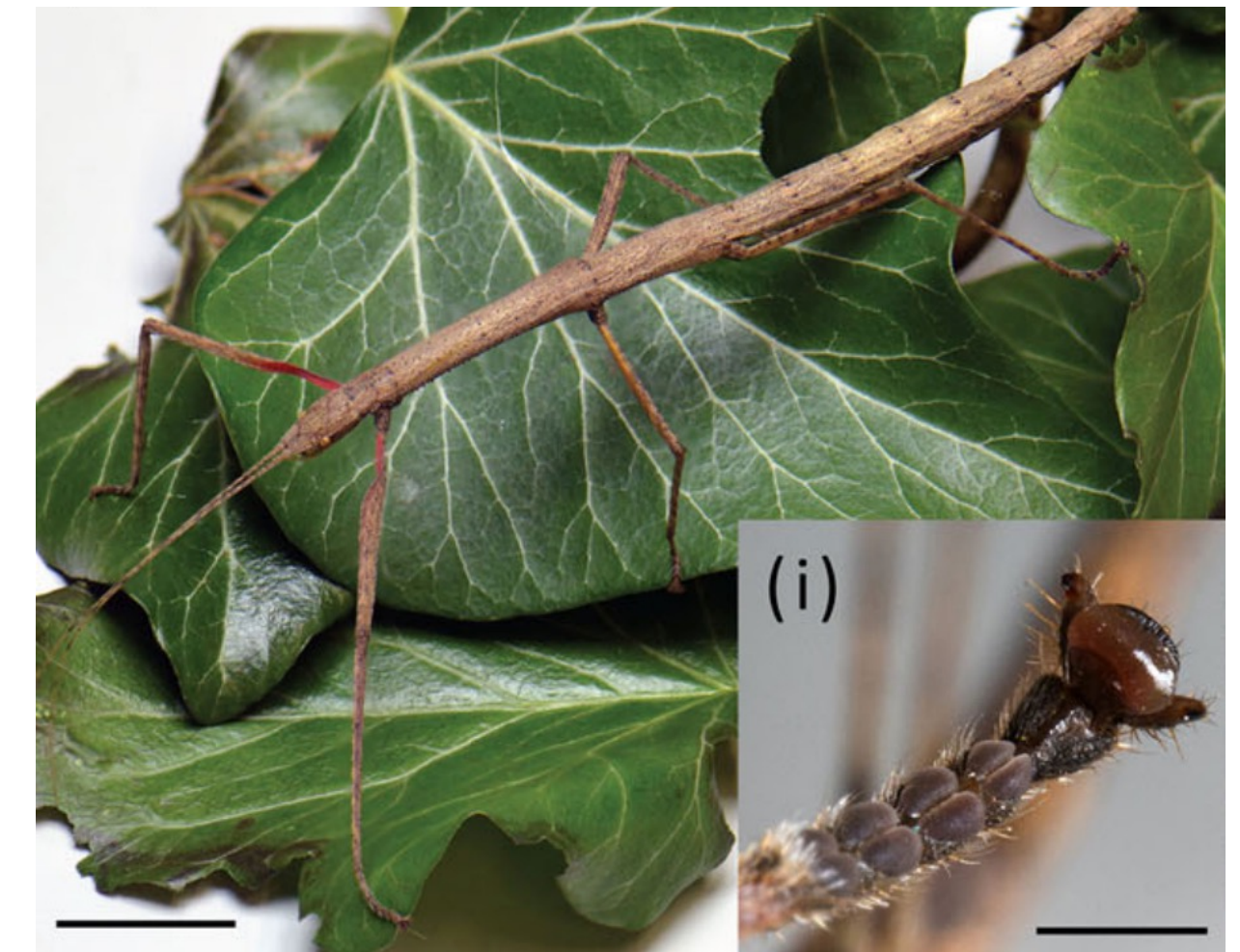
Hypothesis 1: Capillary forces for adhesion (like insects) – condensation of water from atmosphere forming a monolayer of water molecules/insects secreting liquid from their feet can cause significant capillary attraction

ORIGINAL ARTICLE

ANNALS OF THE NEW YORK
ACADEMY OF SCIENCES

Capillary adhesion of stick insects

Guillermo J. Amador¹  | Brett Klaassen van Oorschot¹  | Uddalok Sen² |
Benjamin Karman³ | Rutger Leenders¹

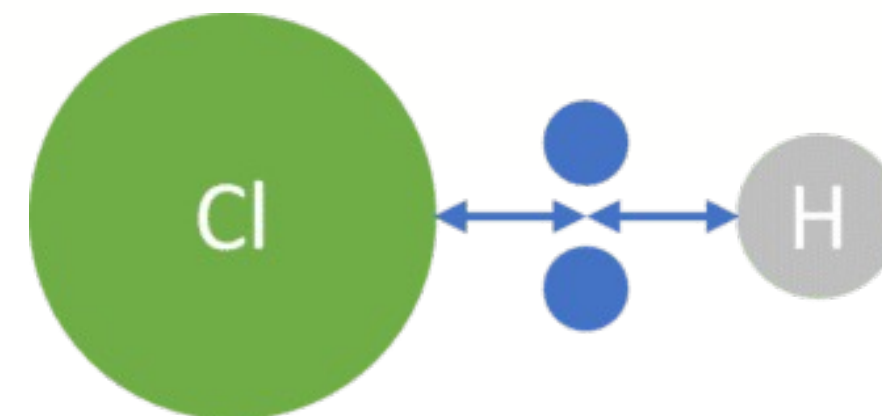
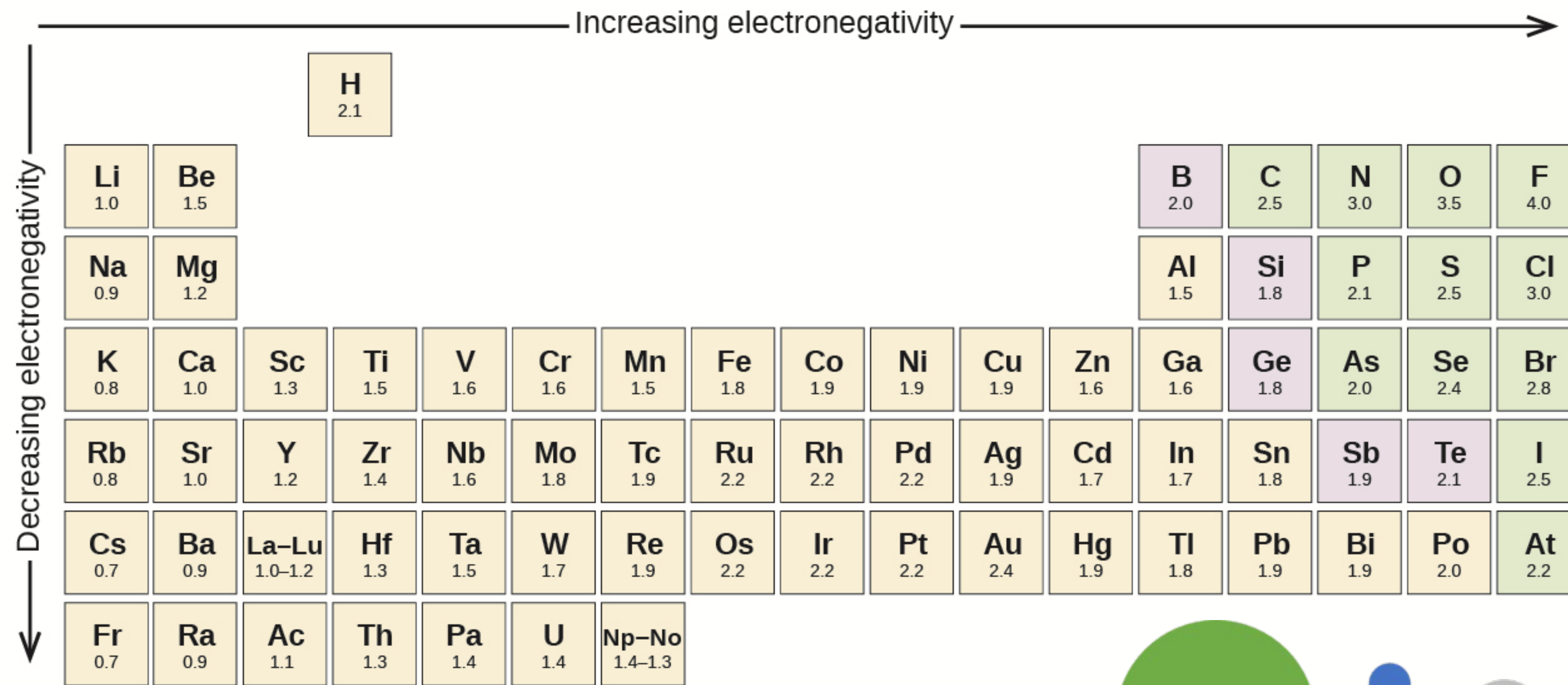


BUT: the toes of geckos are highly hydrophobic unlike insects...

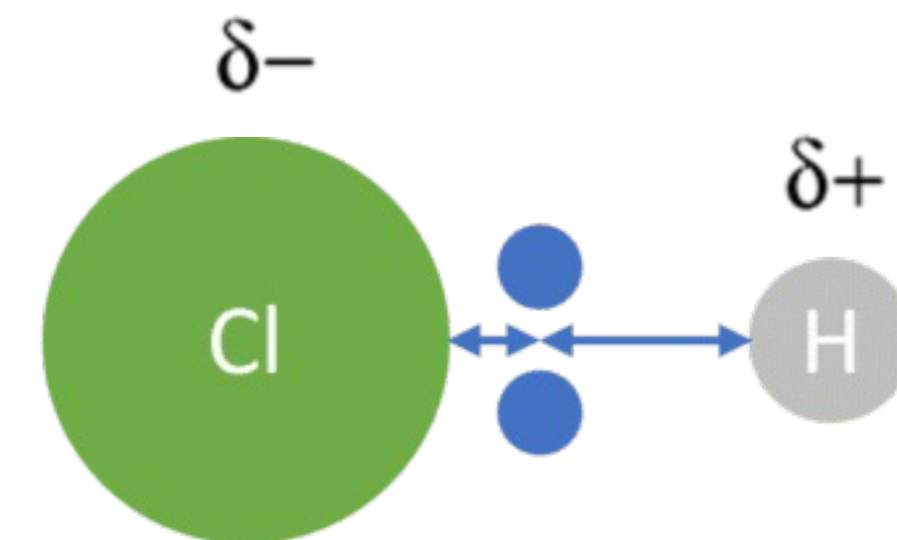
Intermolecular Forces of Attraction – What is At Play for Geckos?

Intermolecular forces make two molecules come closer together and interact

The force of attraction is proportional to the electronegativity (how much the molecule likes electrons)

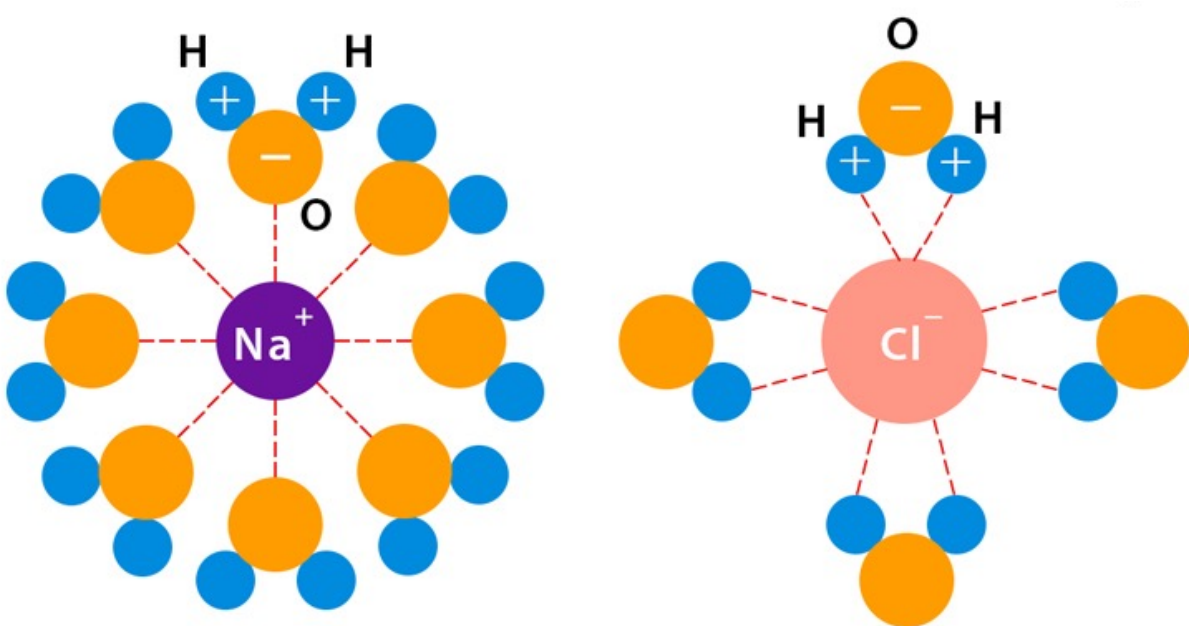


No electronegativity.
Electrons held in the
centre of the bond.

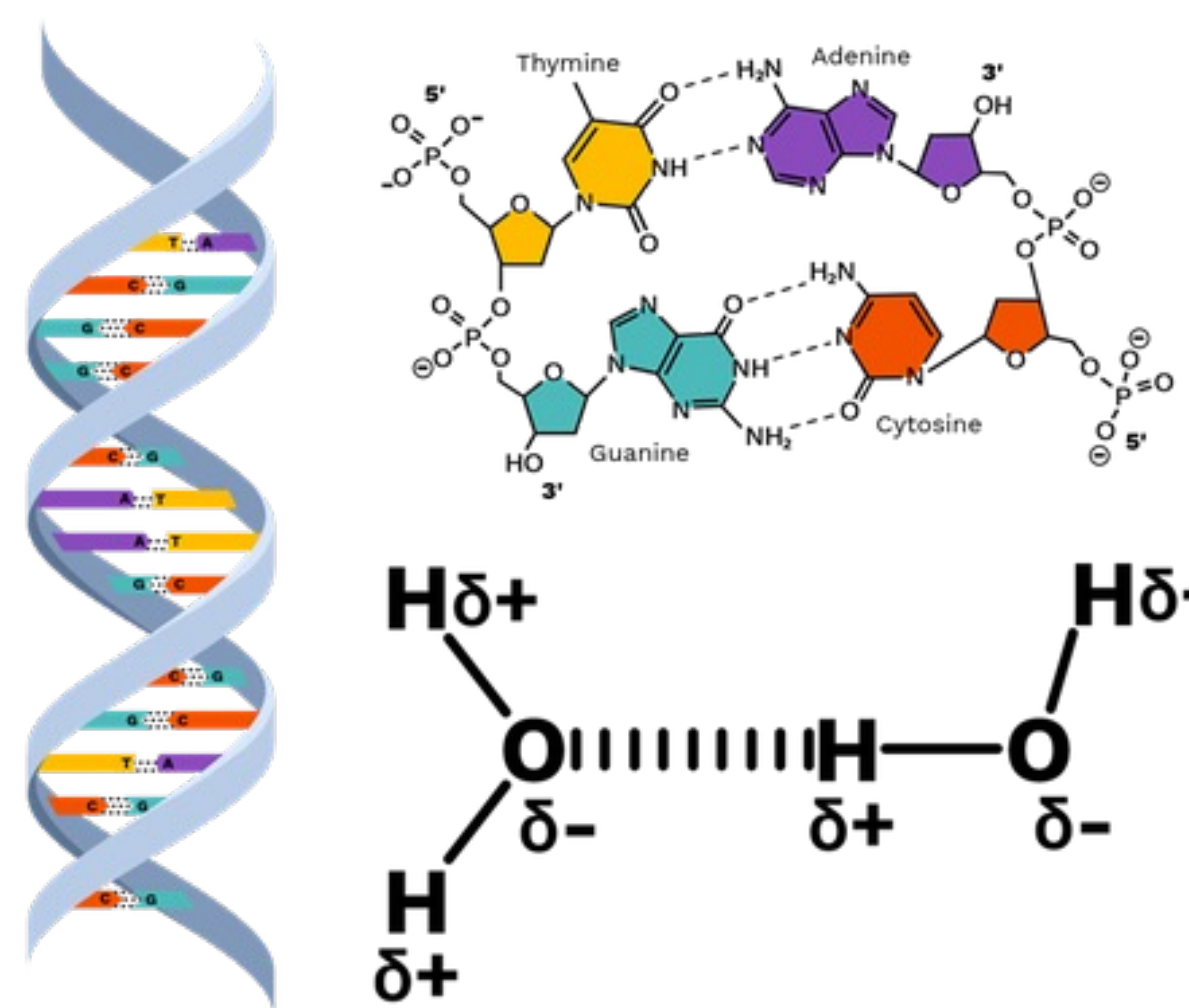


With electronegativity
Electrons are drawn
closer to chlorine.

Different Forms of Intermolecular Interactions/Forces

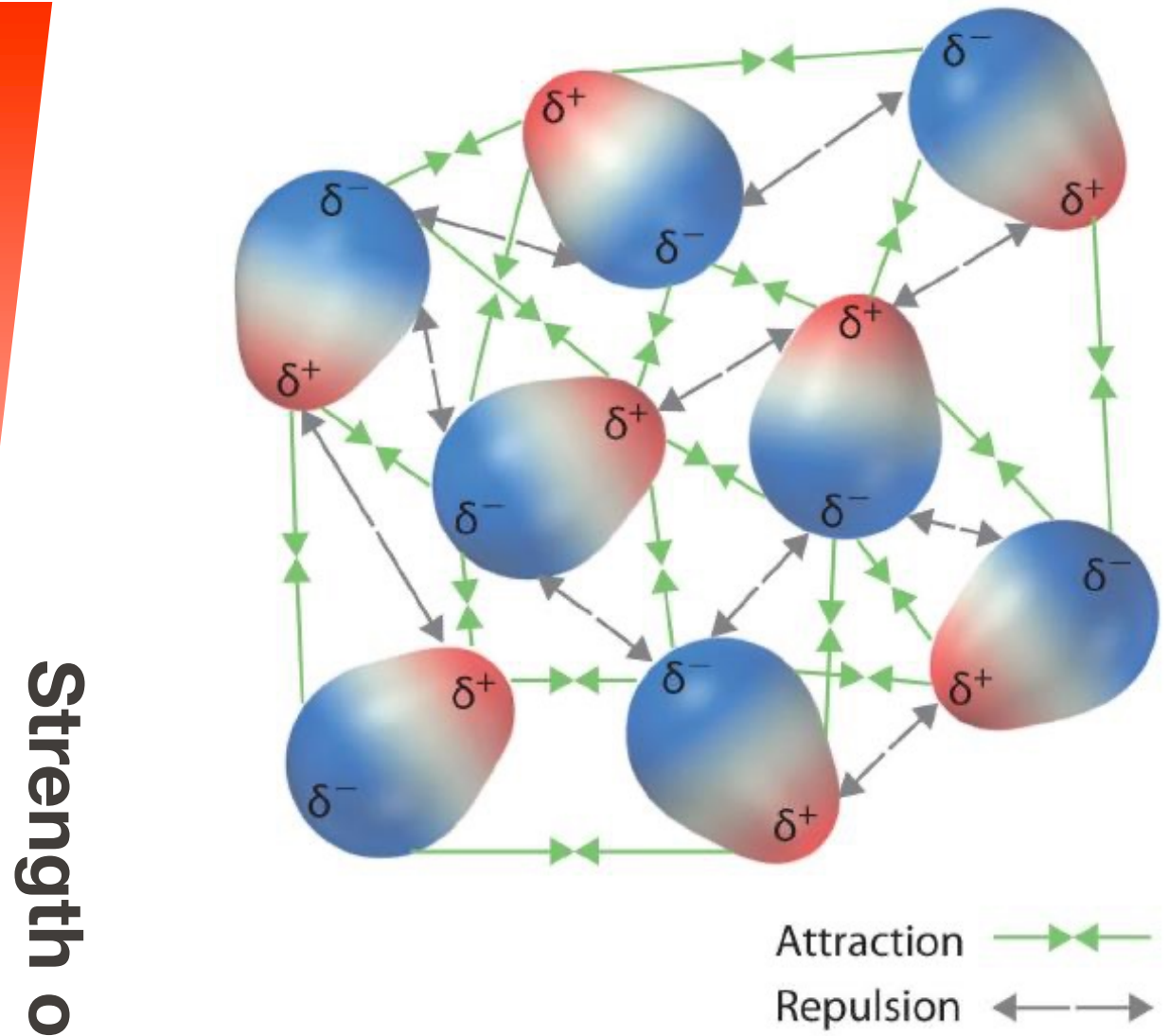


Ion-dipole



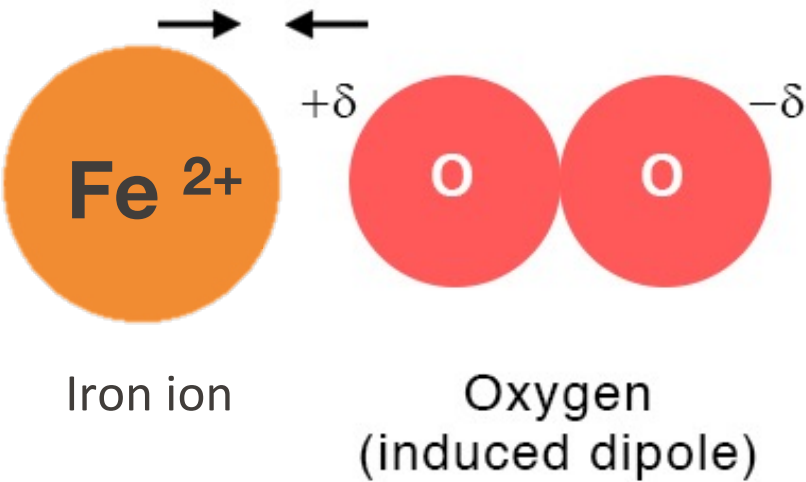
H-bond

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

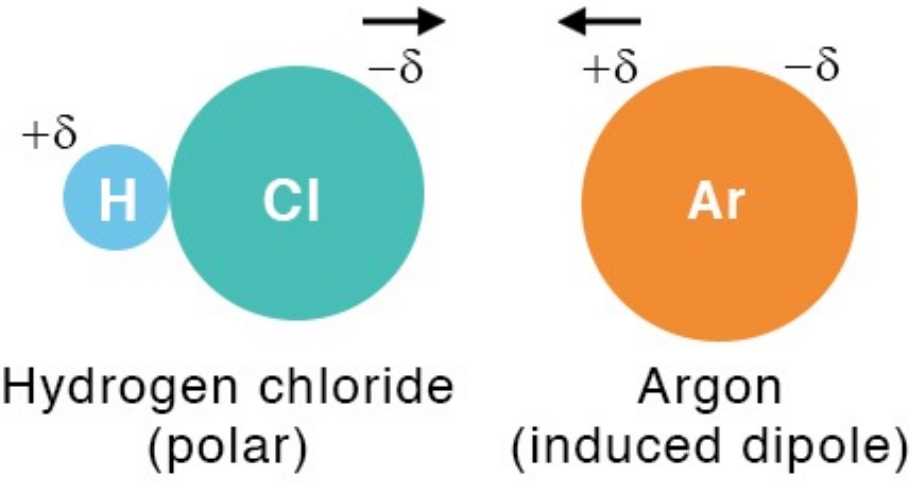


Dipole-dipole

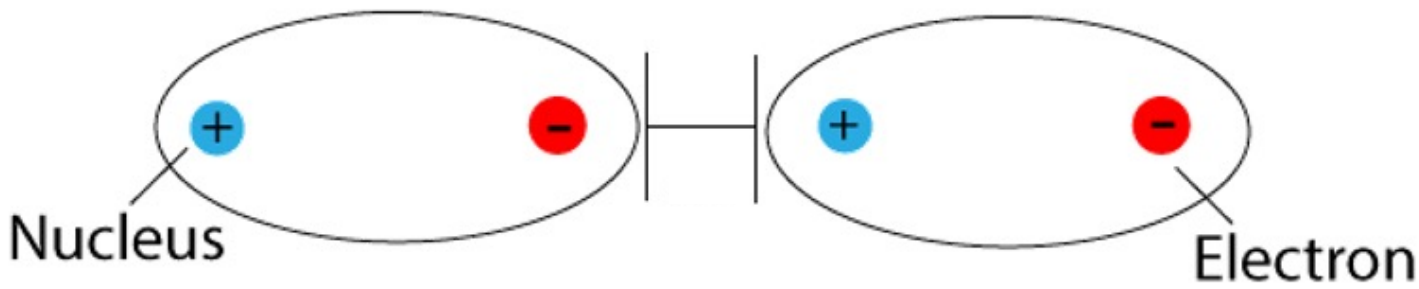
Strength of force



Ion-induced dipole



Dipole-induced dipole



Van der Waals forces

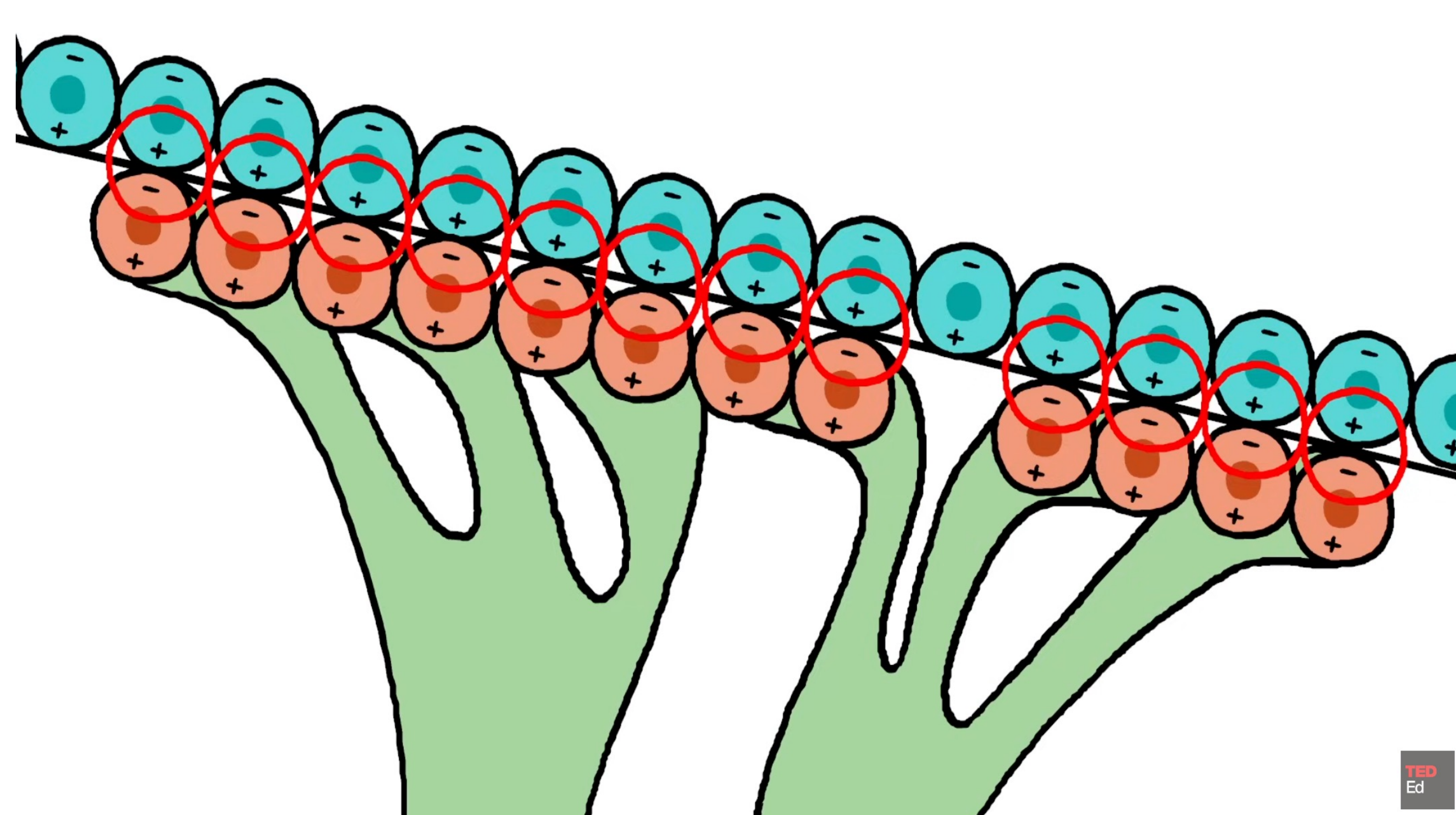
The toes of geckos are hydrophobic and not charged...

How Geckos Stick on der Waals

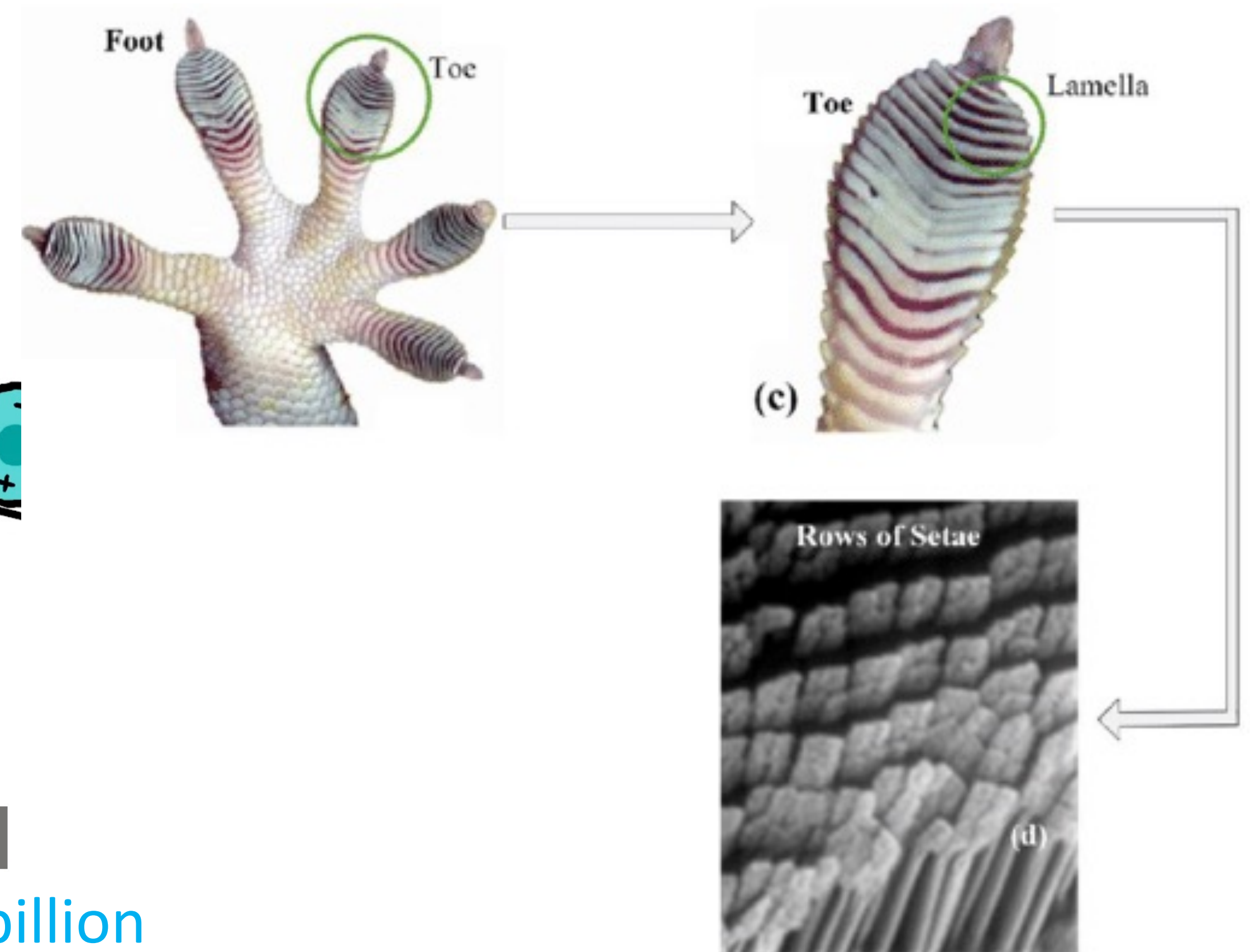
Revealing the lizards' secret, engineers aim to make wall-walking robots

27 AUG 2002 • BY BEN SHOUSE

Science



Adhesion strength from subdividing each toe into 2 billion microstructures → maximize contact area → increase cumulative van der Waals interactions with the surface



Wang *et al.*, *J. Bionic. Eng.*, 18, 1011, 2021

Semiconductor Material Led to Evidence of Interactions

RESEARCH ARTICLE | BIOLOGICAL SCIENCES | ✓

PNAS

Evidence for van der Waals adhesion in gecko setae

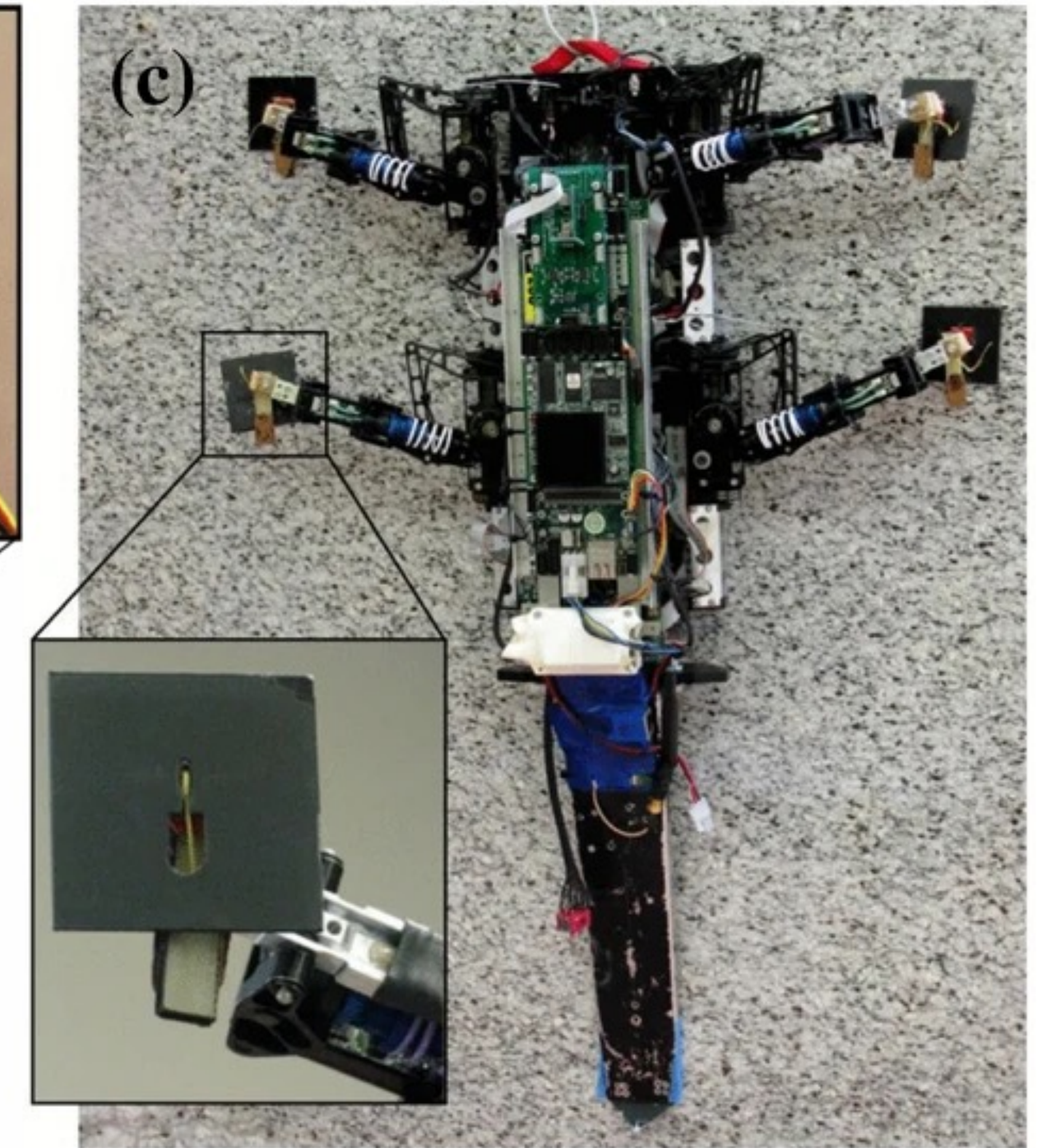
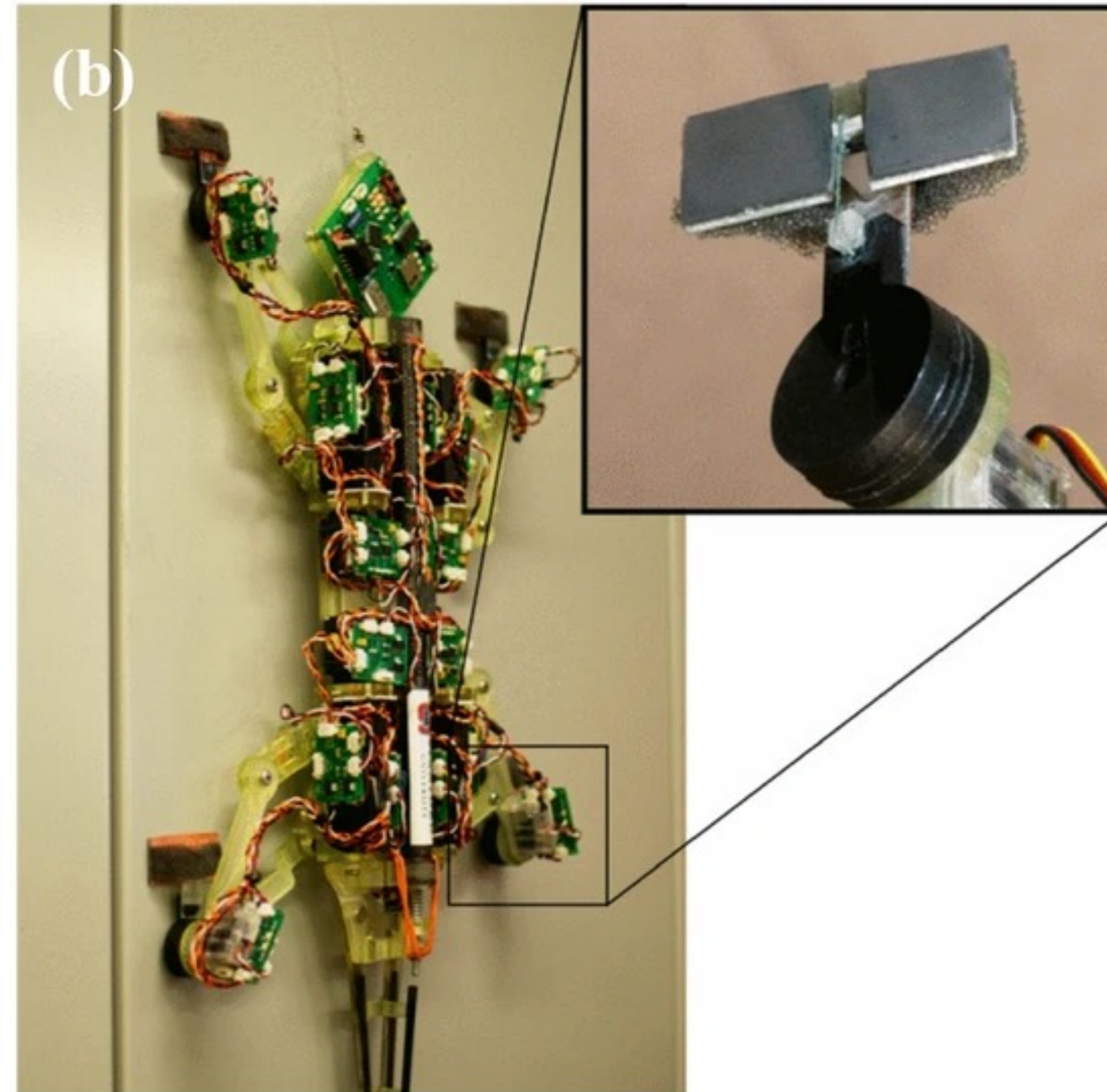
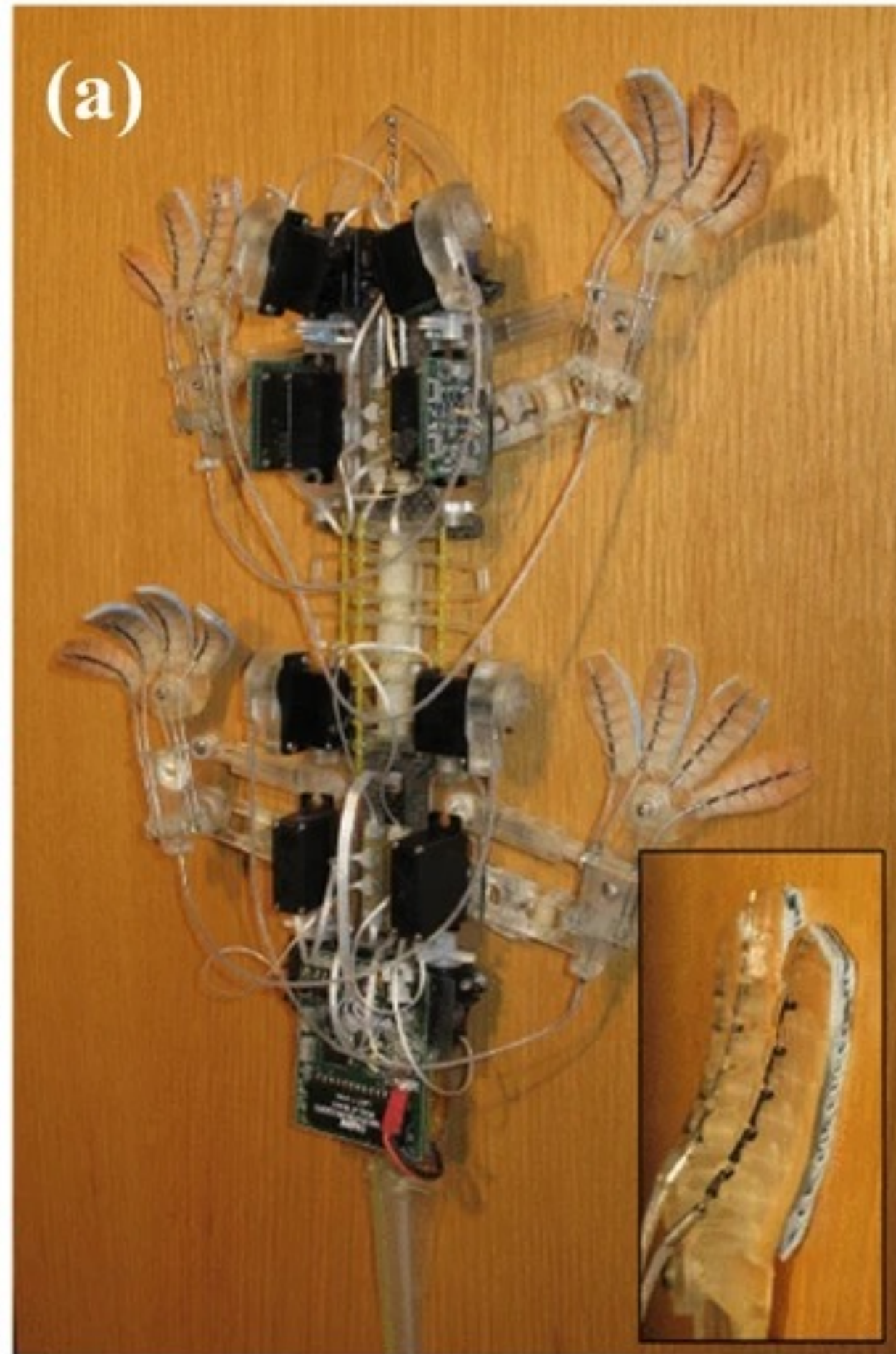
Kellar Autumn, Metin Sitti, Yiching A. Liang, Anne M. Peattie, Wendy R. Hansen, Simon Sponberg, Thomas W. Kenny, Ronald Fearing, Jacob N. Israelachvili, and Robert J. Full -6 [Authors Info & Affiliations](#)

August 27, 2002 | 99 (19) 12252-12256 | <https://doi.org/10.1073/pnas.192252799>



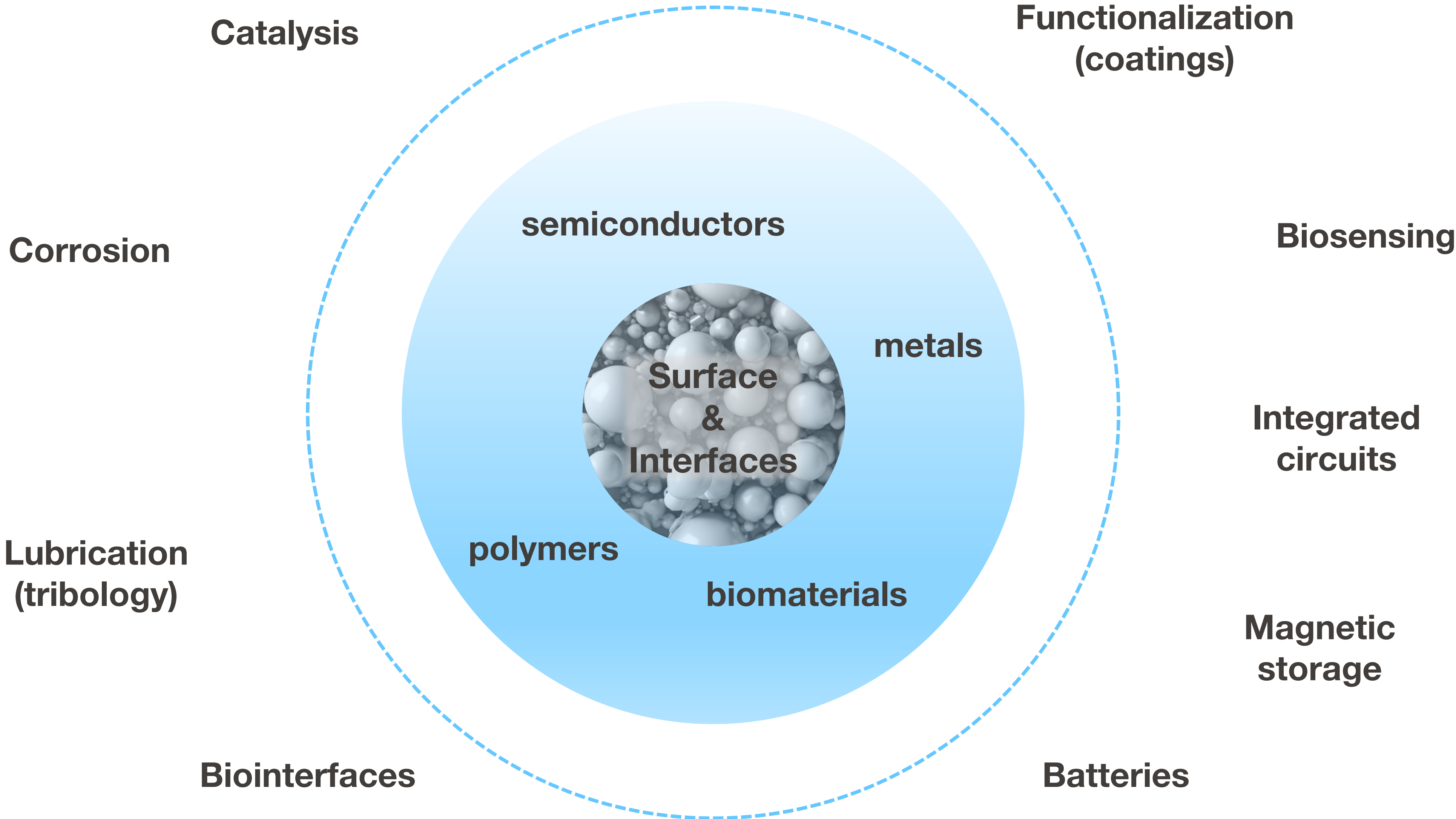
Gecko adhering to
molecularly smooth
hydrophobic gallium arsenide
semiconductor demonstrates
mechanism of adhesion is van
der Waals force

Wall-Climbing Robots Inspired by this Knowledge



Wang et al., *J. Bionic. Eng.*, 18, 1011, 2021

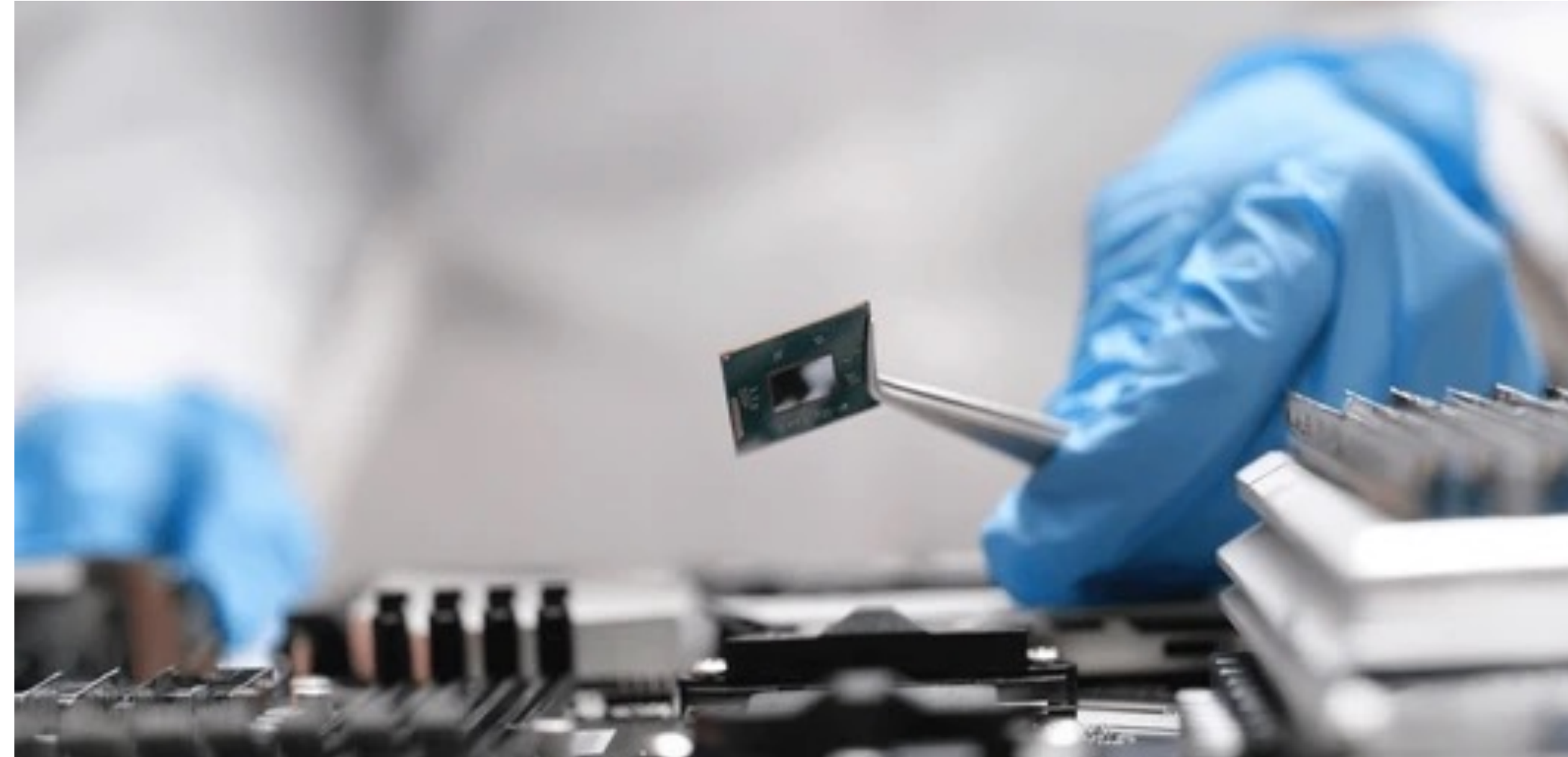
Diverse Applications of Surfaces & Interfaces



Challenge of Studying Surfaces

A freshly cleaned surface remains clean for a very short time interval

Each atom of a 1 cm² metal surface is hit **~10⁸ times/s by a gas particle** (at atmospheric pressure)



The number of molecules that hit the sample surface per unit time (impact frequency) and unit area is calculated as follows:

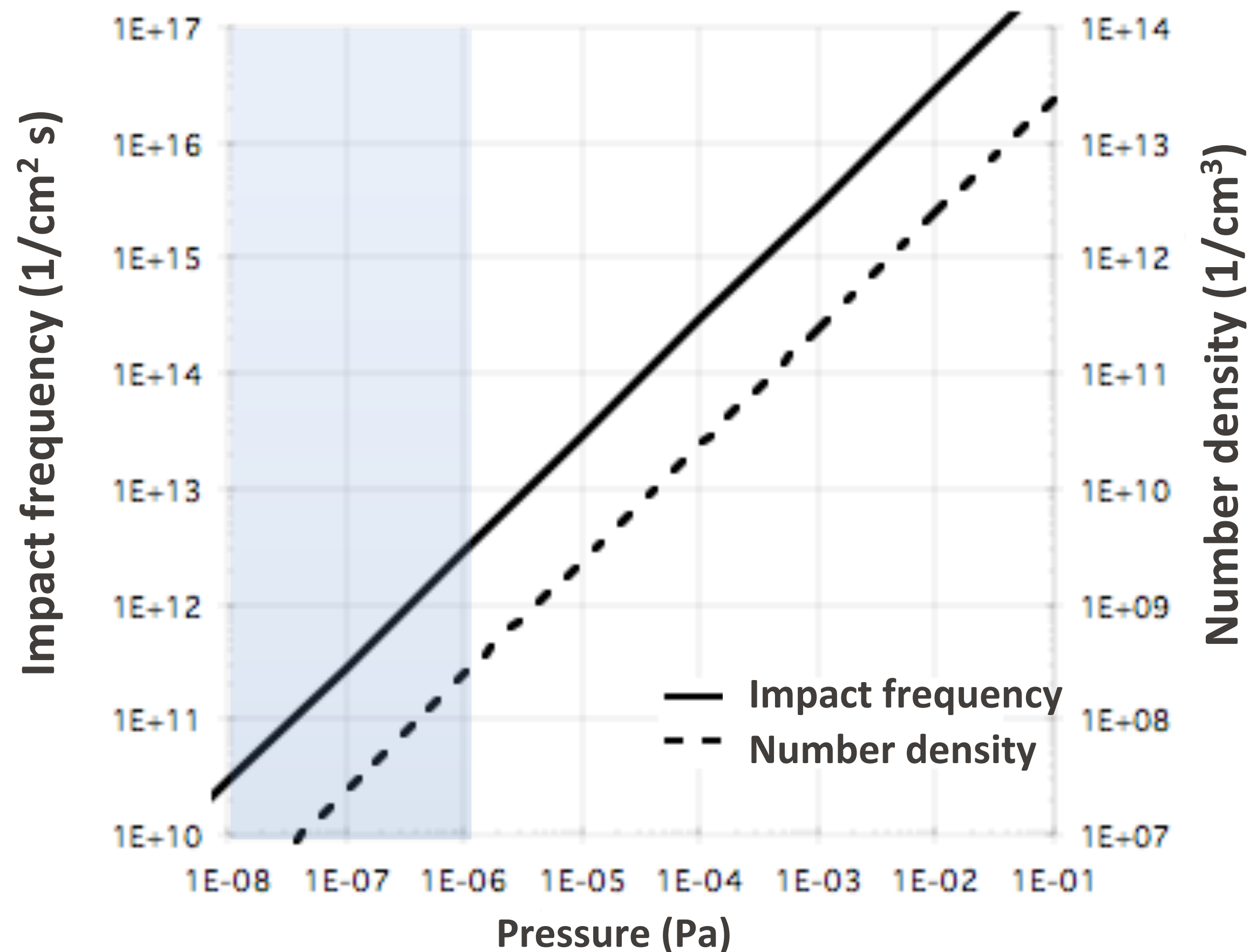
$$\dot{n}_s \approx 2.7 \times 10^{22} \frac{P}{\sqrt{MT}} \text{ cm}^{-2} \text{ s}^{-1}$$

P: pressure
M: molecular weight
T: Temperature

Ultra High Vacuum (UHV) Needed for Ultra Clean Surfaces

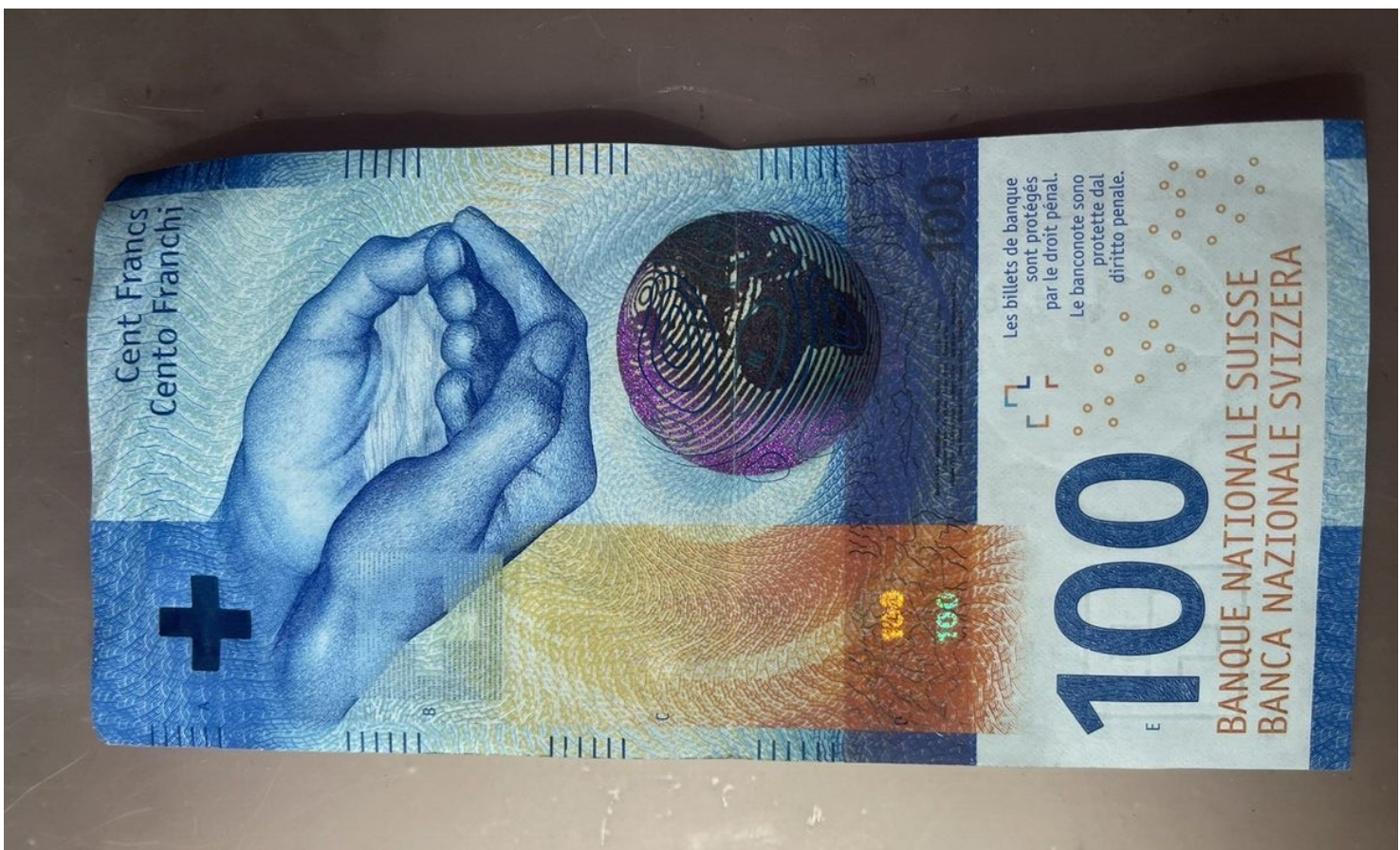
The number of impacts per second per cm² can only be decreased by pressure reduction

UHV



Impact frequency/unit area and number density
as a function of the pressure for an ideal gas

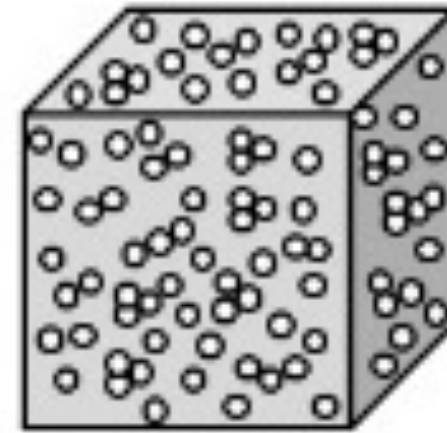
1 Pa is about the pressure exerted by a
CHF 100 note on a table!



1 standard atmosphere = 101,325 Pa

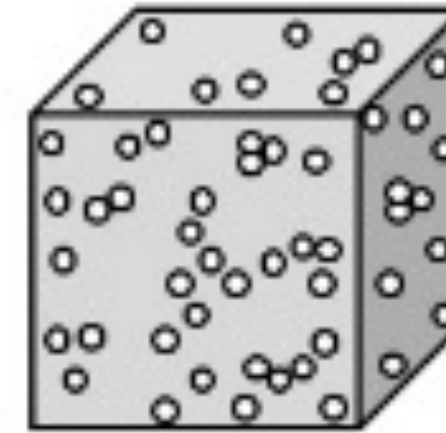
Vacuum Levels Significantly Impacts Monolayer Formation

Rough Vacuum
1 atm – 10^{-3} Torr



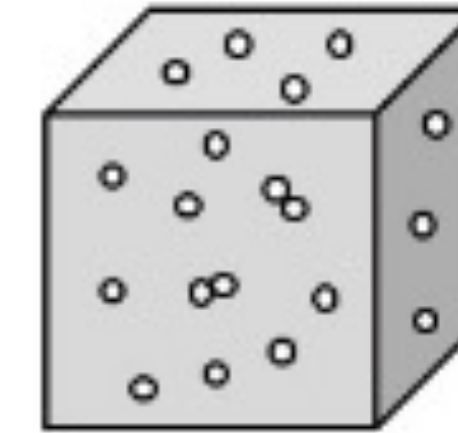
1×10^{-3} Torr
 10^{13} atoms/cm³

High Vacuum
 10^{-3} Torr – 10^{-8} Torr



1×10^{-6} Torr
 10^{10} atoms/cm³

Ultra High Vacuum
 10^{-8} Torr – 10^{-12} Torr

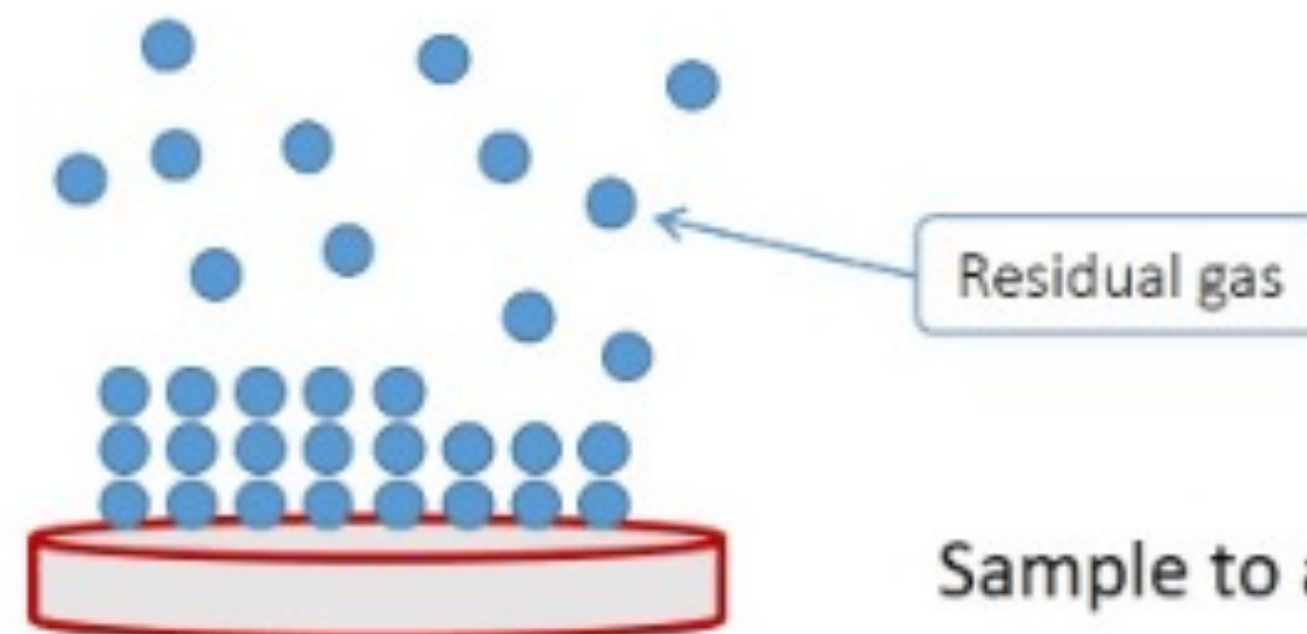


1×10^{-11} Torr
 10^5 atoms/cm³

1 residual gas monolayer
every 4 SECONDS

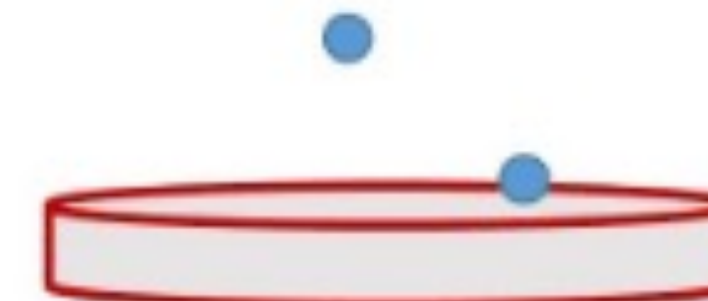
1 residual gas monolayer
every 4 DAYS

High Vacuum



Sample to analyze

UHV



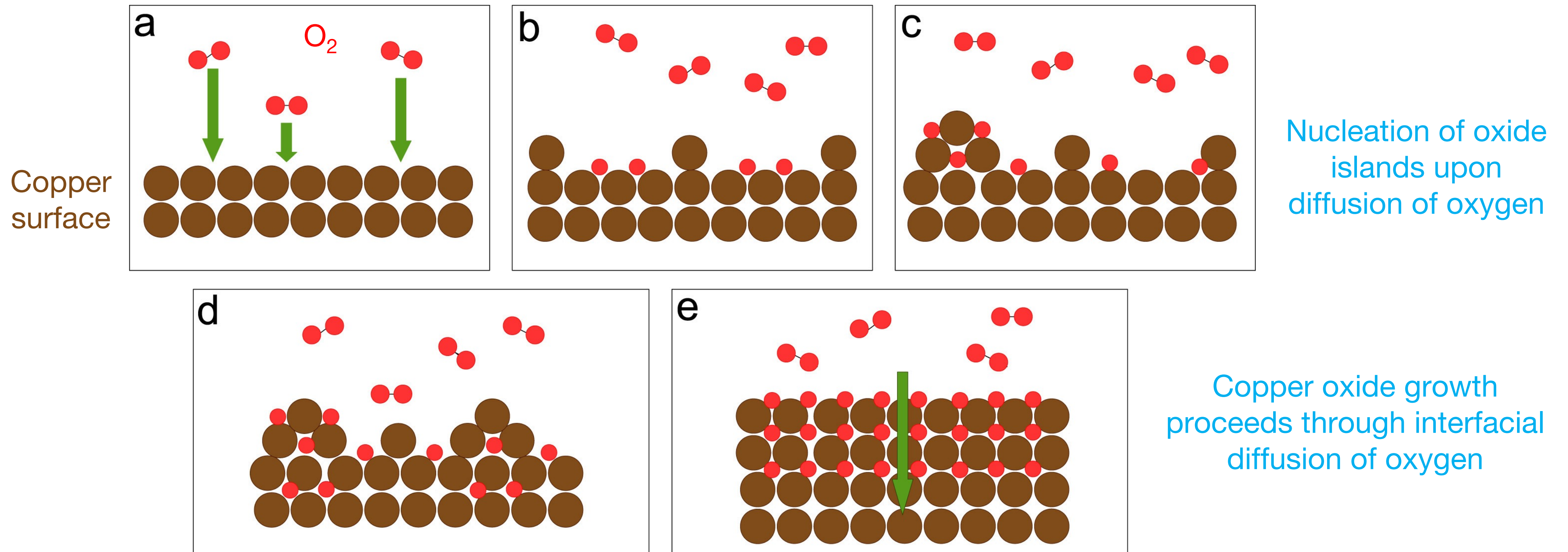
VAC COAT

CHEM\$NA

So How Clean Are Surfaces? (They're Not!)

Surfaces in air are mostly covered with multilayers of molecules from the gas phase
(H₂O, hydrocarbons, air components)

Metals (except Au) are mostly oxidized
(*i.e.* the surface atoms are in a different oxidation state from most of the bulk atoms)



Gattinoni & Michaelides, *Surf. Sci. Rep.* 70:424-447, 2015

Oxidation of Surfaces Leads to Corrosion

Surfaces in air are mostly covered with multilayers of molecules from the gas phase (H_2O , hydrocarbons, air components)

Metals (except Au) are mostly oxidized
(*i.e.* the surface atoms are in a different oxidation state from most of the bulk atoms)

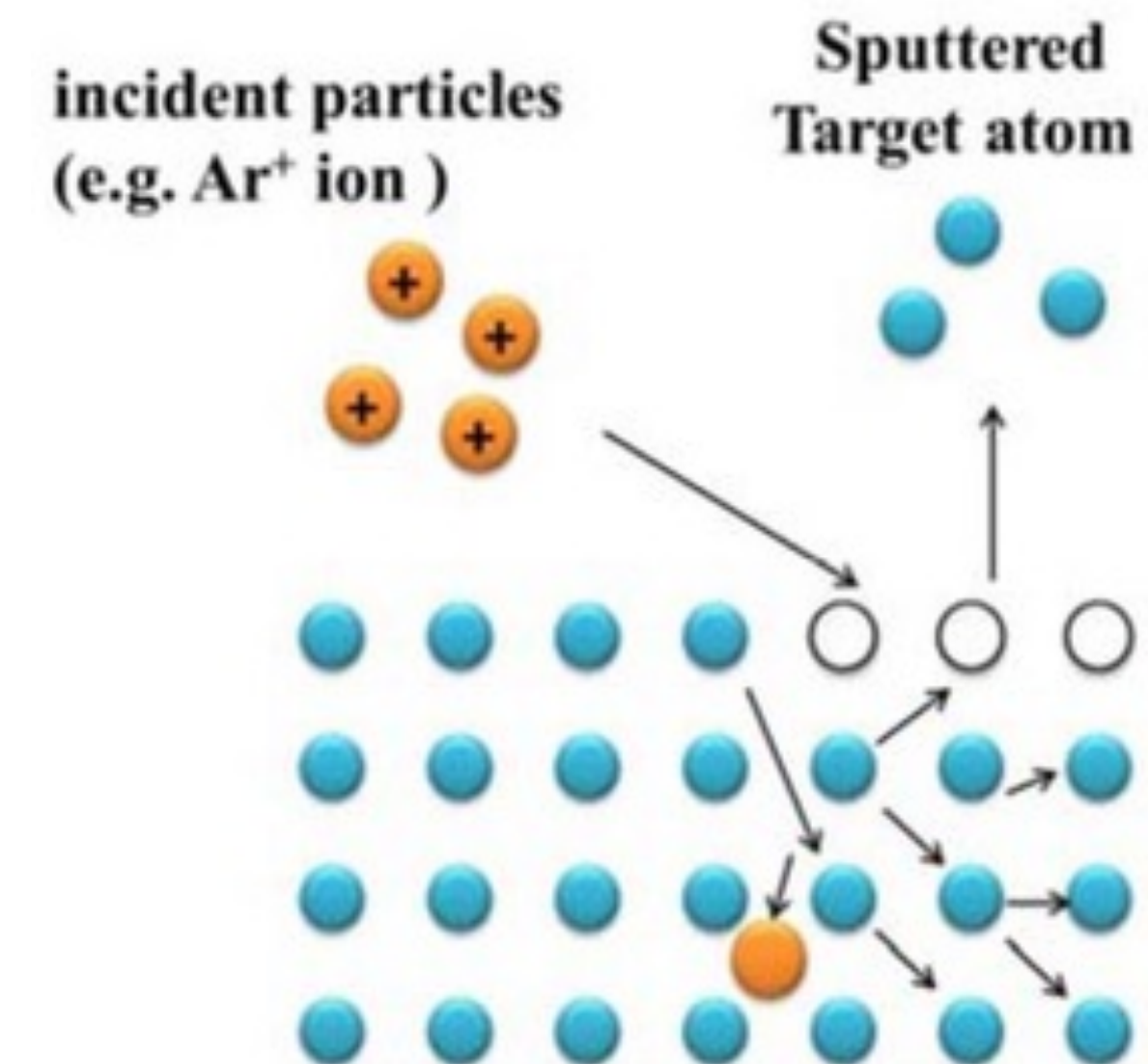


Contact with water or oxygen in the presence of an electrolyte (salt or sulfuric acid)



How Can we Obtain Clean Surfaces?

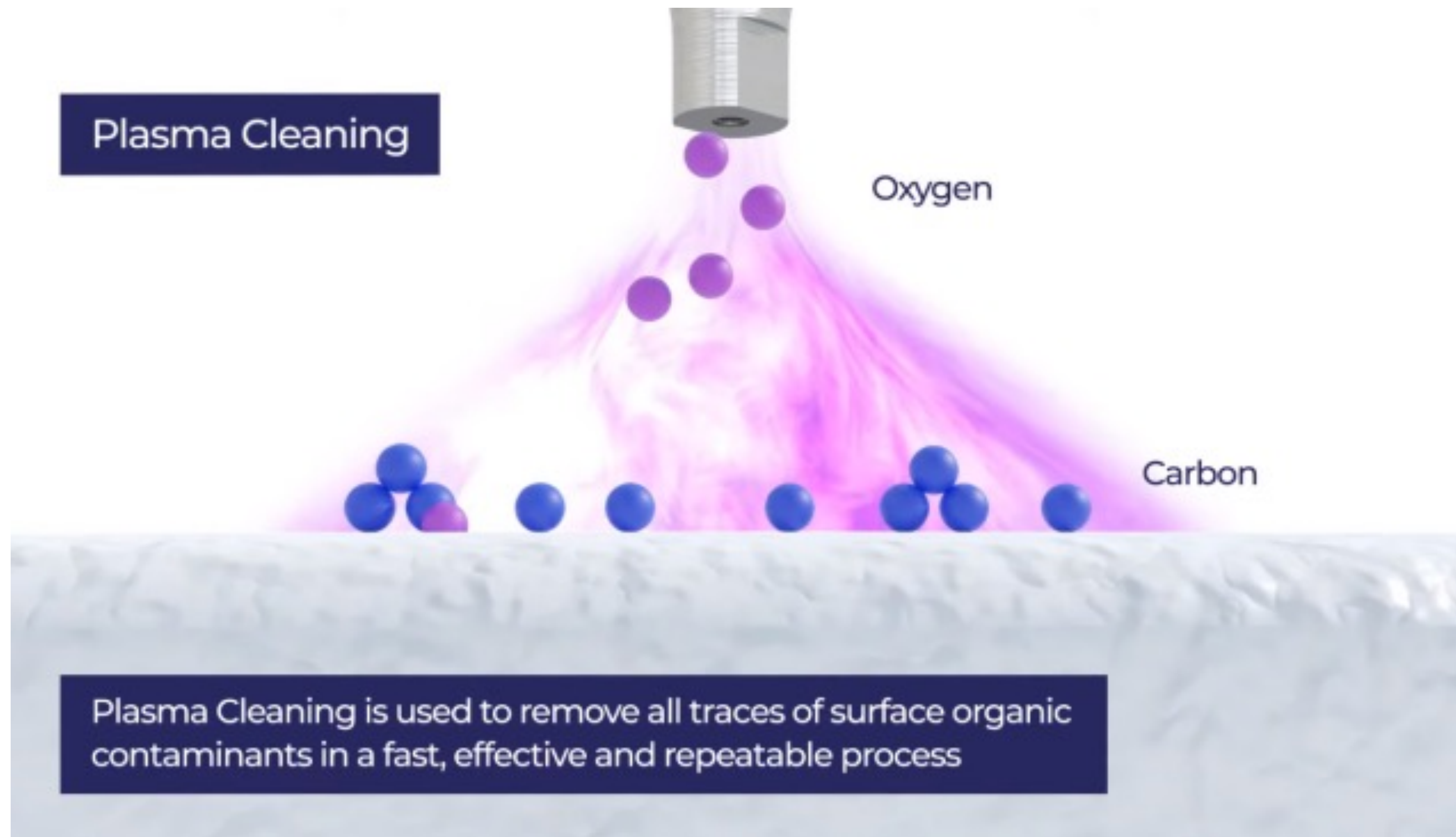
1) **Heating:** suitable for samples covered by an oxide layer, which are not stable at high temperatures (*e.g.*, flame annealing of substrates)



2) **Argon sputtering:** removing the top layer of a sample by sputtering with Ar ions, with subsequent heating to remove surface defects

How Can we Obtain Clean Surfaces?

3) Plasma cleaning to remove surface contaminants



Plasma is generated by applying an electric field to a gas in a vacuum chamber

Oxygen radicals interact with carbon-based (organic) contaminants, breaking down into volatile compounds such as CO_2 and H_2O

Reaction products often in gas form are carried away by vacuum system

4) Fracture of a material: possible to obtain pure and very smooth surfaces (mica)

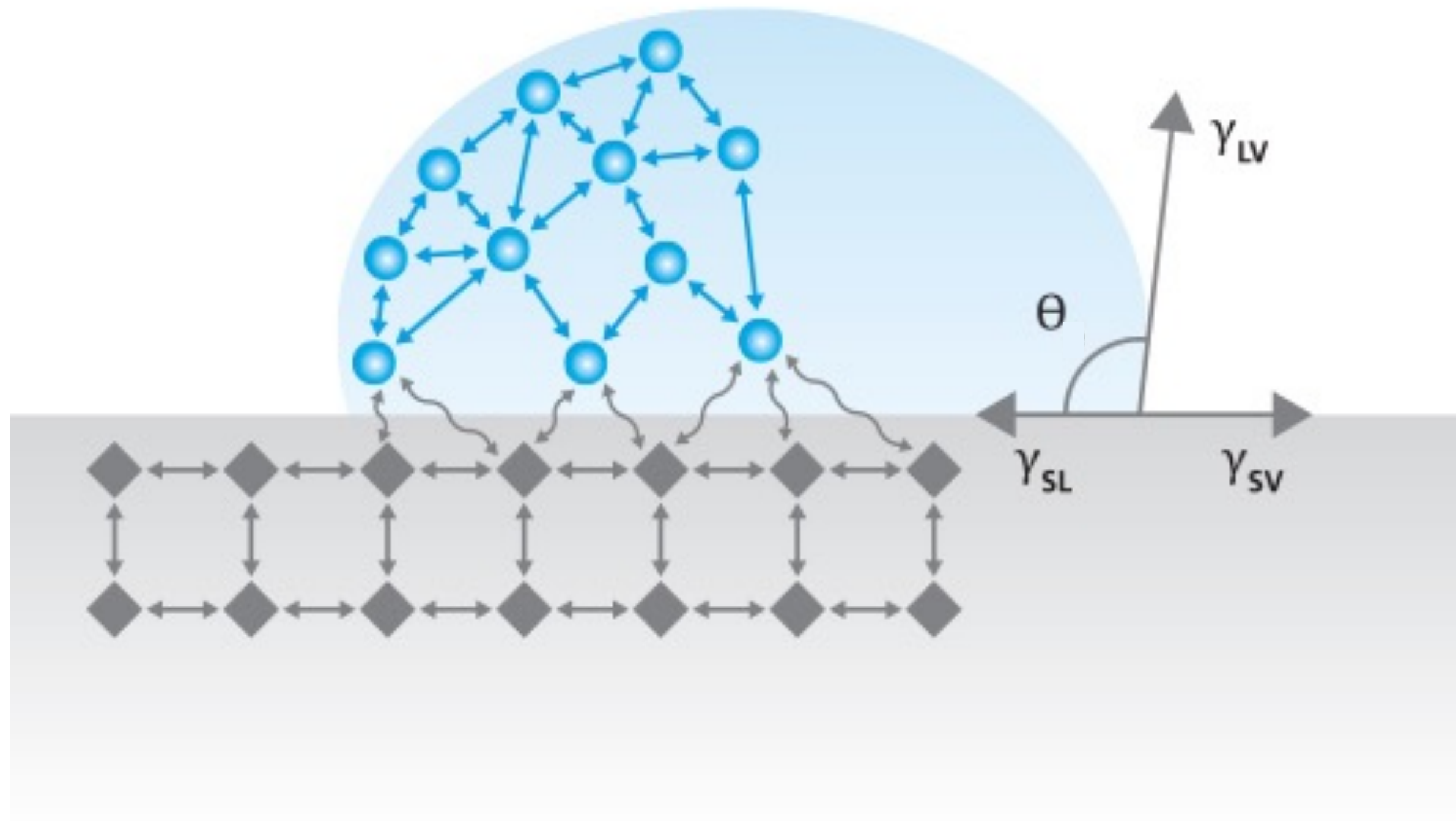
How Can We Check the Cleanliness of a Surface?

Contact angle (θ): quantifies the wetting of a solid by a liquid. Angle formed by a liquid at the three-phase boundary point where the liquid, gas, and solid intersect (thermodynamic equilibrium)

Young Equation

$$\gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta = 0$$

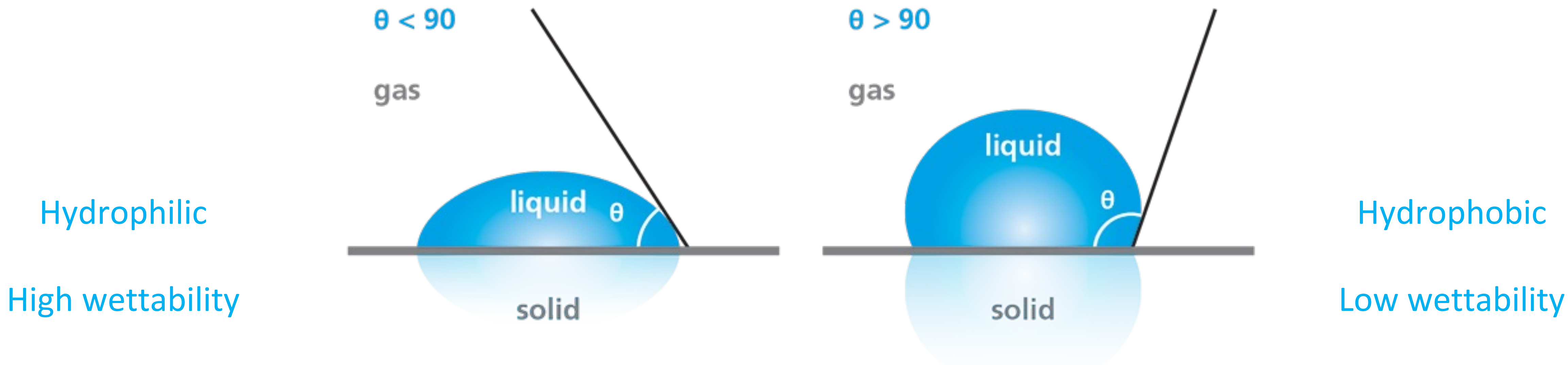
Relating interfacial energies with contact angle



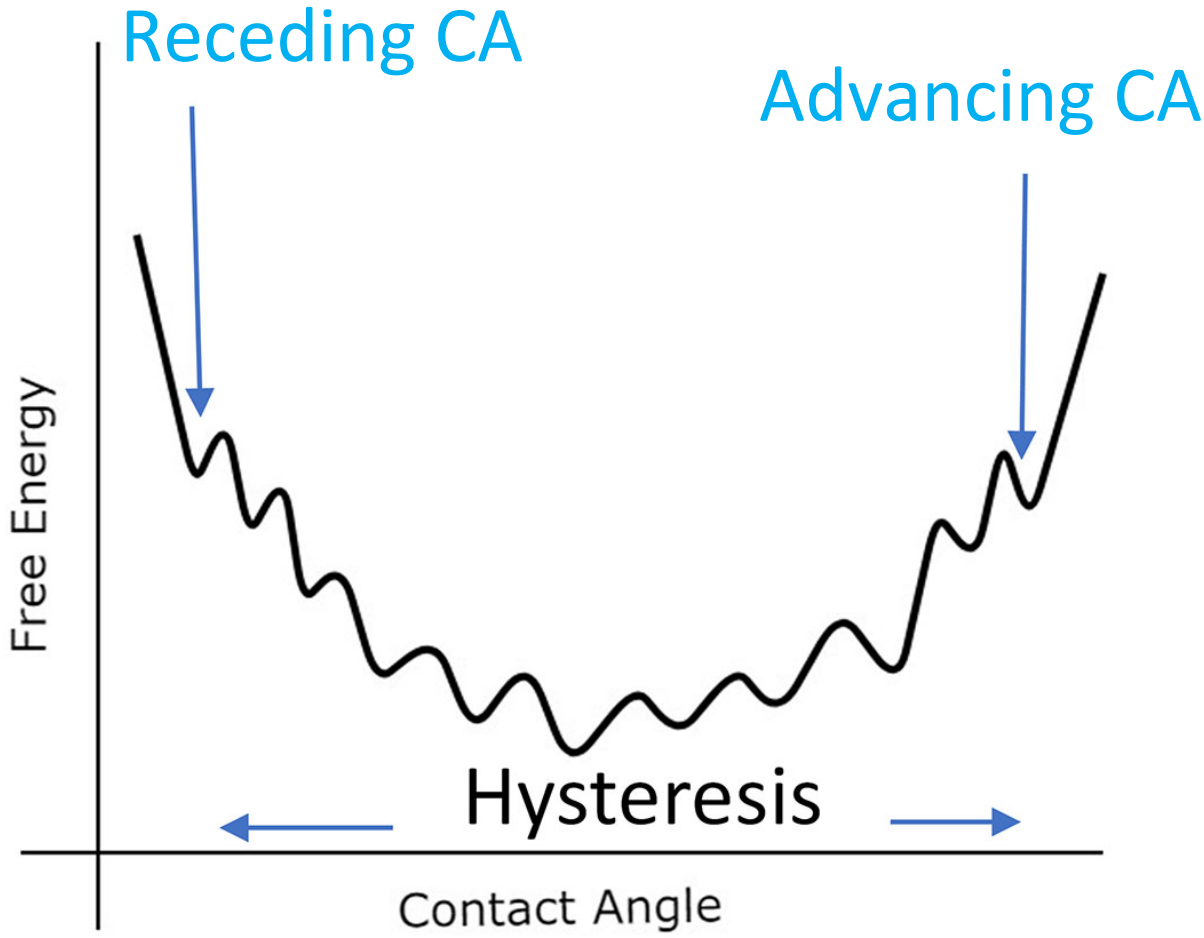
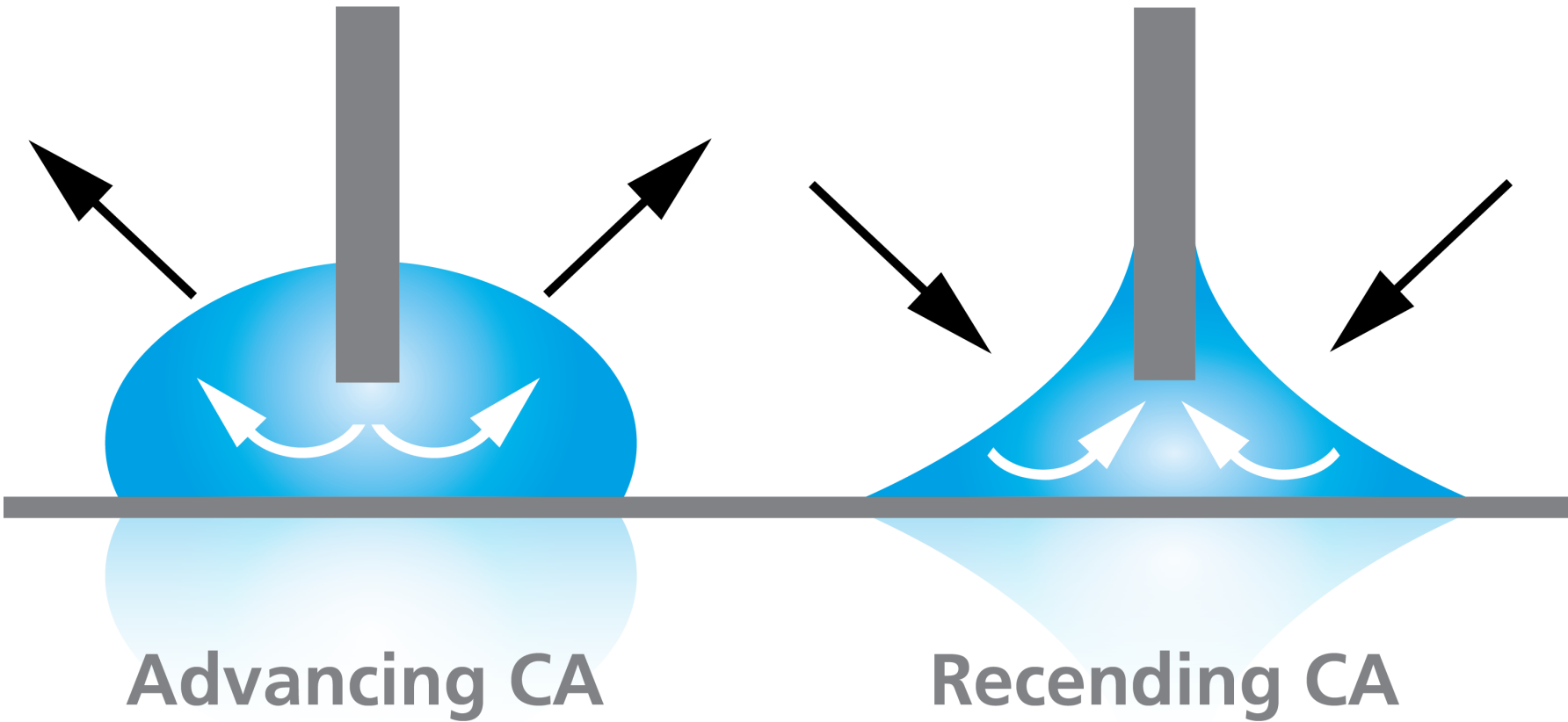
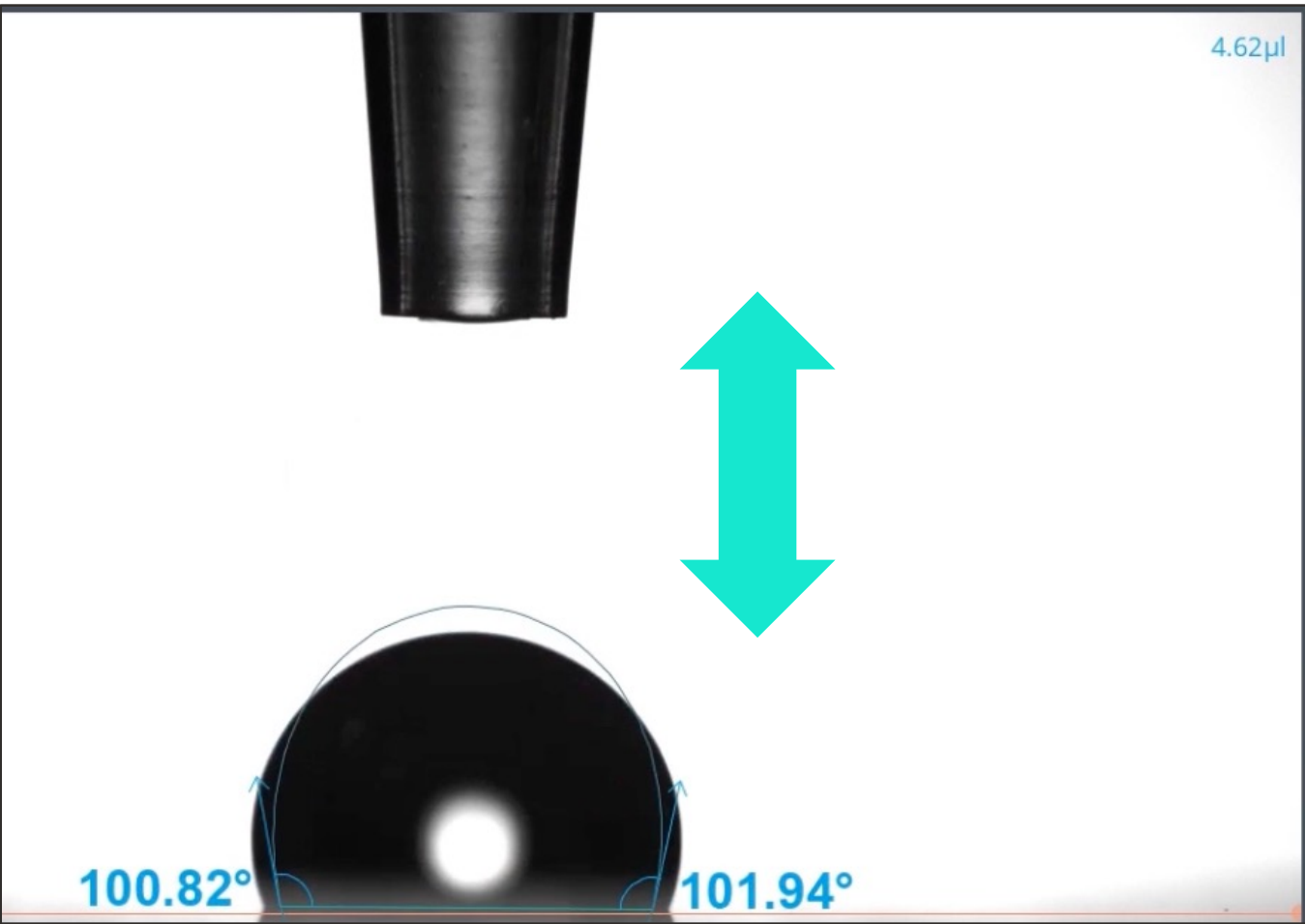
Ideal surface assumptions:

- Smooth
- Rigid
- Chemically homogeneous
- Insoluble
- Non-reactive

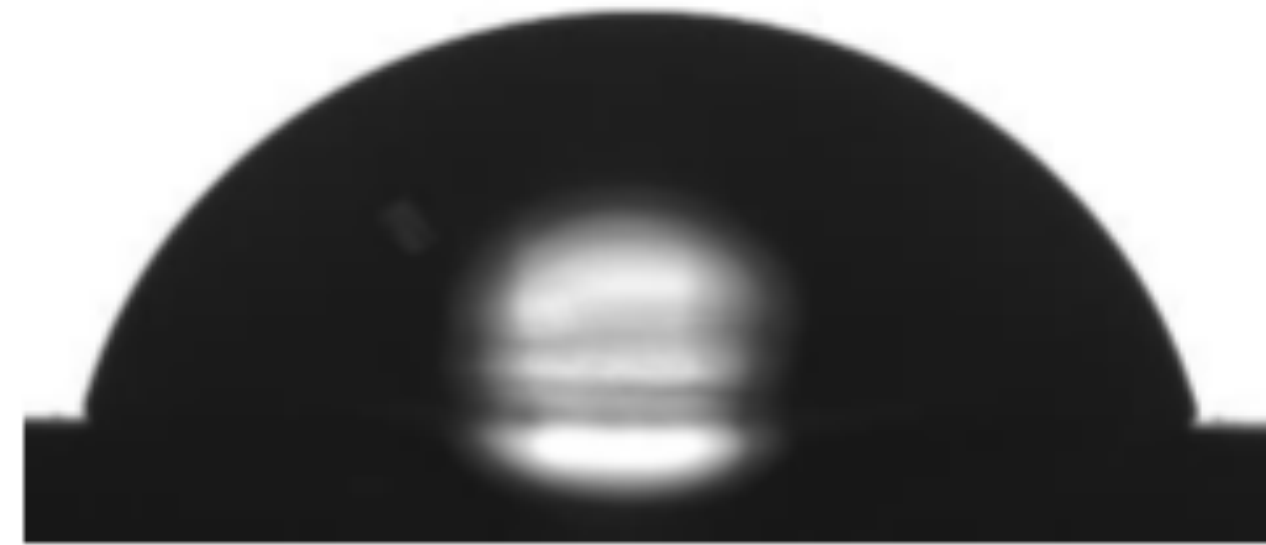
Wettability – Tendency of Liquids to Spread Across Surface



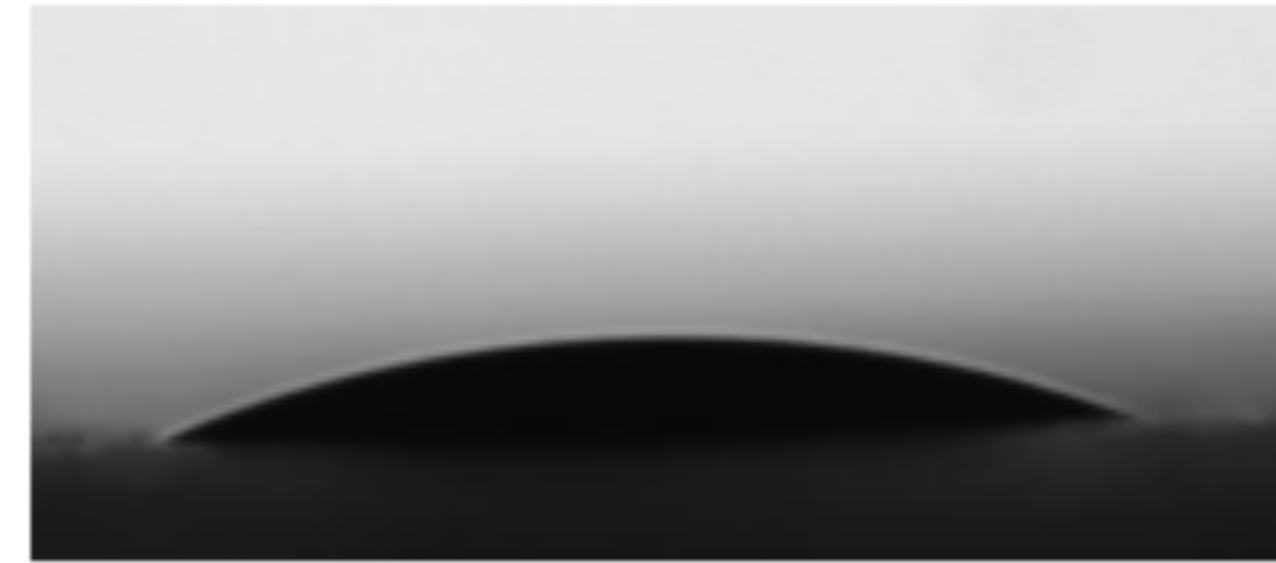
Static Contact Angle / Sessile Drop measured by an Optical Tensiometer



Contact Angle on Glass Surface Higher with Contamination



Before cleaning



After cleaning

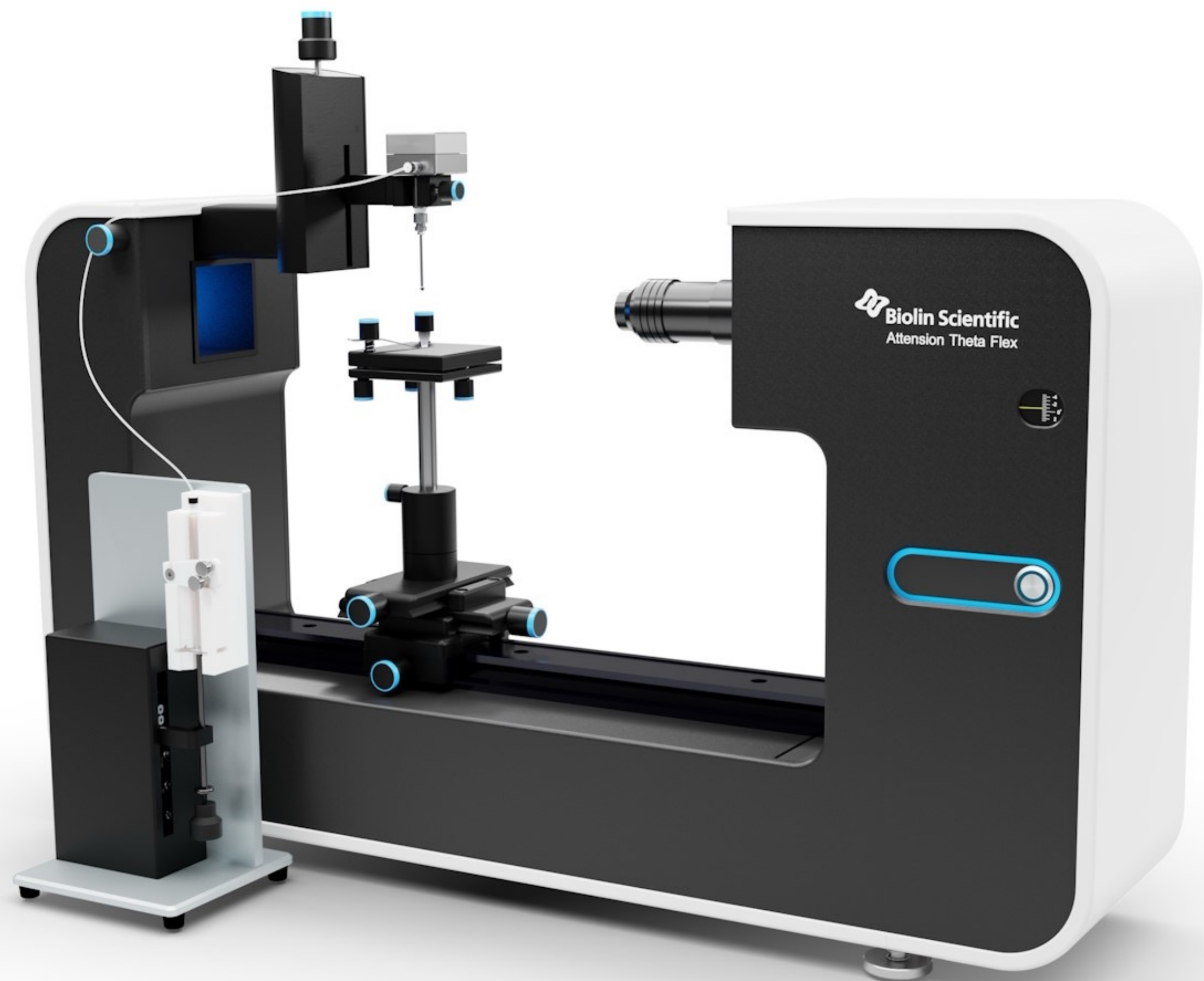
If a metal surface were perfectly clean, the contact angle would approach 0 degrees, indicating a surface that is completely wettable.

Let's see if this is the case?

Contact angle advantages: Quick, non-destructive

Contact angle limitations: Limited information

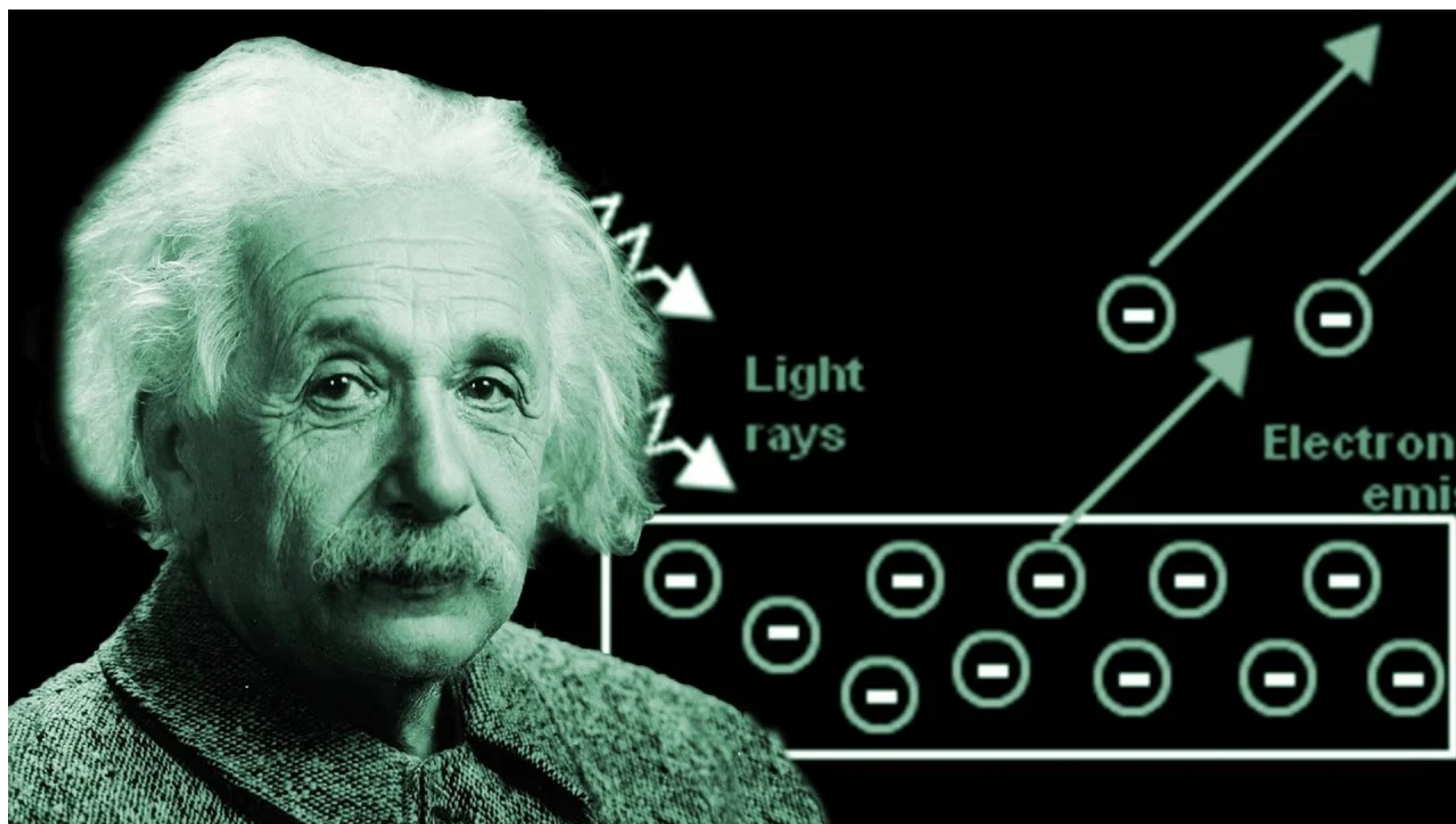
Contact Angle Instruments



Electron Spectroscopy to Monitor Surface Species

X-ray Photoelectron Spectroscopy (XPS)

Photoelectric Effect



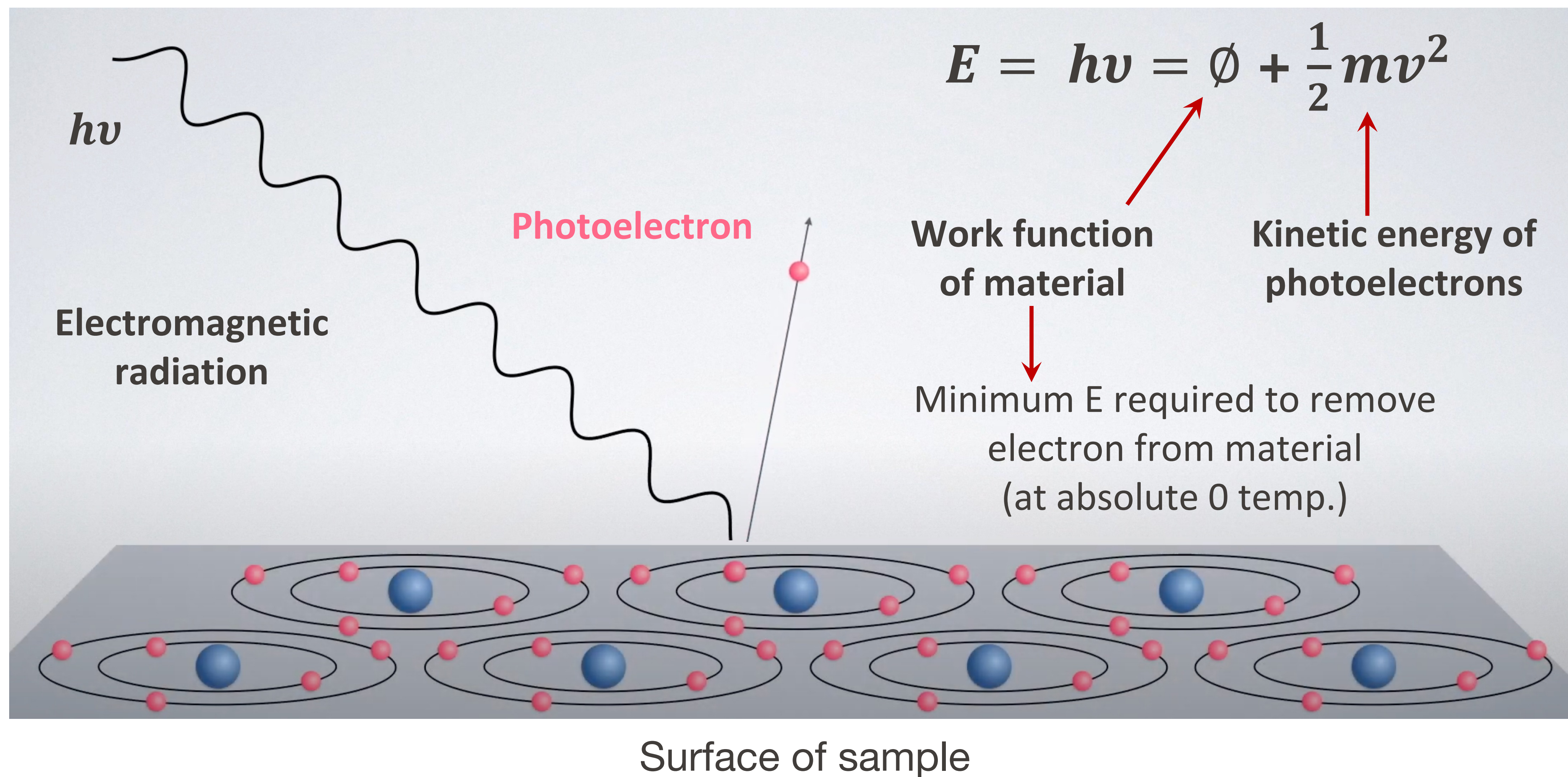
Albert Einstein



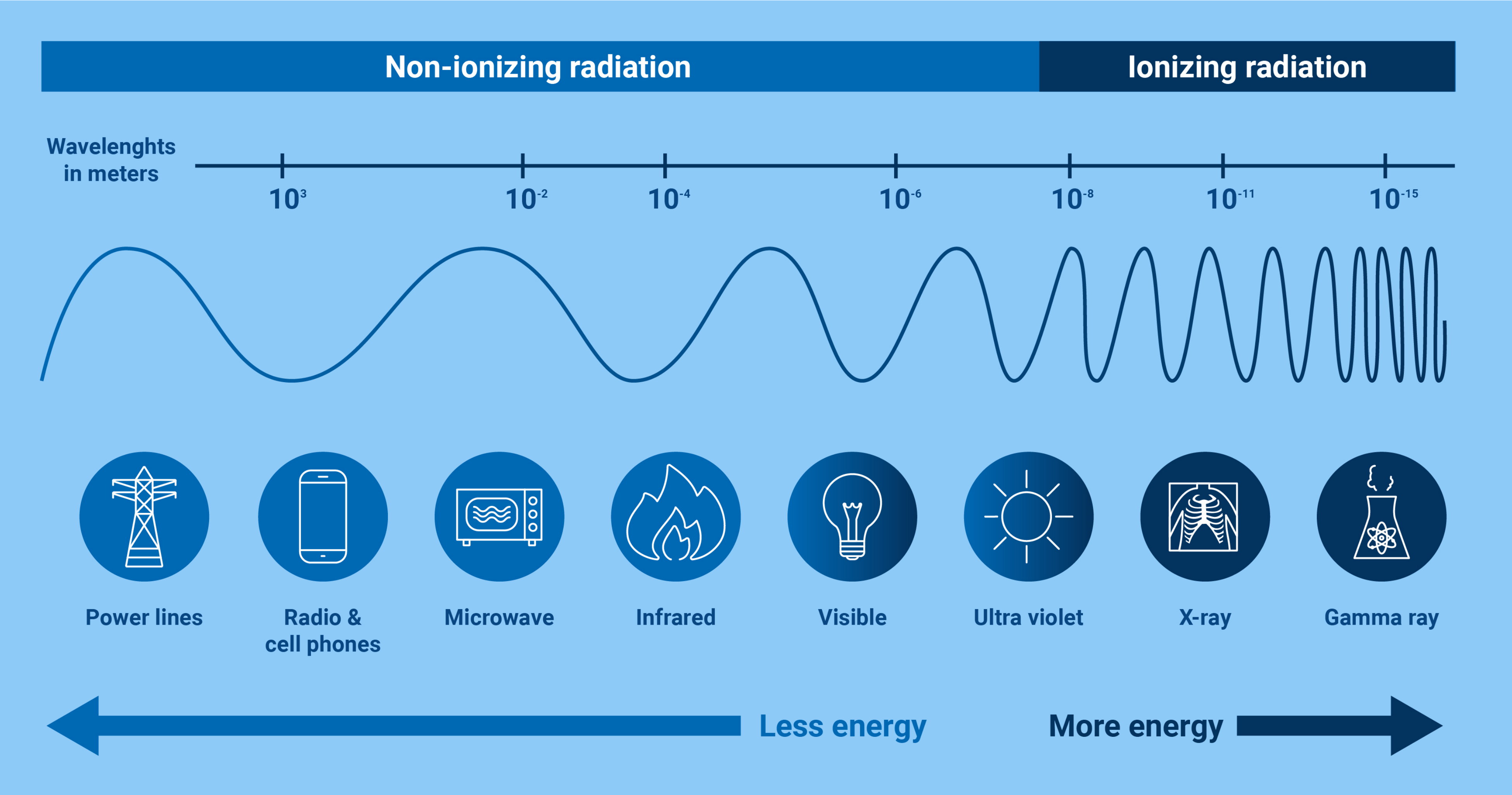
Nobel Prize in Physics for his discovery of the Photoelectric Effect (1921)

Electron Spectroscopy to Monitor Surface Species

X-ray Photoelectron Spectroscopy (XPS)

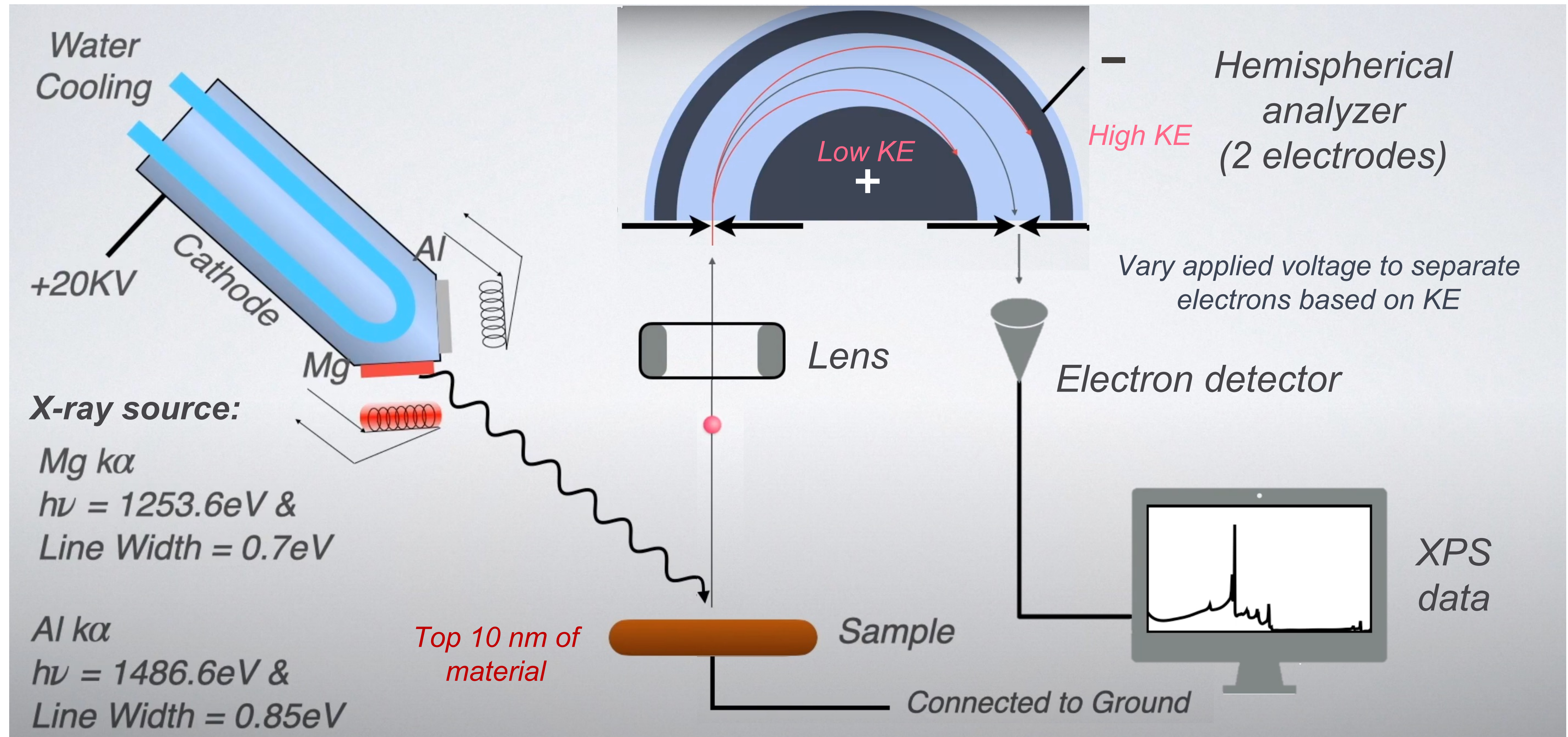


Electromagnetic Radiation – Ionizing Radiation for XPS



Valence electrons : UV light
Core electrons: X-rays

How Does XPS Analyze Surface Elements?



**Counteract sample charging*

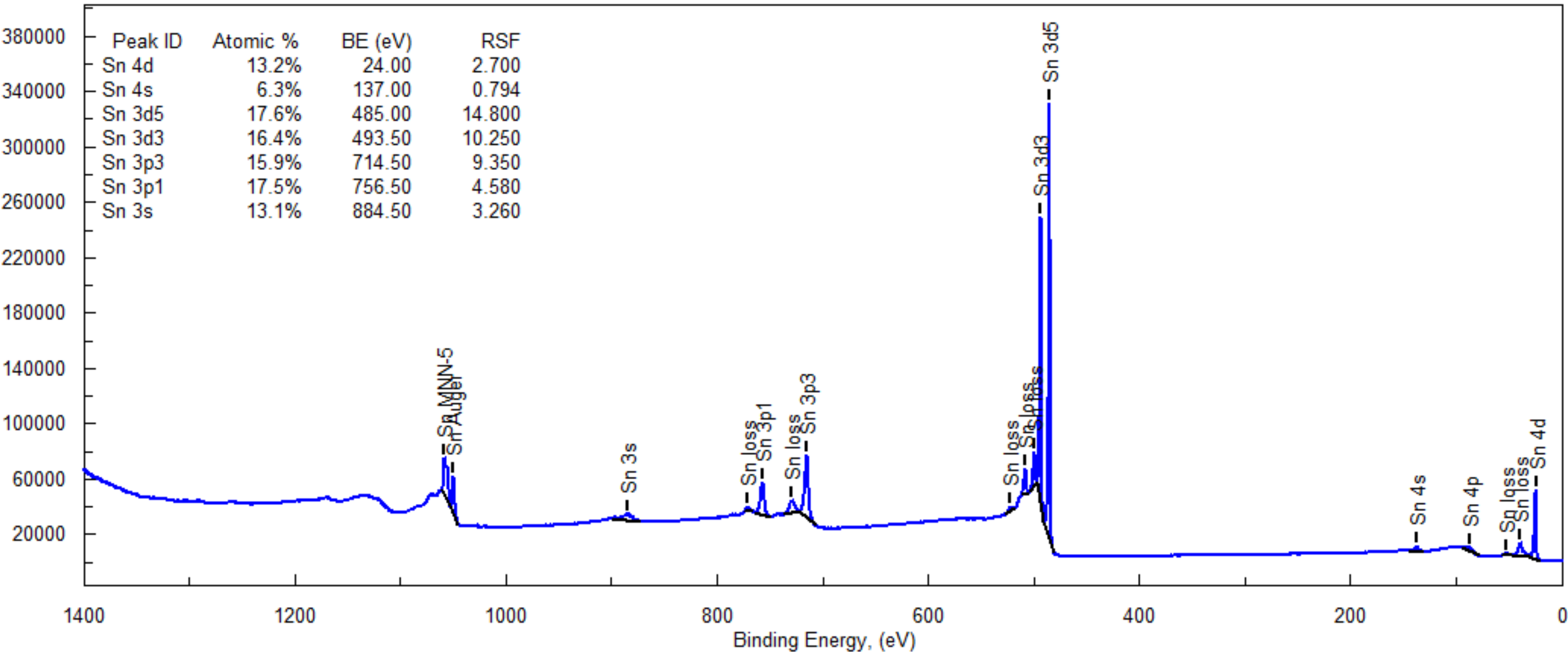
Binding Energy (eV) vs. Number of Electrons Counted

Kinetic energy of ejected electrons is related to the binding energy of the electron in the atom, which is unique to each element

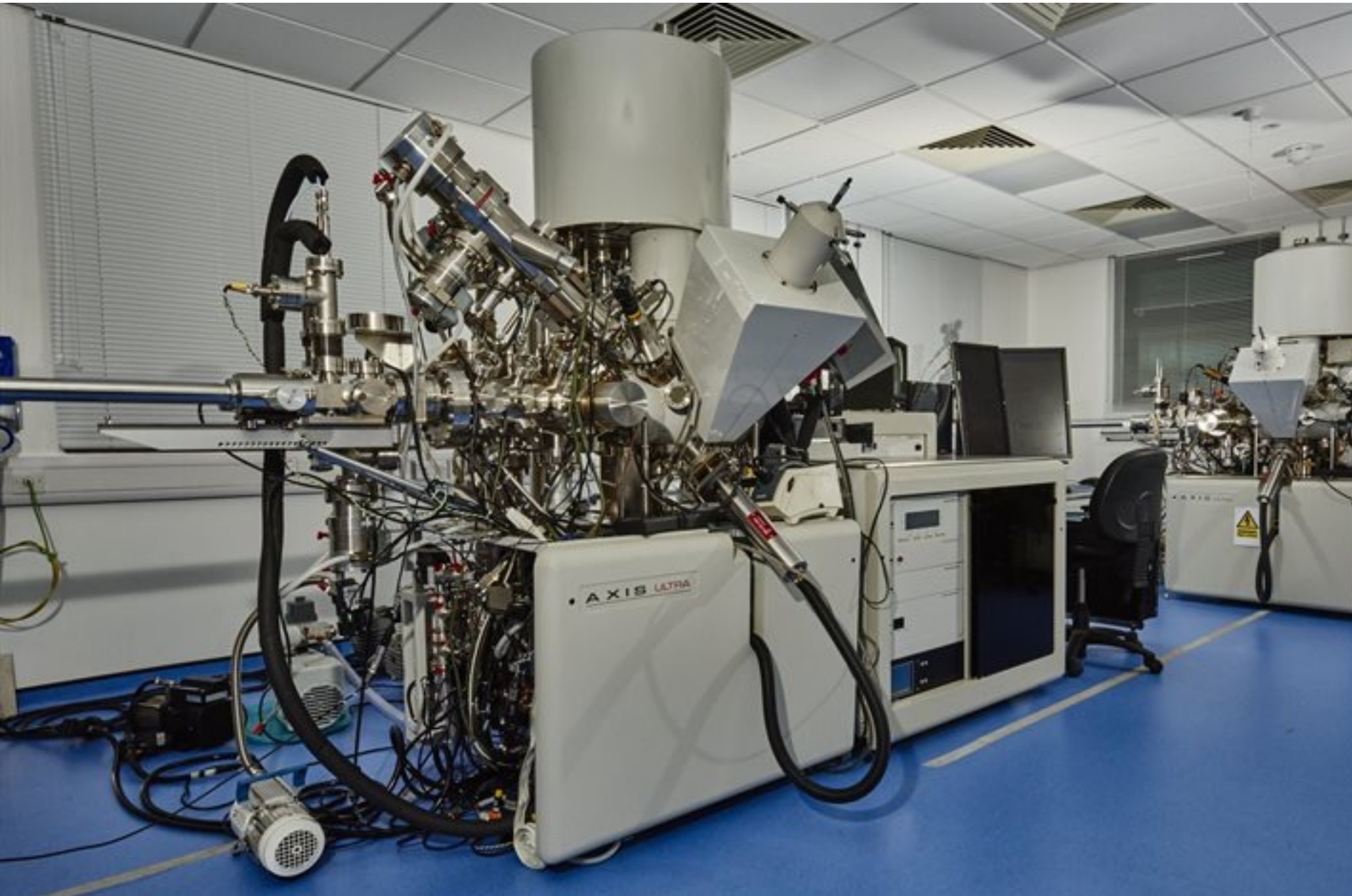
$$E = h\nu = \phi + \frac{1}{2}mv^2$$

Sample Description: Sn, tin

Counts



XPS Instrument

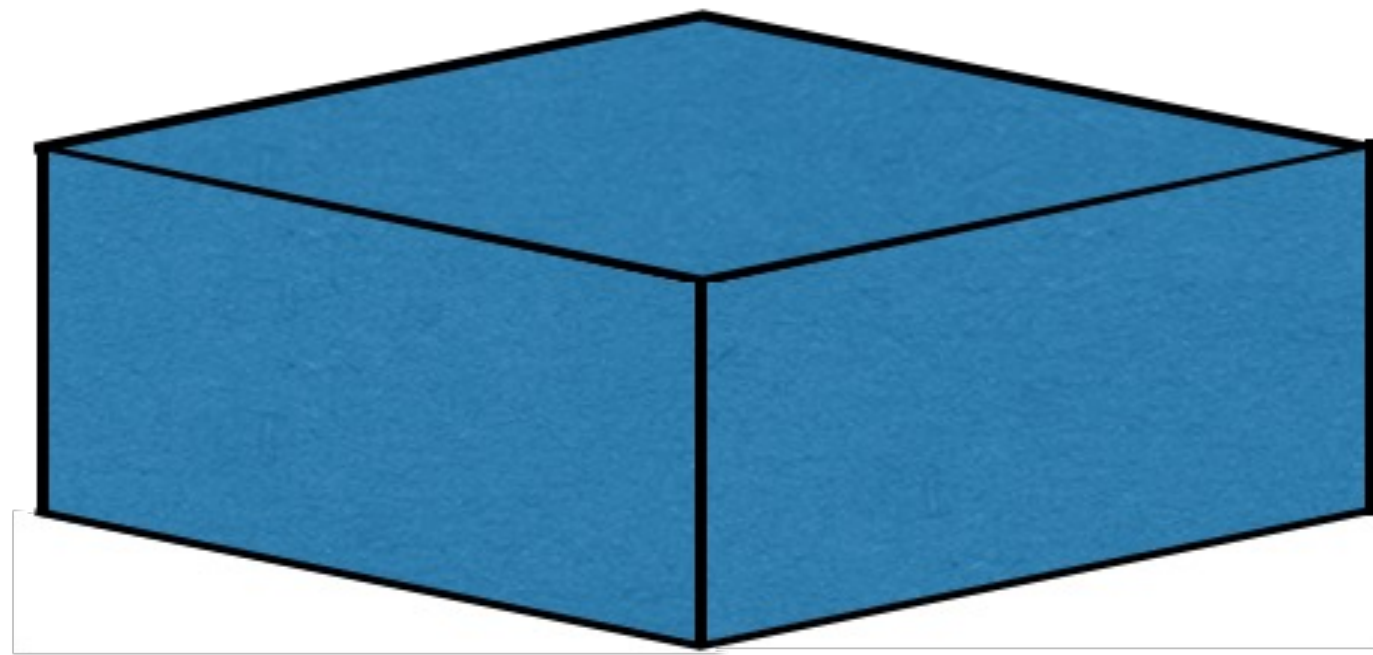


XPS advantages: Quantitative analysis – elemental composition

XPS limitations: Requires UHV (complicates sample handling), expensive

Surface Chemistry – Why Functionalize Surfaces?

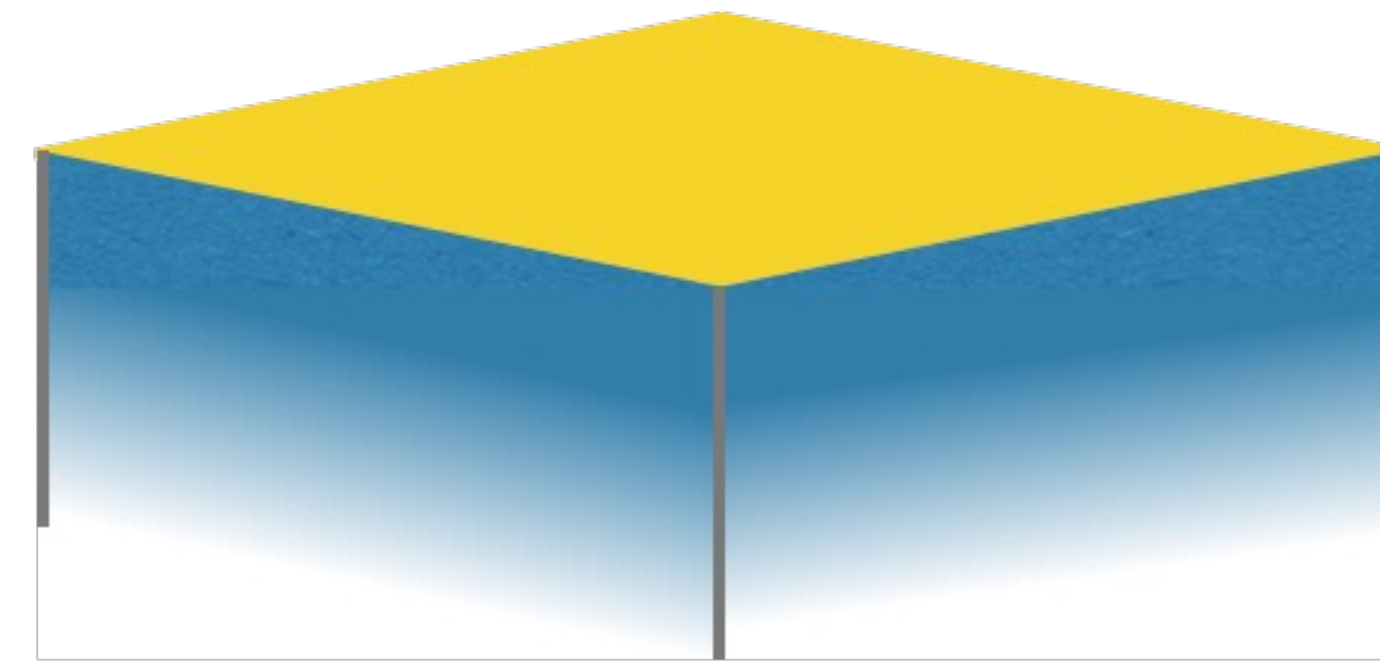
The goal is to combine ideal bulk properties with ideal surface properties



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

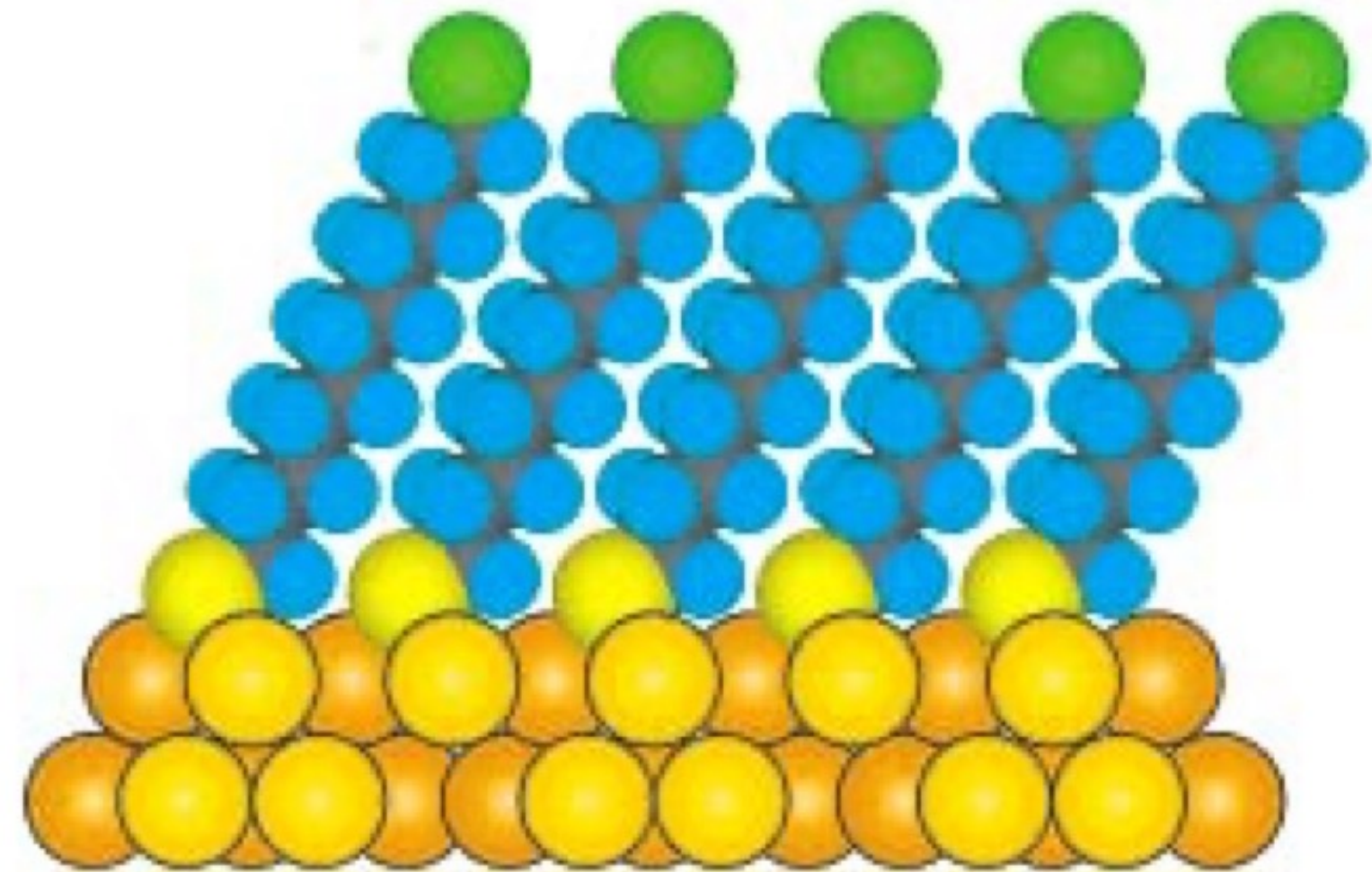
Wettability
Biocompatibility
Corrosion resistance
Roughness
Lubricity/ease-of-cleaning
Catalytic activity

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.*



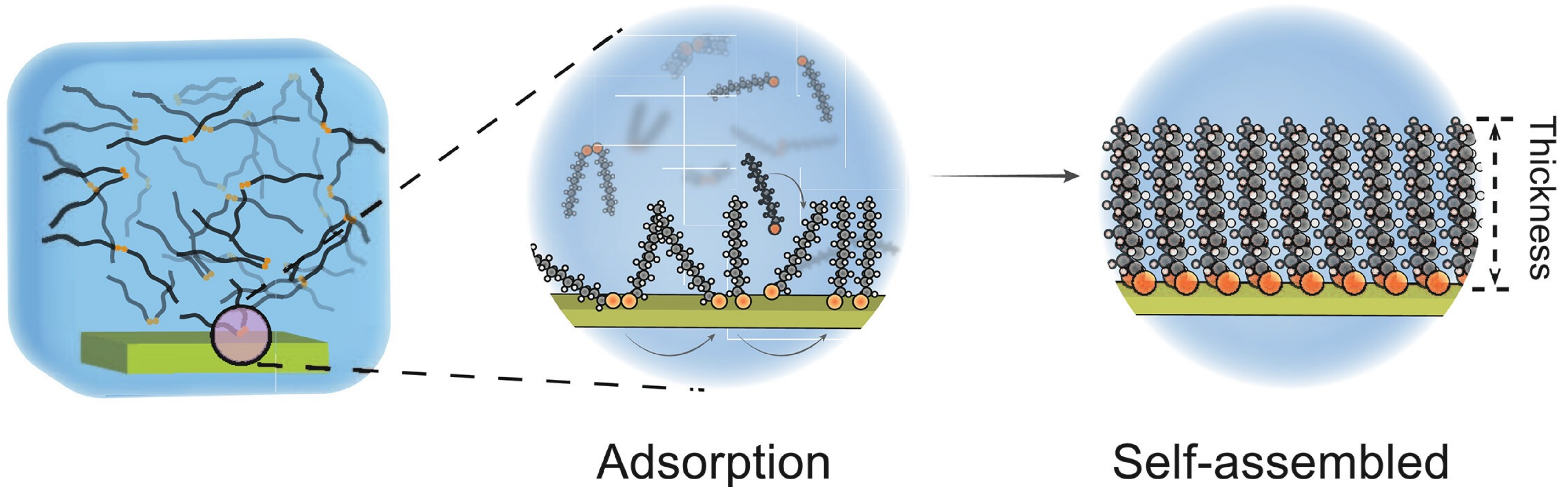
Functional group: mainly determines surface properties

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

Self-Assembled Monolayers Form by Themselves



Source: Chen *et al.*, *Sci. Adv.*, 9, 42, 2023

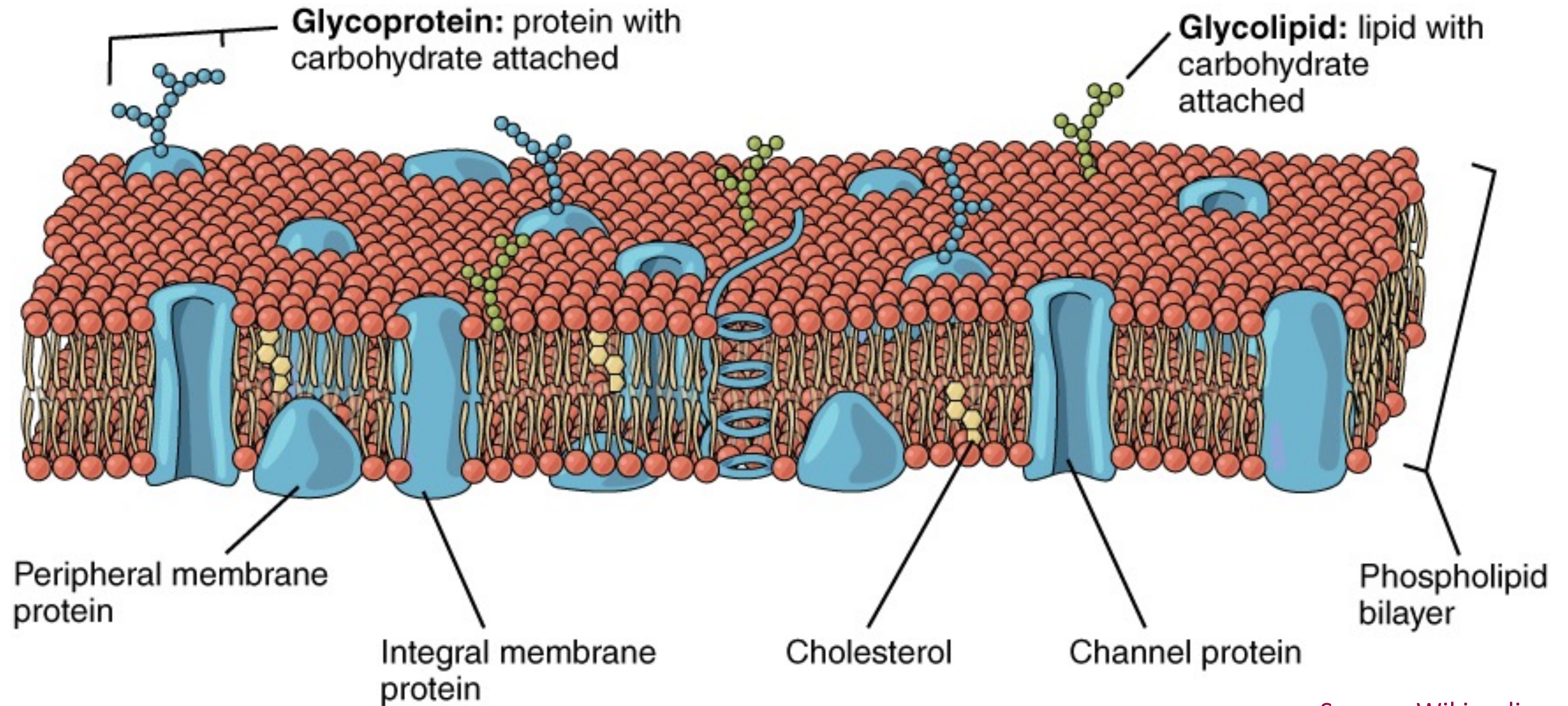
Technically simple “dip and rinse” process

No external driving force needed

Large choice of anchor groups, substrates, and functional groups

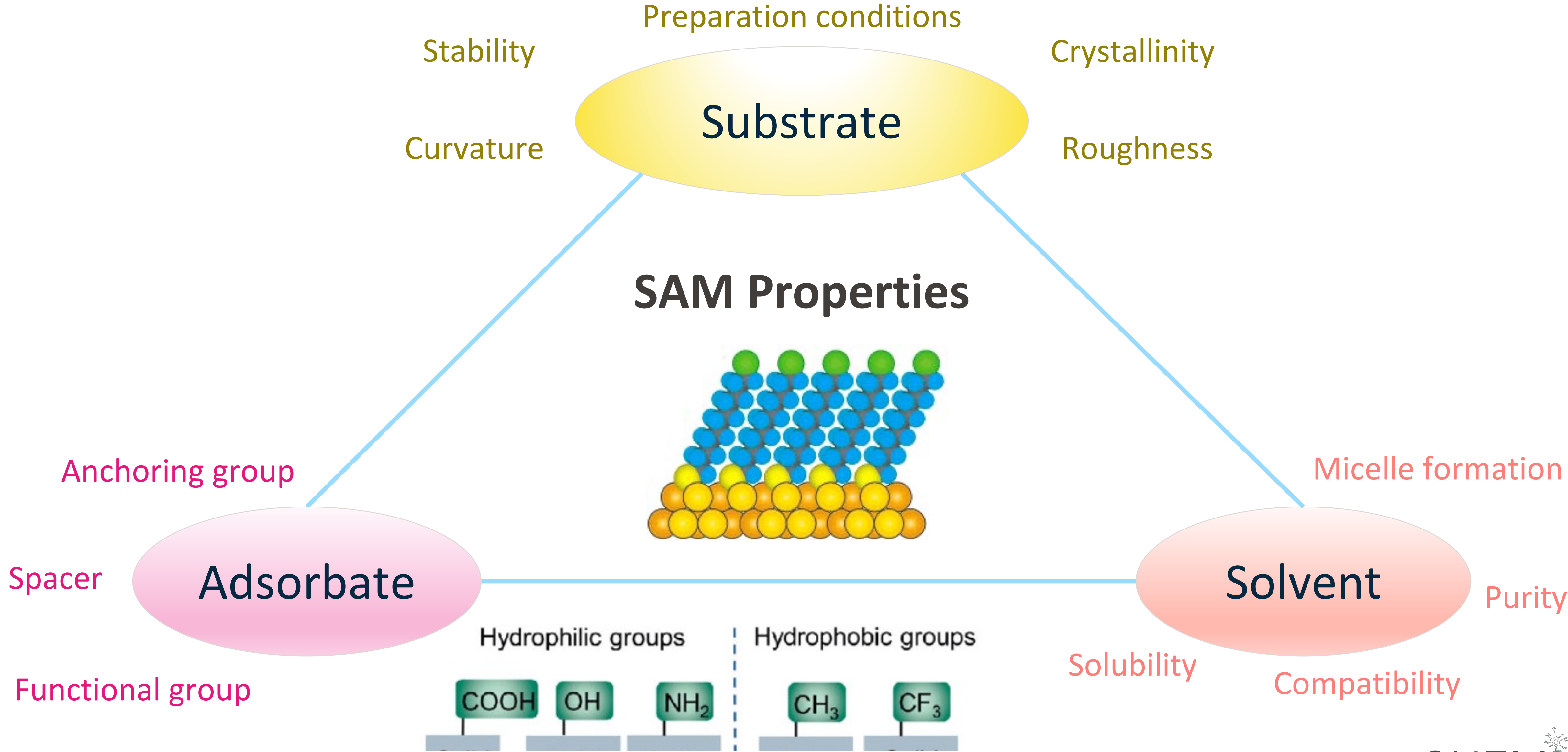
Easily modified and patterned

Example of Spontaneous Self-Assembly in Nature



Source: Wikipedia

Factors Governing Self Assembly

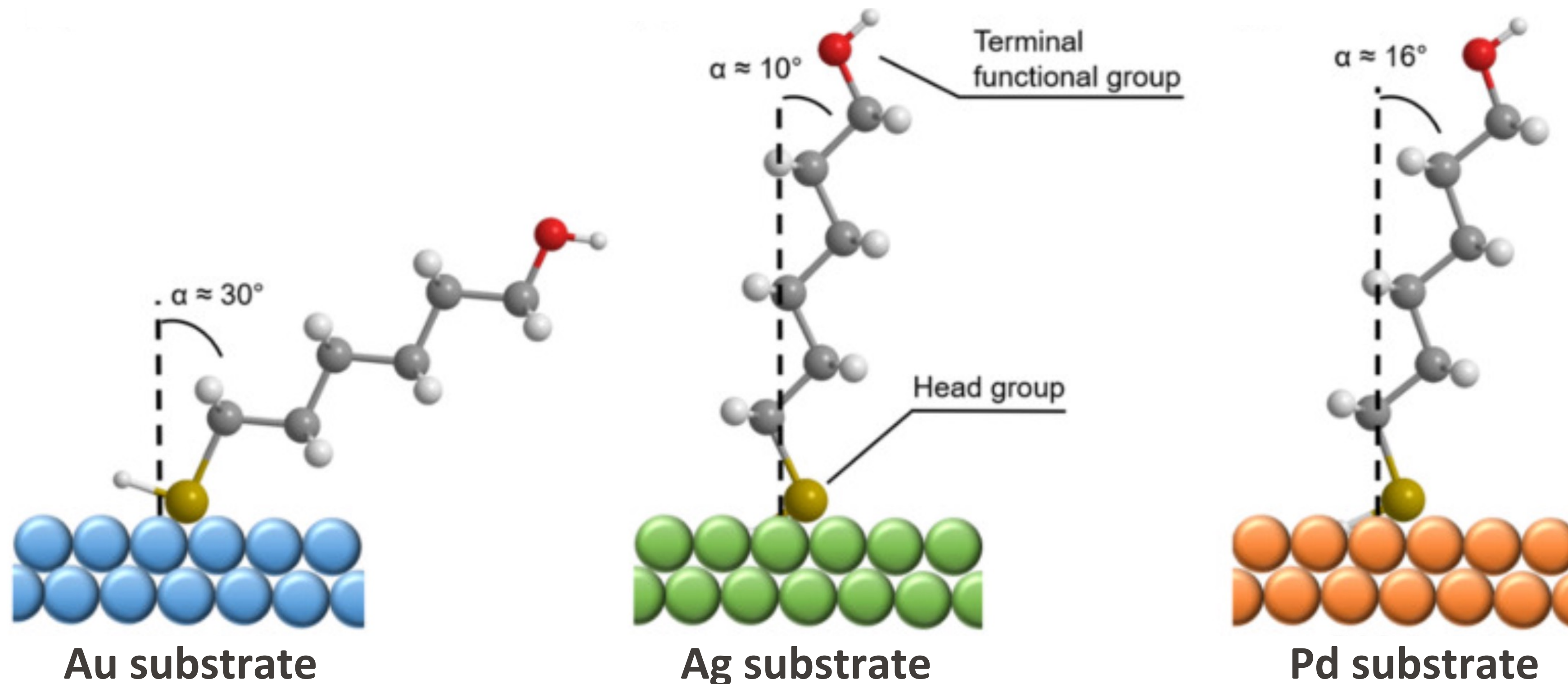


Overview of Surface Binding Chemistries

Adsorbate	Substrate
<u>Thiols:</u> R-SH	Au, Ag, Cu, Pt, Pd, Ru, Hg, AuAg, AuCu, Ni, Ir, Zn, ZnSe, CdSe, CdS, CdTe, Ge
<u>Disulfides:</u> R-S-S-R'	Au, Ag, Pd
<u>Silanes:</u> R-SiCl ₃ , R-Si(OR') ₃ R-Si(CH ₃) ₂ Cl	SiO₂, TiO ₂ , Au
<u>Phosph(on)ates:</u> R-PO ₄ H ₂ R-PO ₃ H ₂	Al₂O₃, TiO ₂ , Nb ₂ O ₅ , Ta ₂ O ₃ , ZrO ₂

Adsorbate	Substrate
<u>Ammonium :</u> R-NH ₃ ⁺ R-N(CH ₃) ₃ ⁺ R ₂ -N(CH ₃) ₂ ⁺	Mica
<u>Carboxylic acid:</u> R-COO-/R-COOH	Al₂O₃, Ni, Ag, Ti/TiO ₂
<u>Alkyne:</u> R-C≡CH	Si(111):H
<u>Alcohols:</u> R-OH	Si:H

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

Intrinsic and Extrinsic Defects Found in Polycrystalline SAMS

Chem. Rev. 2005, 105, 1103–1169

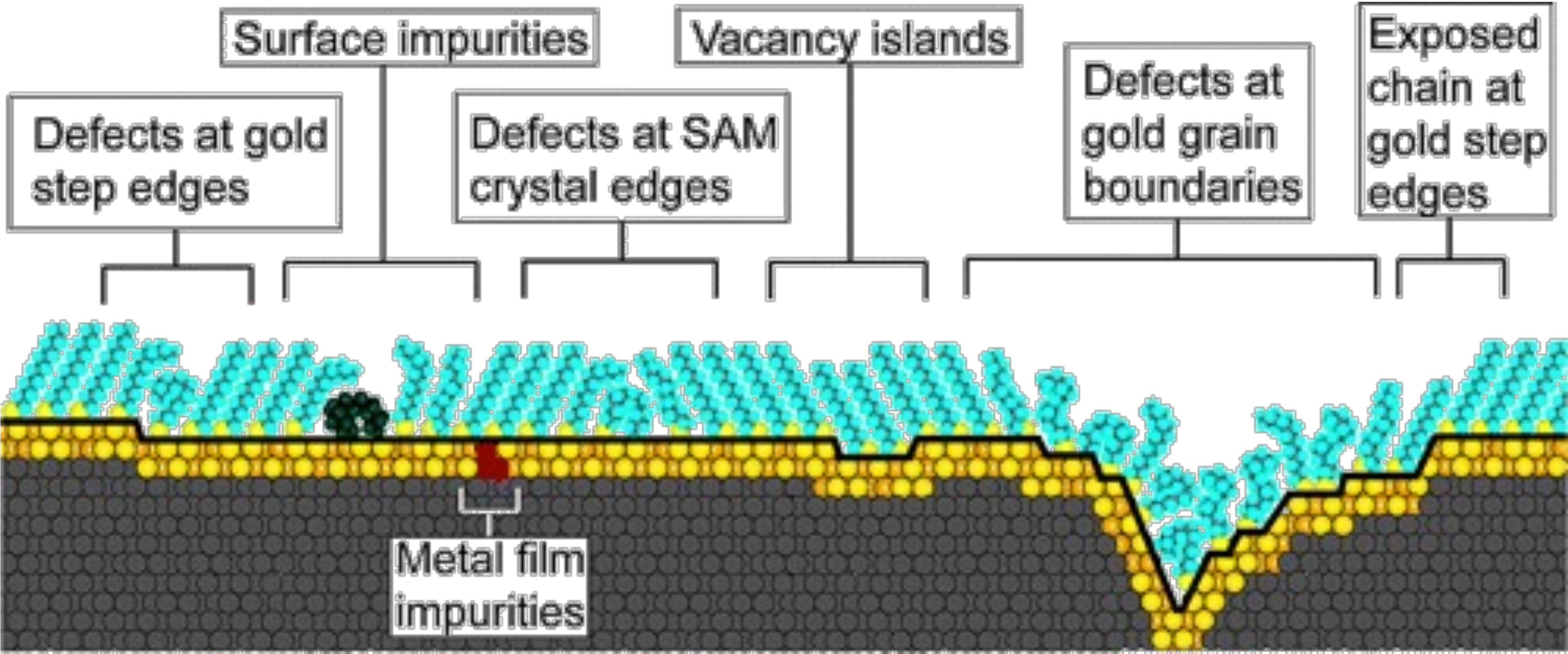
1103

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

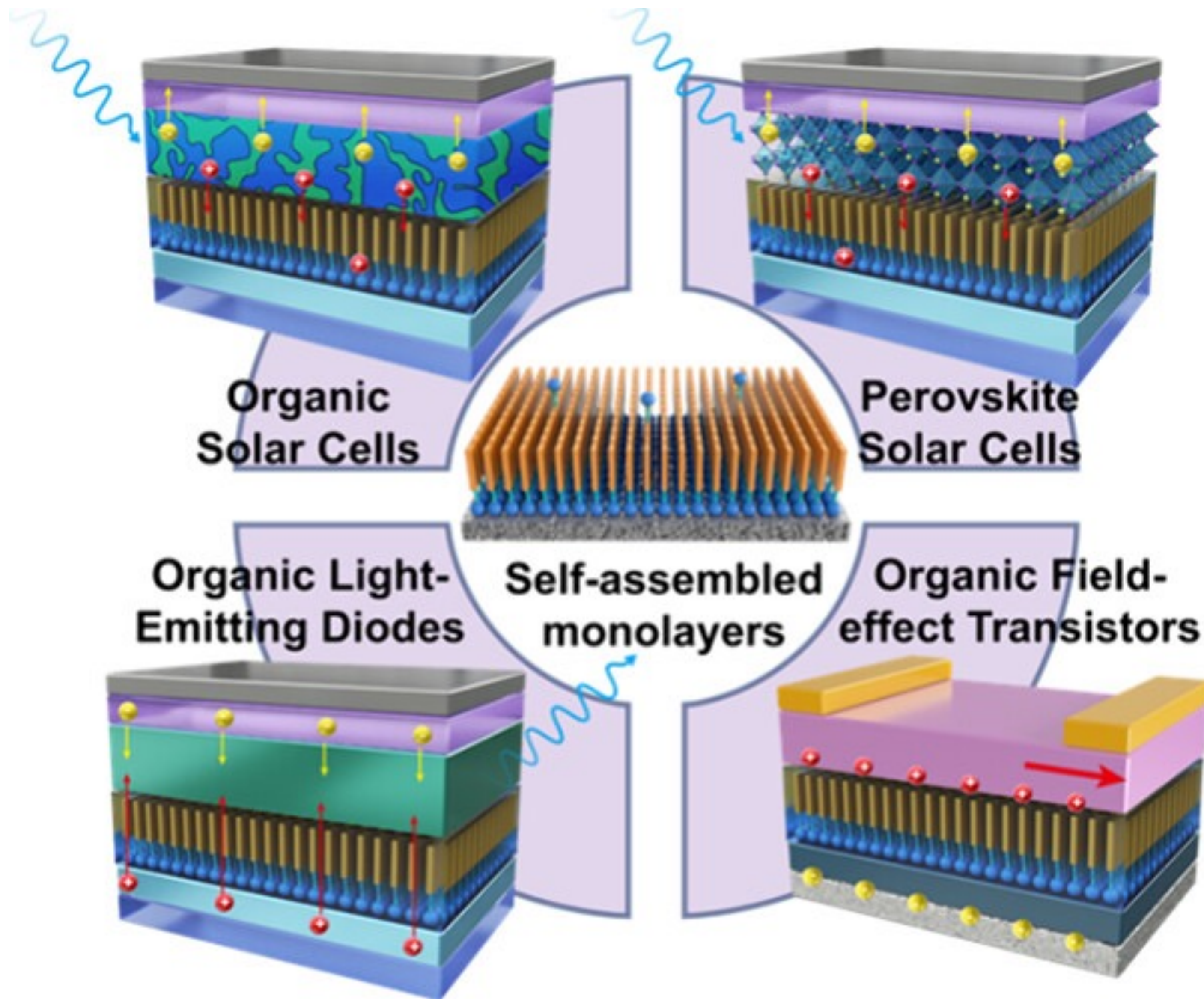
Cited > 10,000 times!

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*



Self-Assembled Monolayers in Electronic Devices



Transparency
Diversity
Stability
Sensitivity
Selectivity
Surface passivation ability

Summary of Today's Class

- 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

Exercise Session: Importance of UHV for obtaining clean surfaces