

Surface Phenomena at the Nanoscale

Lesson 11

MSE 304

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November 28th 2025



Oral Exams in January

Wednesday 21.01.2026: 9 – 6 pm

Thursday 22.01.2026: 9 – 6 pm

Goal: To test your fundamental understanding of key topics and ability to bring together the difference course material to solve problems.

Please let me know ASAP if you have **time conflicts** or **special requirements**



Oral Exams in January

Process: A random number generator will pick a number associated with a question. You have ONE opportunity to request another number, but then you must keep that question.

Format: 20 min preparation (MXG032), 20 min oral exam (MXG 030)

During preparation, you may use whatever resources (internet, slides)

During the exam, you may not use any of these resources

Suggested review: Recap the questions you practiced answering during your TA exercise sessions with the understanding that questions may come from all the different topics covered during the semester!



Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Energetics & Interfacial Phenomena

4: Atomic Structure of Real Surfaces

5: Solid-Solid Interfaces

6: From Ideal Planes to Real Materials (Recap)

7: Characterization of Surfaces & Interfaces

8: Surface Chemistry

9: Surface Patterning and Polymer Chemistry

10: Probing Functional Interfaces

11: Surface Phenomena at the Nanoscale

12: Biosensor Fundamentals

13: Biosensing applications

14: Chemistry of Semiconductor Surfaces & Beyond



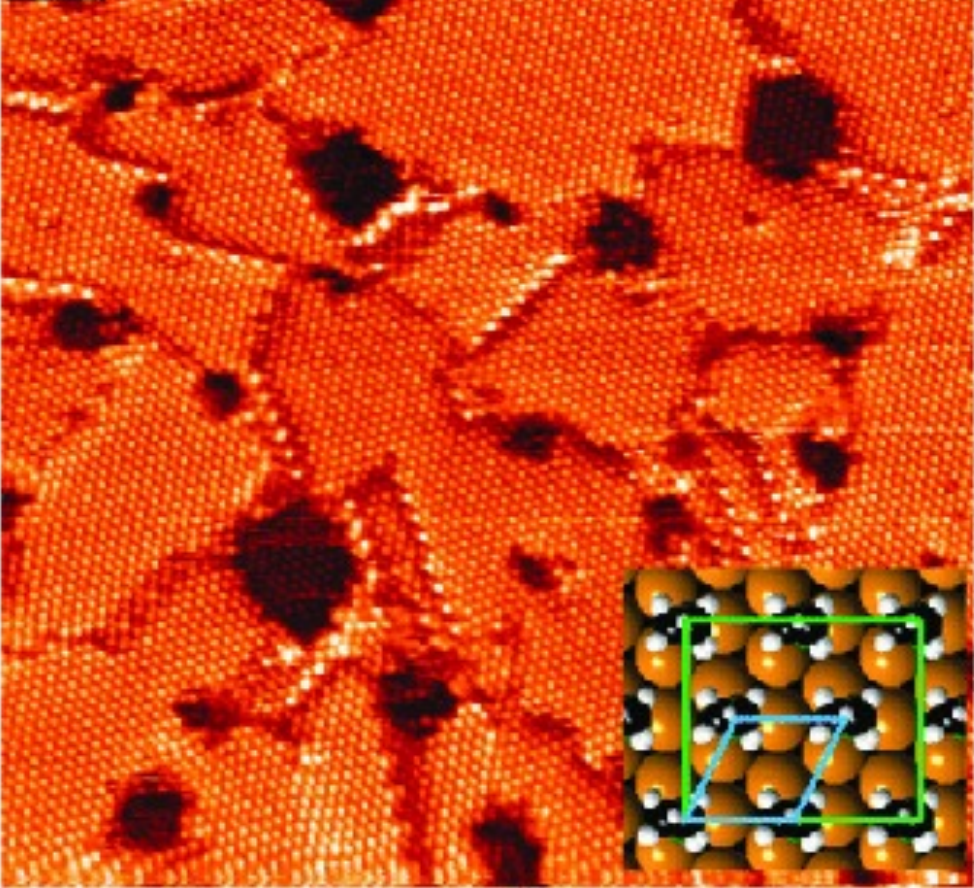
Recap from Lesson 10 – Tools to Extract Surface Properties

- **AFM** can extract mechanical properties (forces) of surfaces
- **FluidFM** (AFM + fluidics) can interact with biology
- **QCM-D** can characterize the viscoelastic properties of surfaces and monitor real-time assembly of “wet mass”
- **Ellipsometry** can extract optical properties and precise layer thickness
- Real-time monitoring of “dry mass” changes can be conducted with **SPR/OWLS**



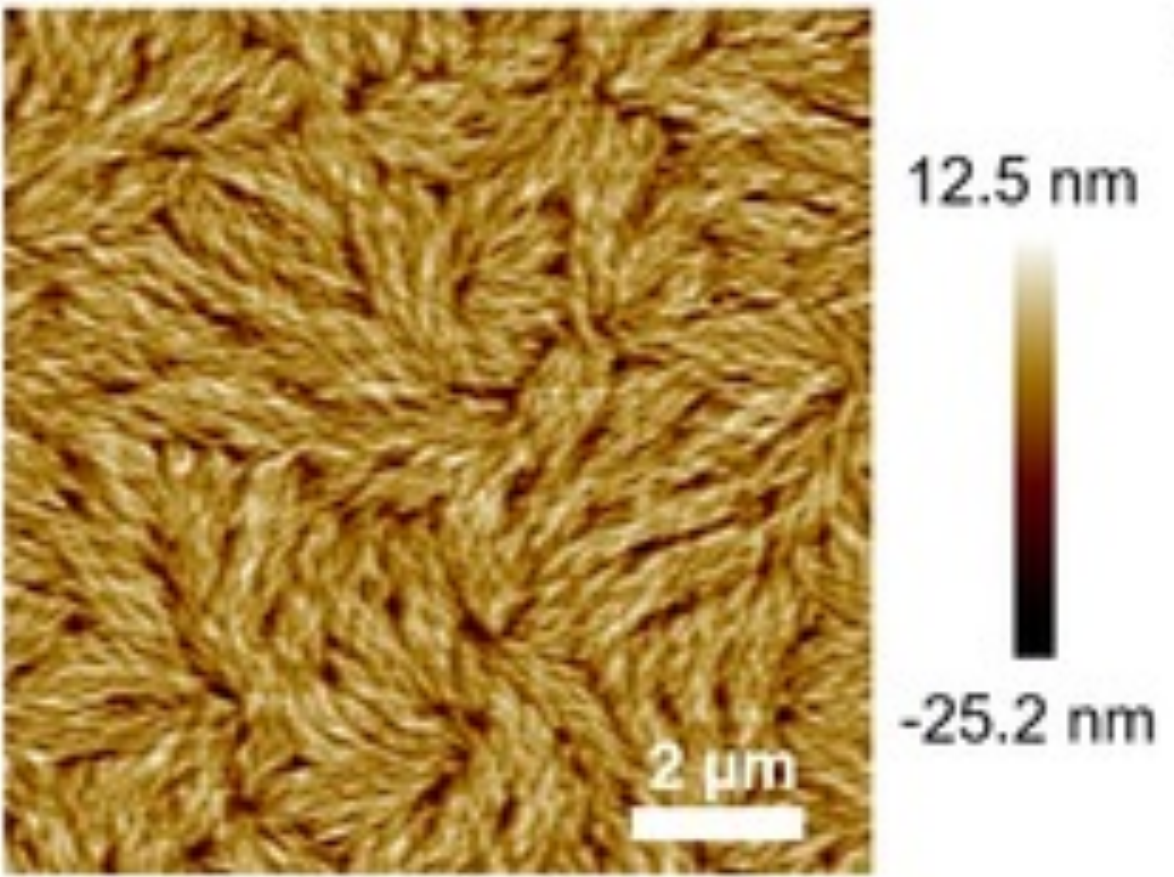
Recap from Lesson 10 – Repertoire of Characterization Tools

STM



5 nm

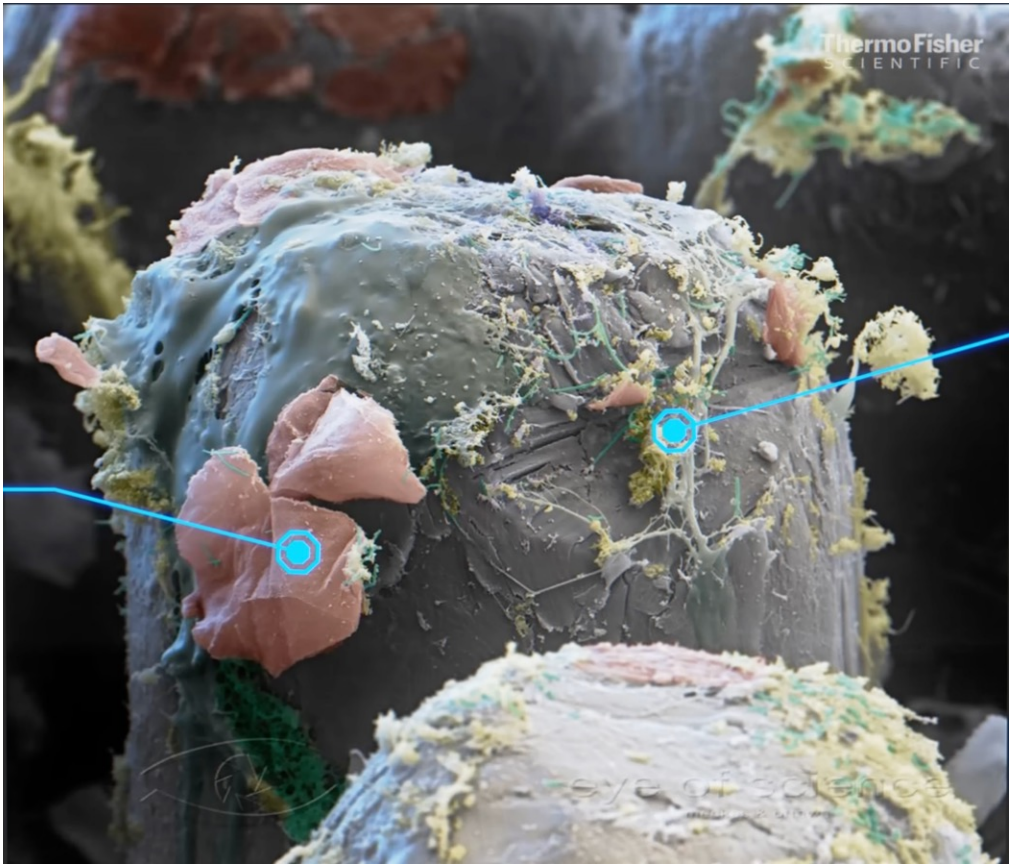
AFM



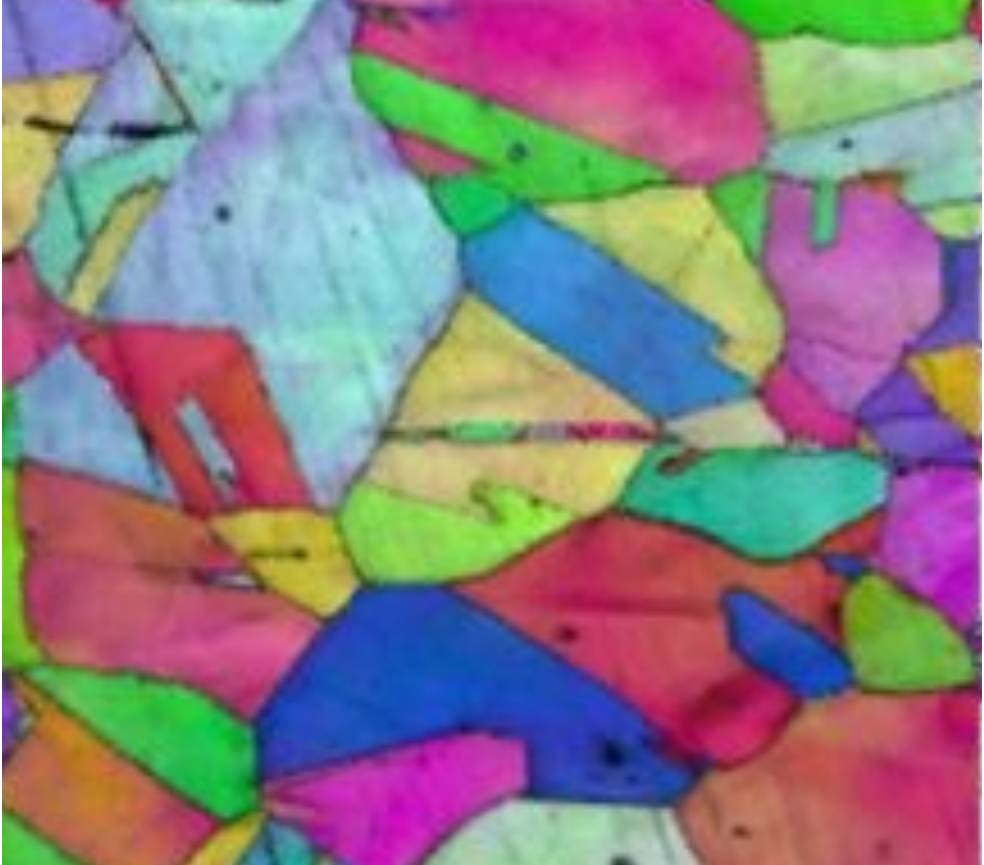
TEM



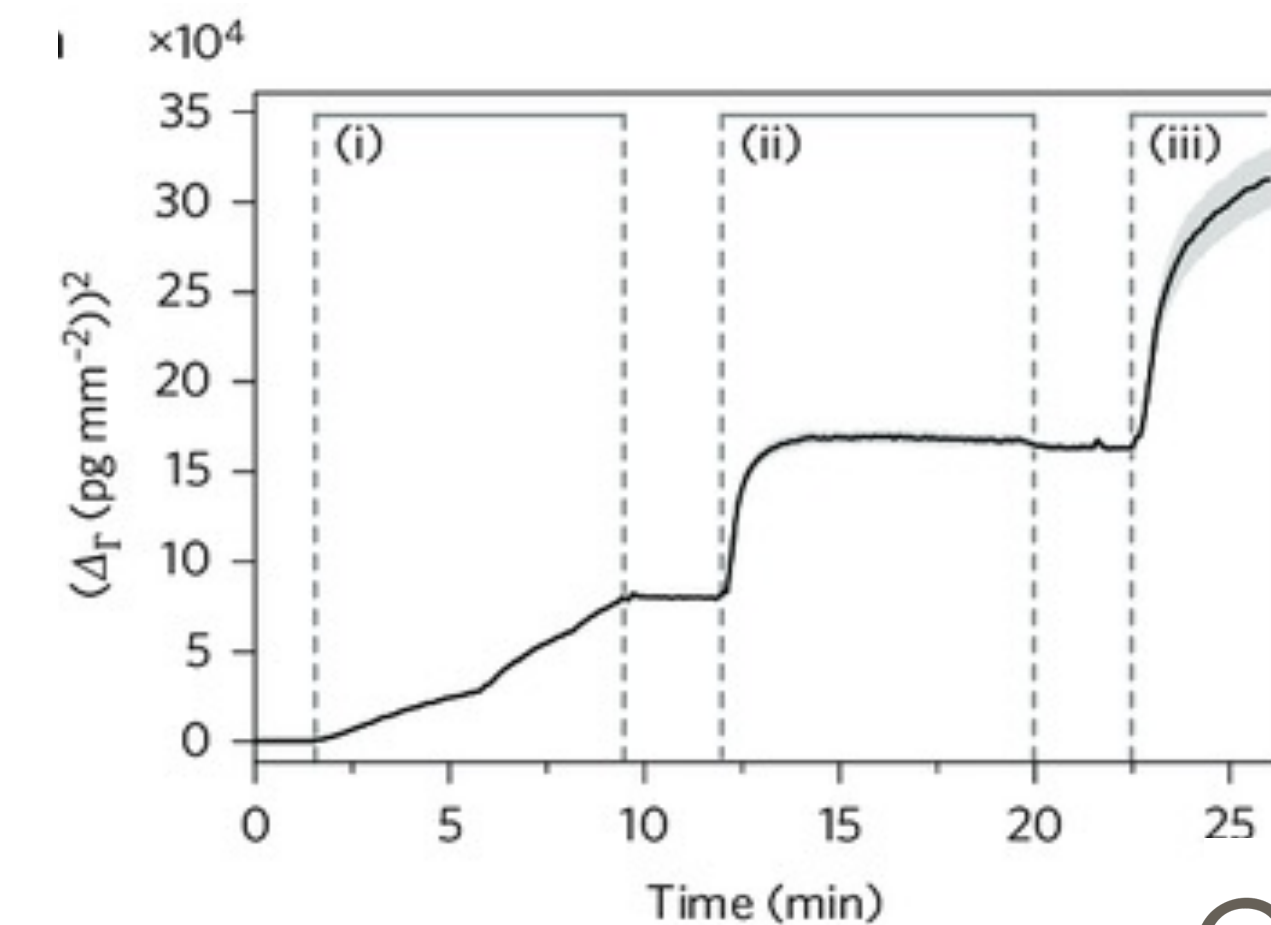
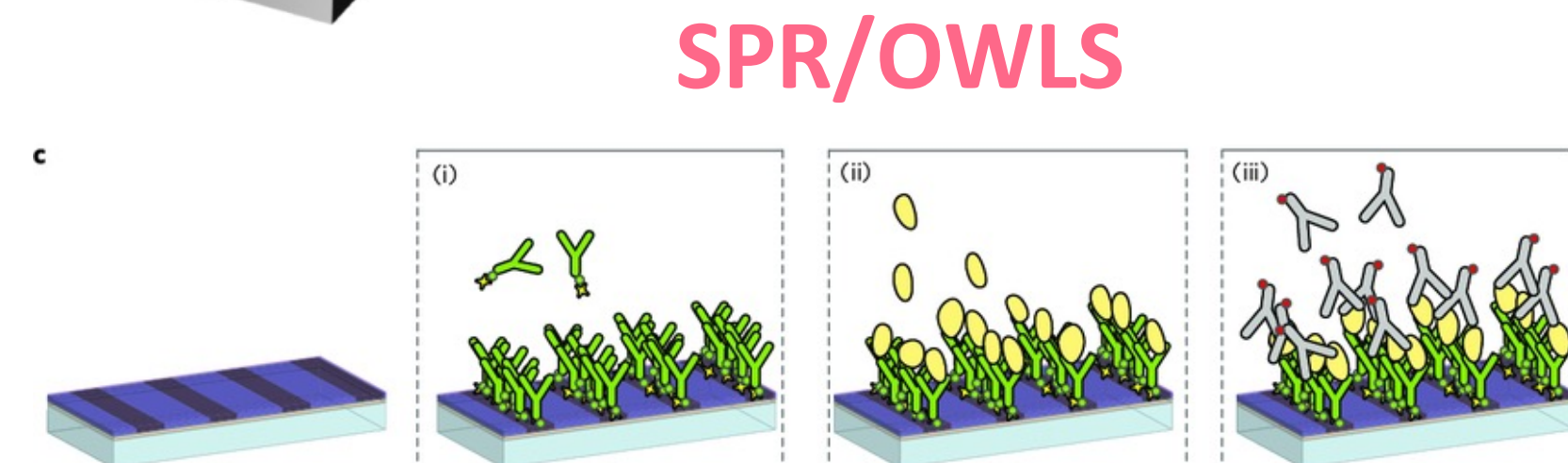
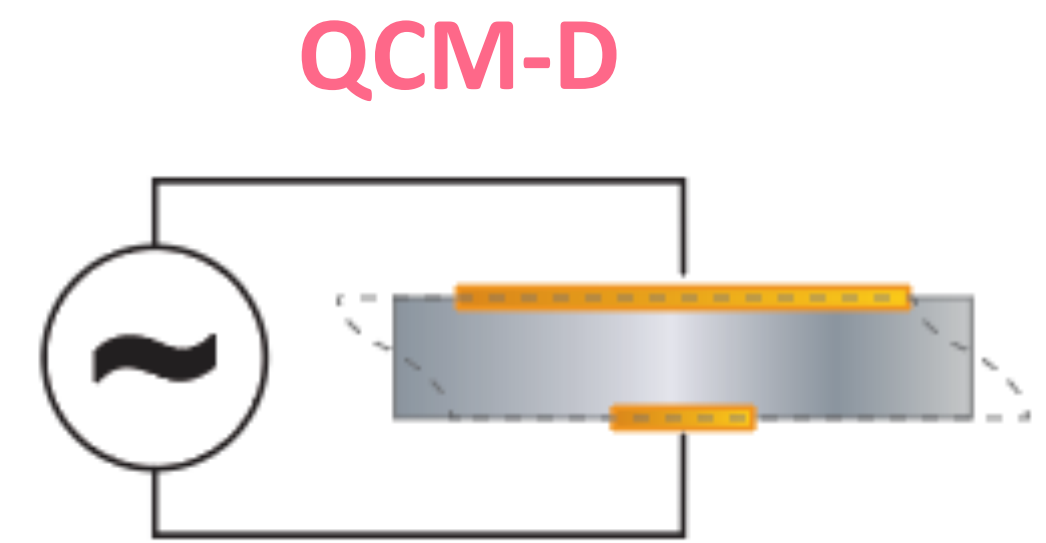
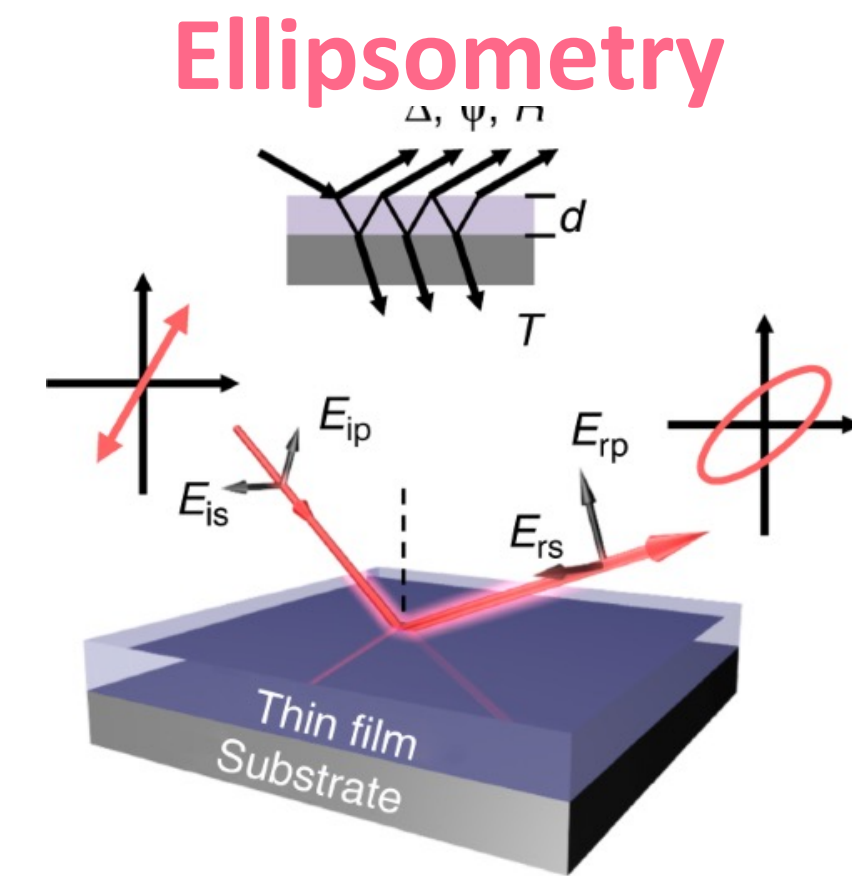
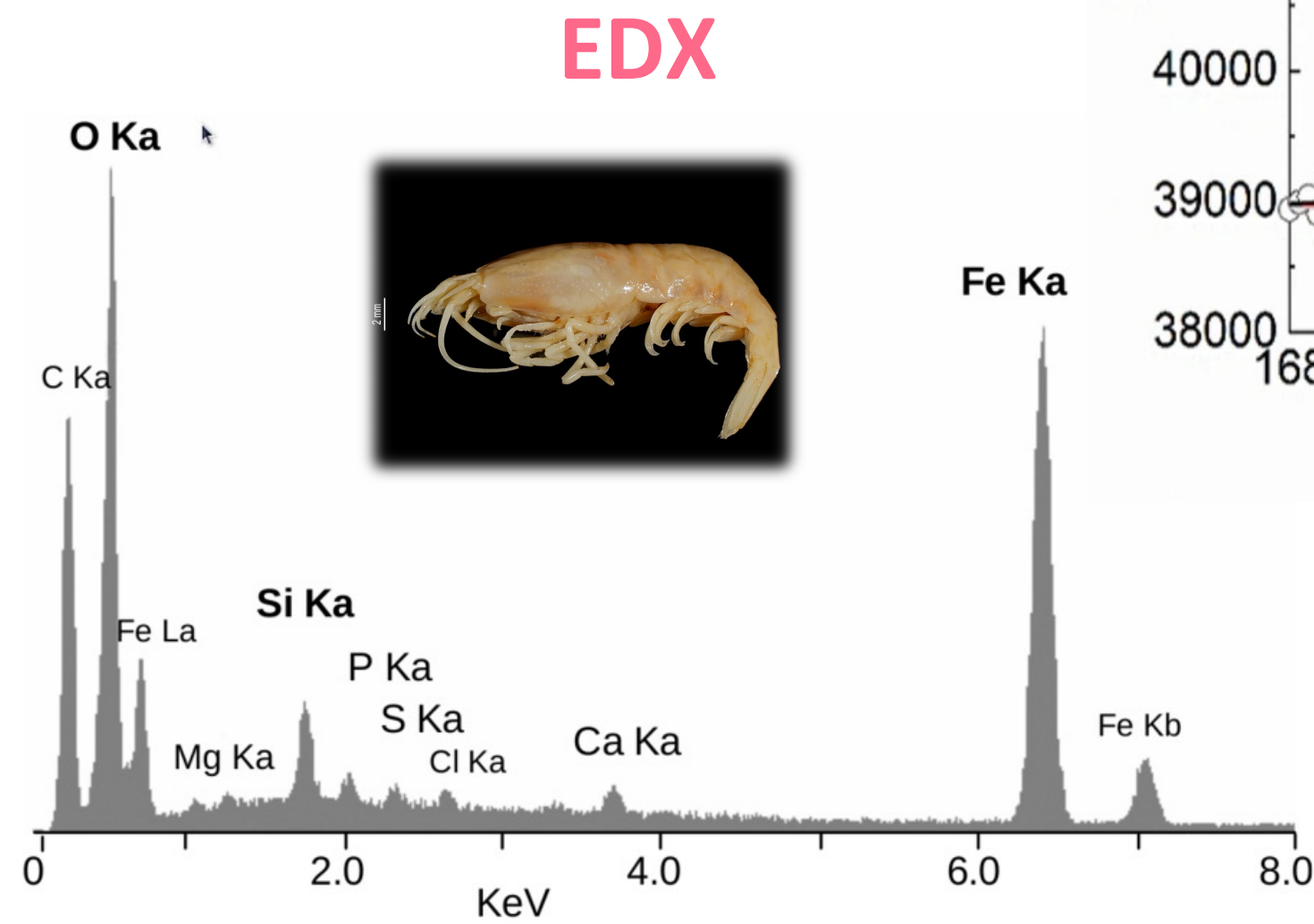
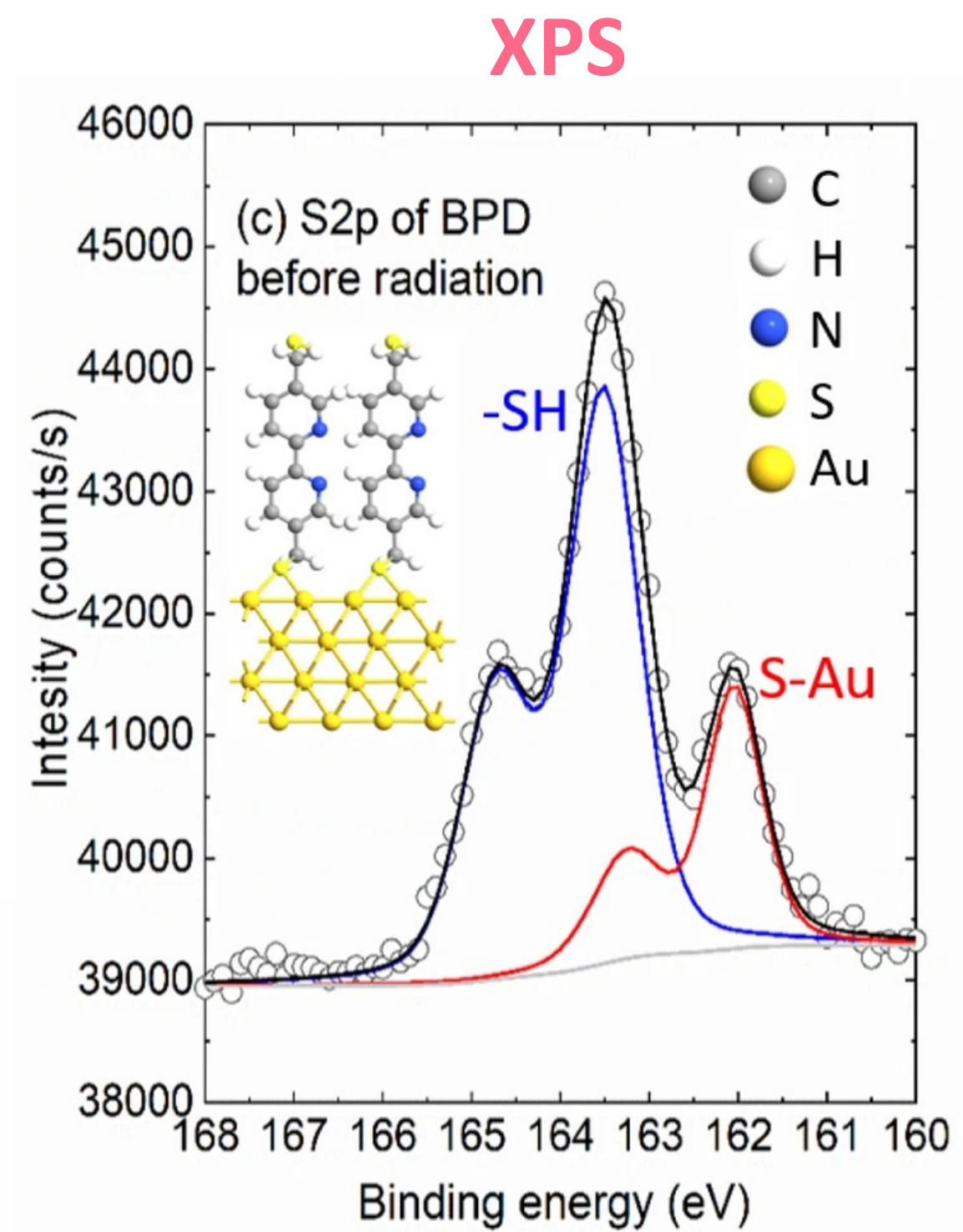
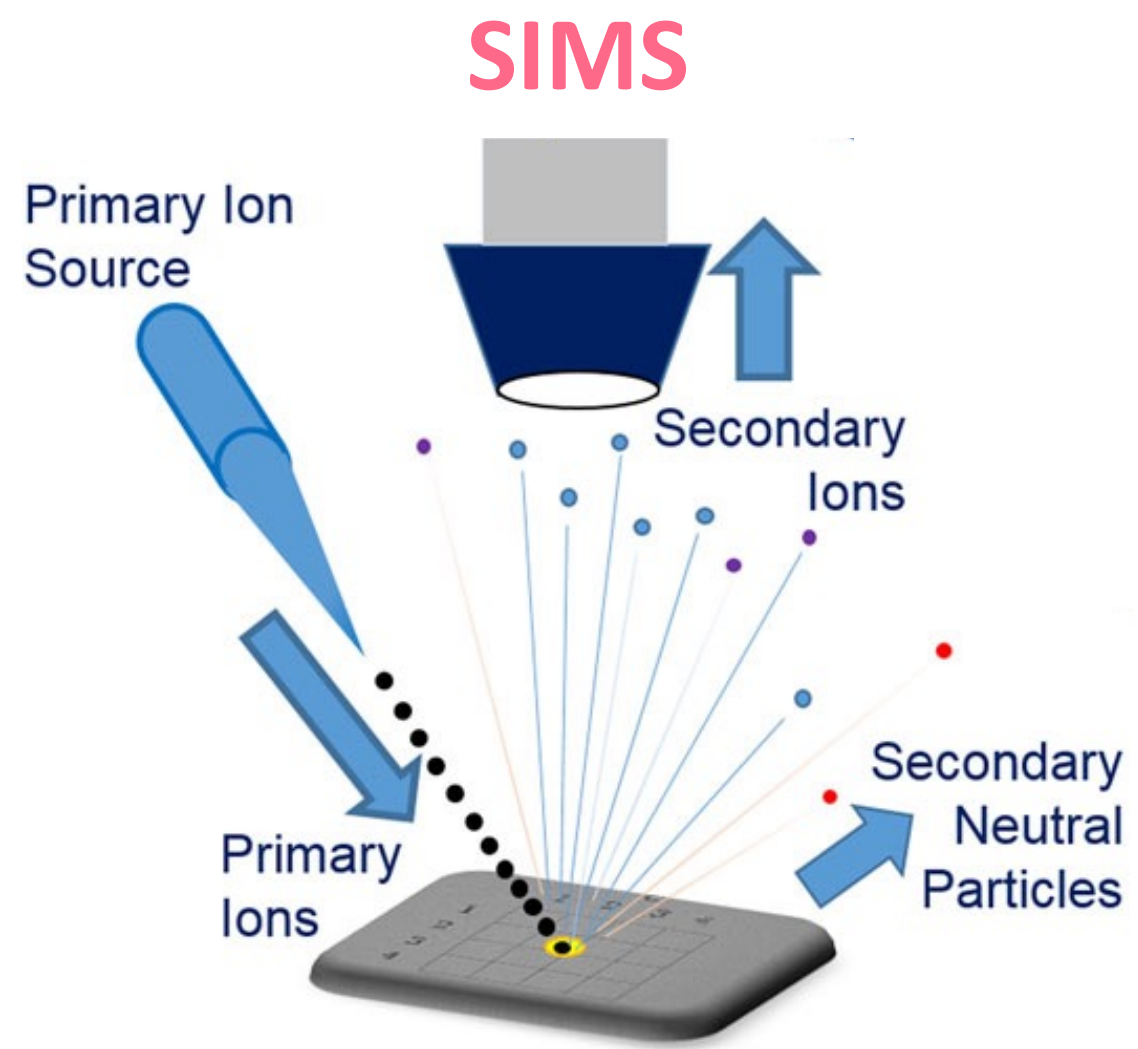
SEM



EBSD



Recap from Lesson 10 – Repertoire of Characterization Tools



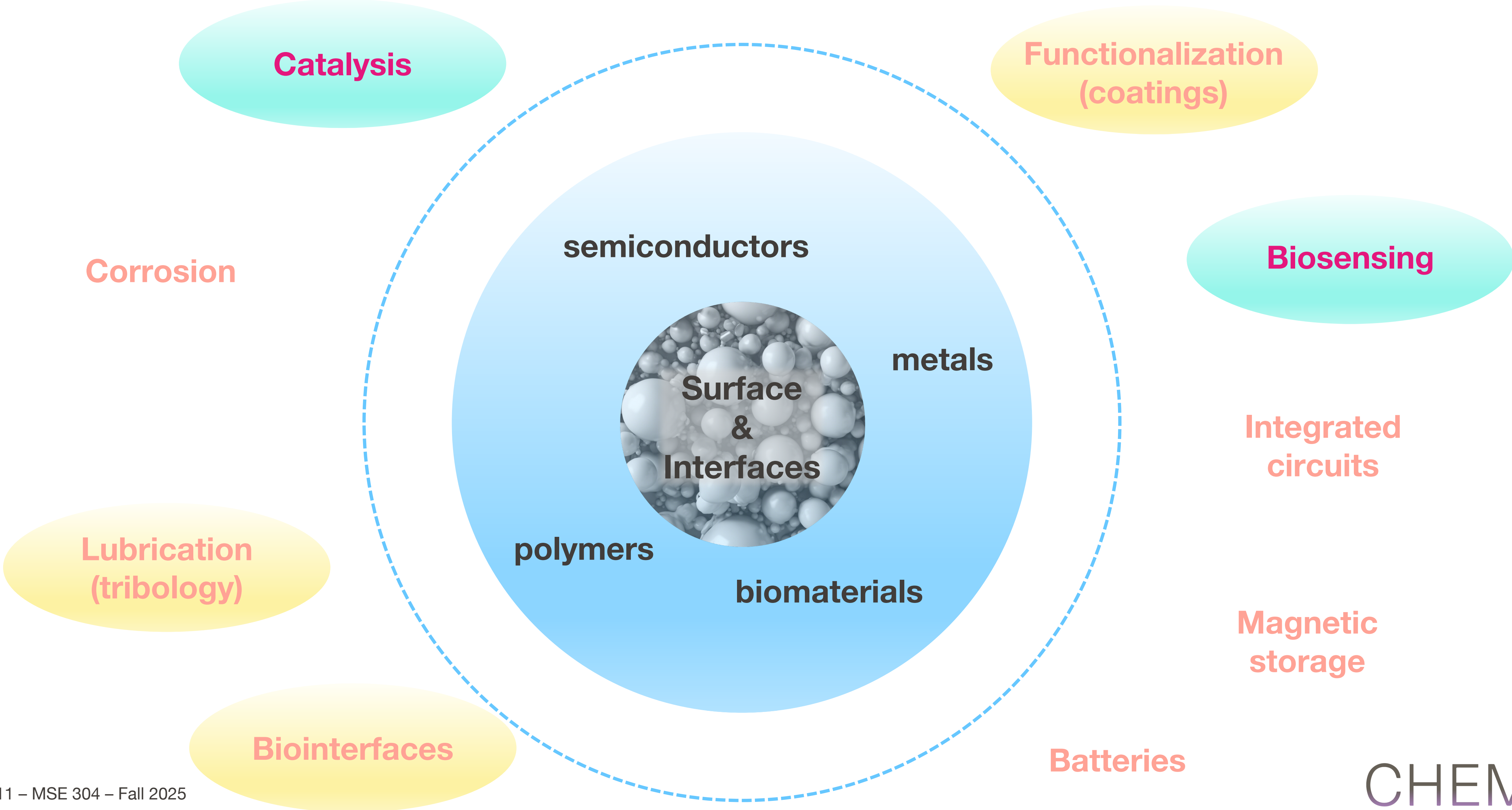
Outline of Lesson 11

- How material properties change at nanoscale dimensions
- Quantum dots and metal nanoparticles as case studies
- How different nanoparticles interact with light
- Effect of plasmon resonance that leads to color in metal nanoparticles
- Synthesis of nanoparticles
- How surfaces serve as catalysts (MO theory recap)



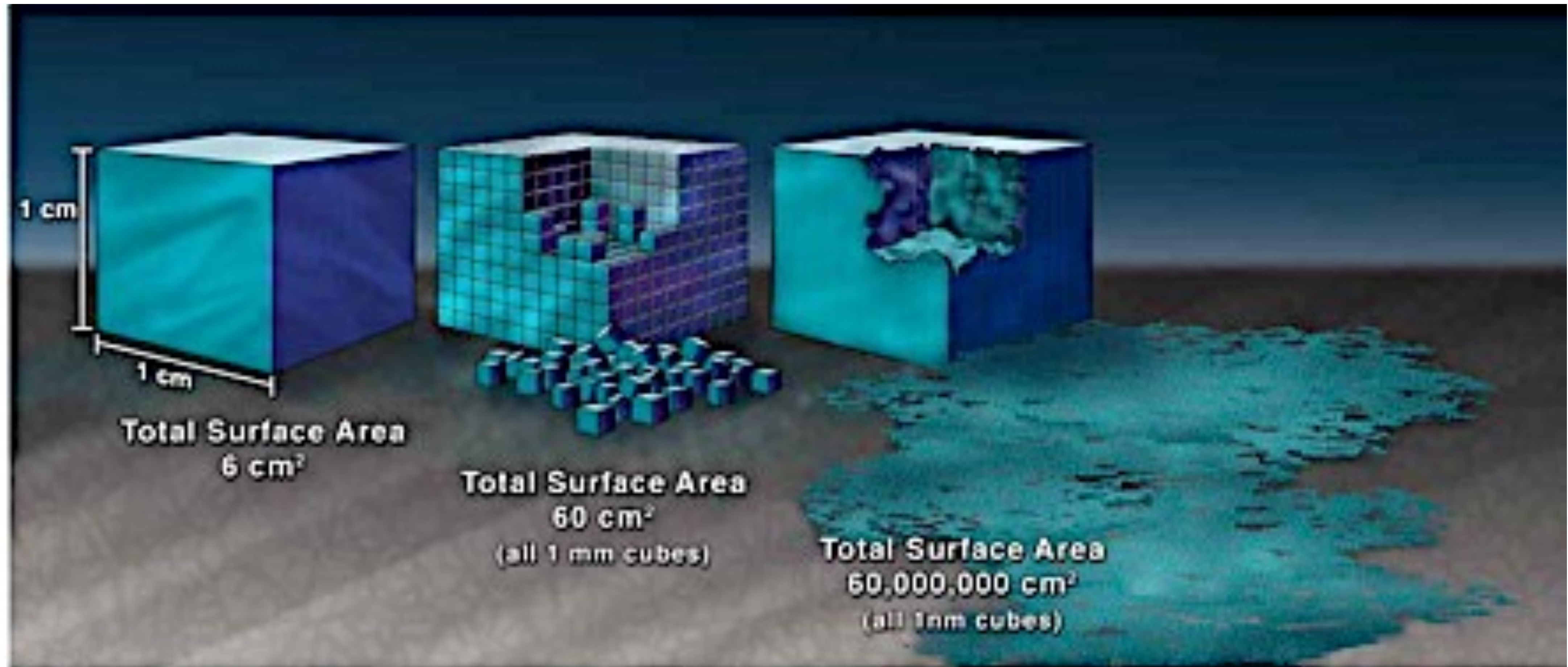
Where We Started: Why Should We Study Surface Science??

Diverse applications in our lives



How Size Controls Surface Area

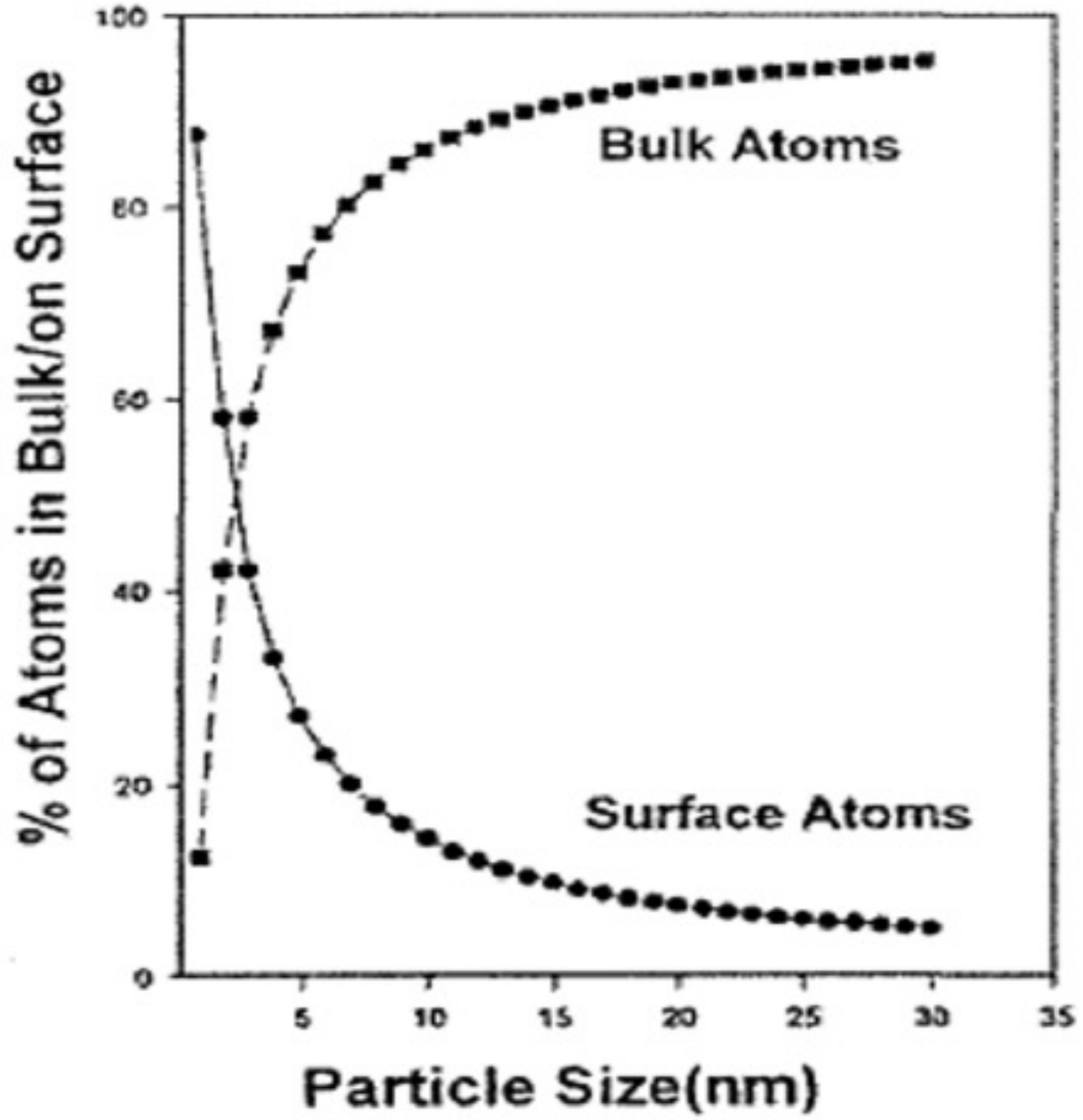
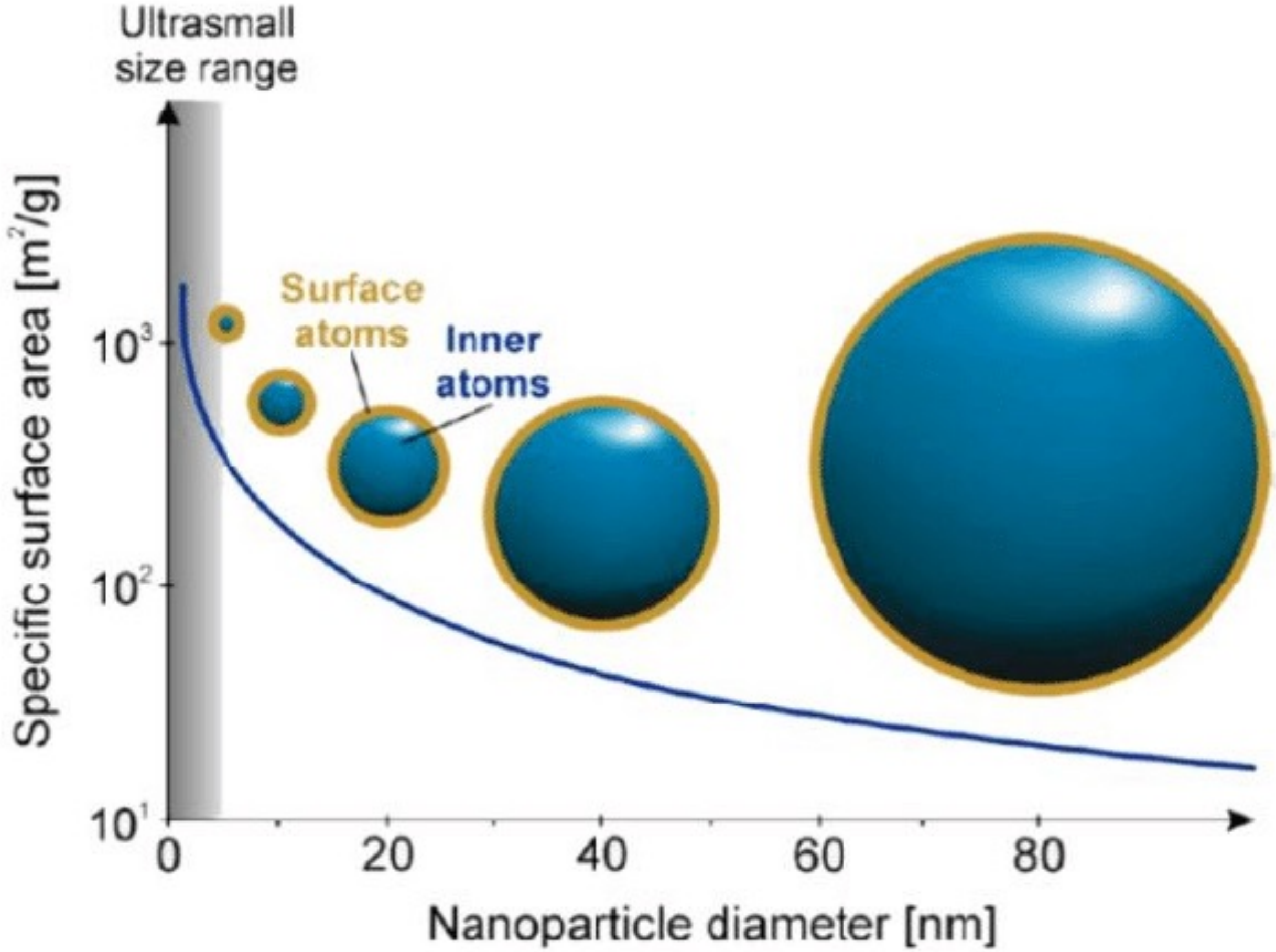
Breaking a material into smaller pieces massively increases surface area
At the nanoscale, almost every atom becomes a surface atom



10 million-fold increase in surface area!

Fraction of Surface Atoms Dramatically Increase at Nanoscale

As particles shrink, the percentage of atoms on the surface increases, making nanoscale materials surface-dominated and more reactive



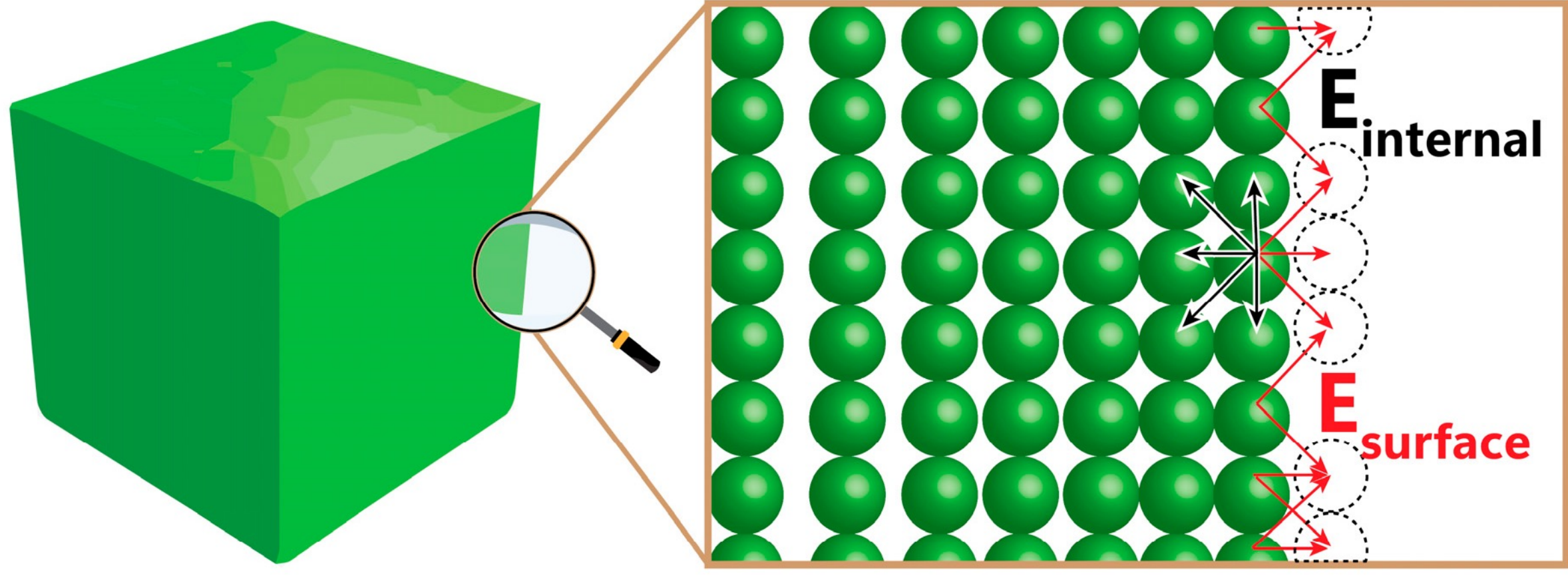
Sharma *et al.* | AIP Conf. Proceed. | 2019

Fuller | 2002

Nanoscale = Surface-Dominated

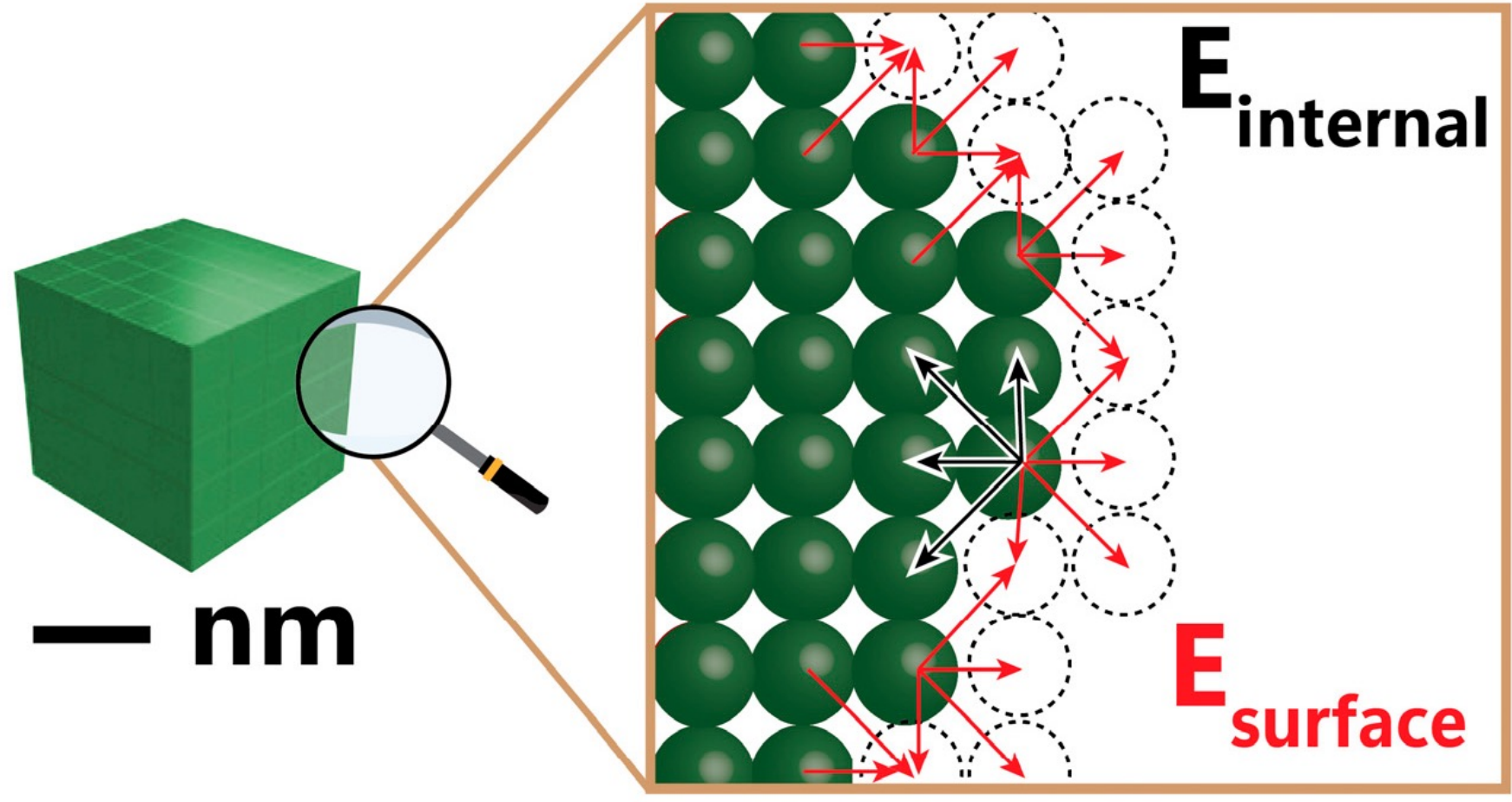
Dangling bonds make surface less stable and higher in surface free energy

Macroscale



Many interior atoms keep structure stable and maintain spacing between atoms

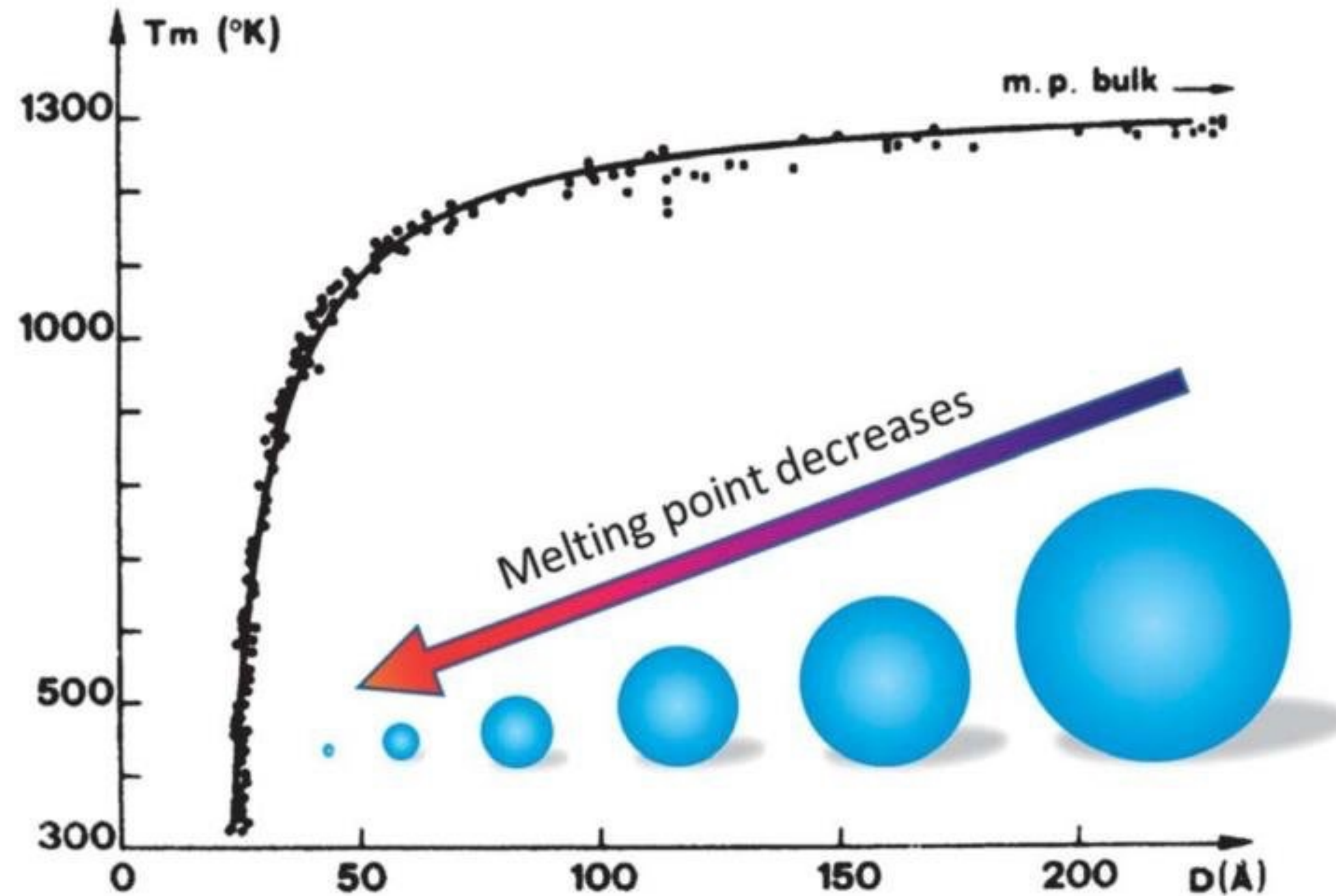
Nanoscale



Almost all atoms become surface atoms with fewer internal atoms to balance surface energy

When Surface Atoms Dominate, Material Properties Shift

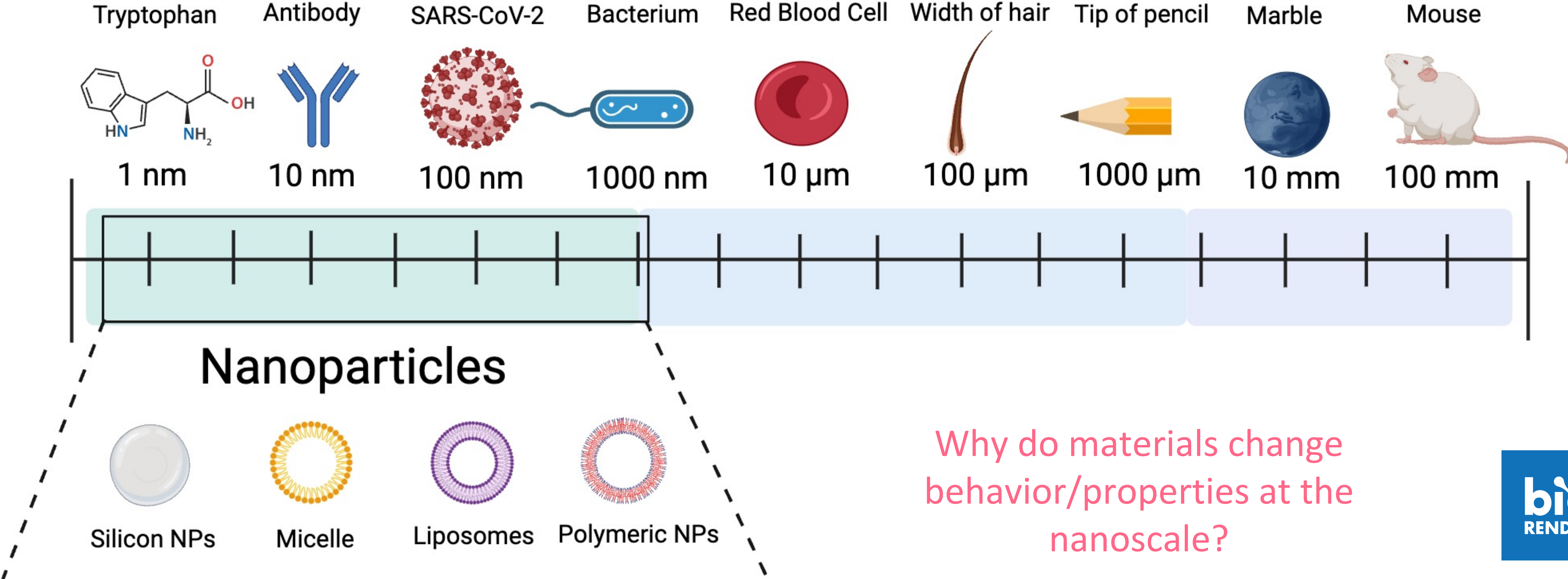
Surface atoms have fewer neighbors
→ weaker bonding
→ easier to melt



Bulk melting point constant
→ atoms well bonded
→ high stability

Surfaces Dominate at Small Sizes - Welcome to Nanoscience

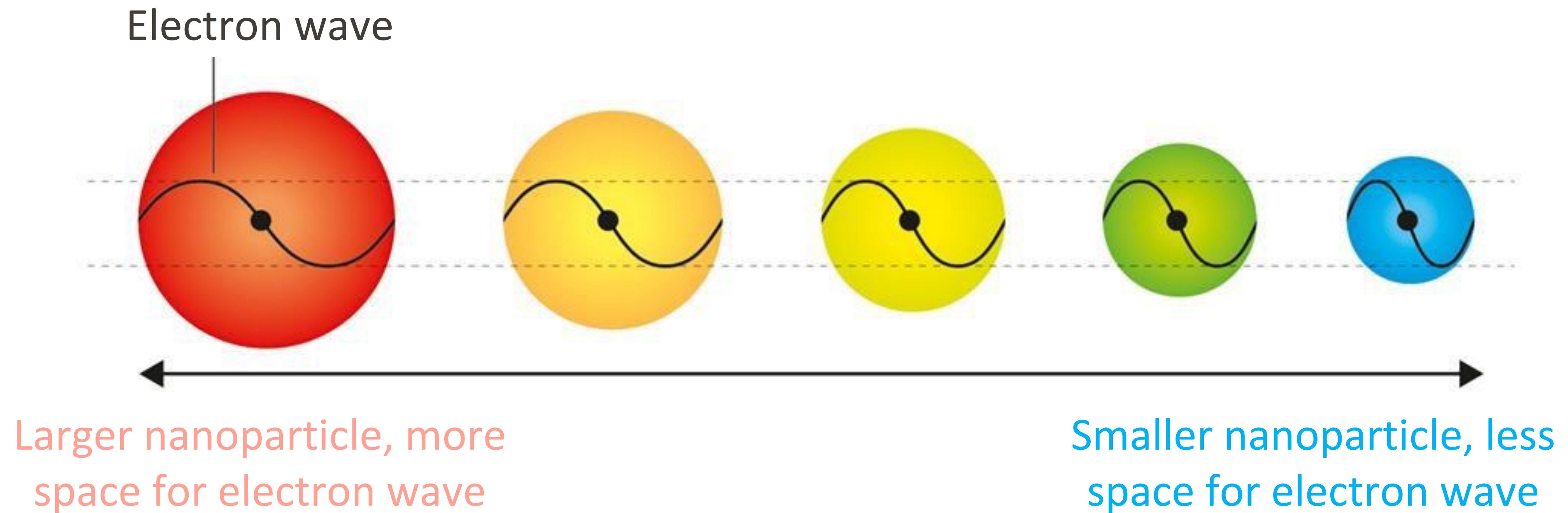
Study of objects and systems in which at least one dimension is 1-100 nm



Why Properties Change at the Nanoscale

Two main reasons:

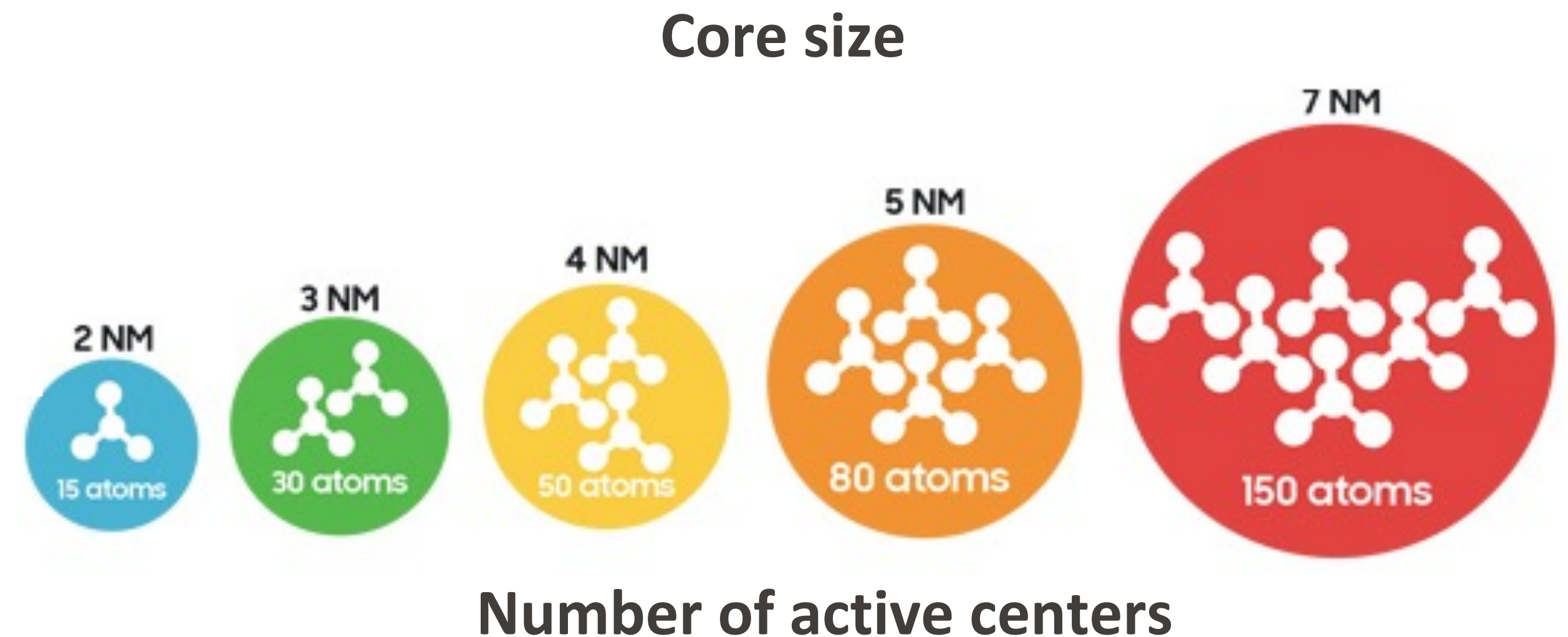
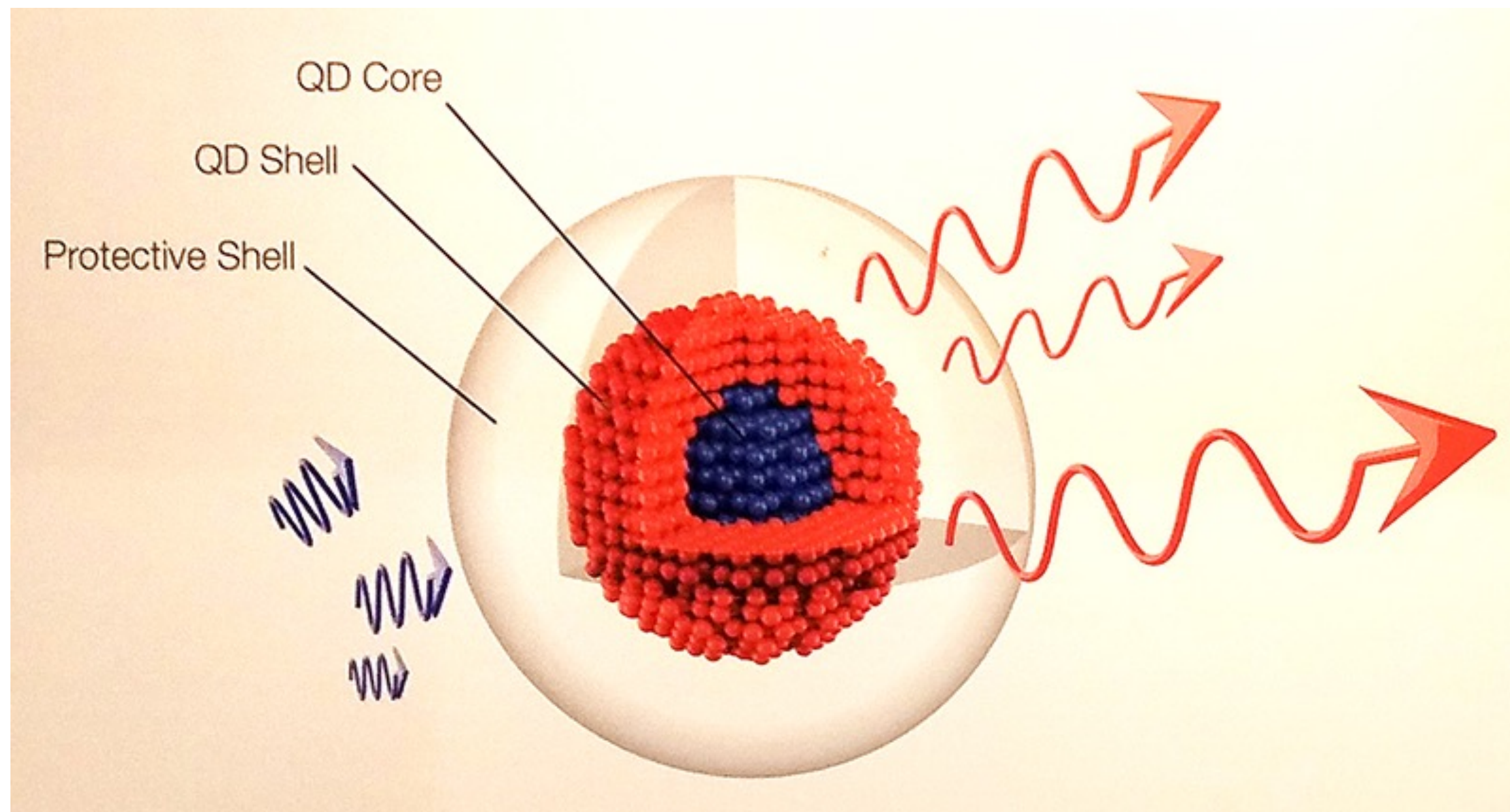
1. High fraction of surface atoms
2. Quantum confinement effect



When particles are just a few nanometers in diameter, the space available to electrons shrink → affects optical properties

Size Controls Color (Optical Properties): Quantum Dots

Quantum dot: crystal of a semiconductor material typically 2-10 nm in size



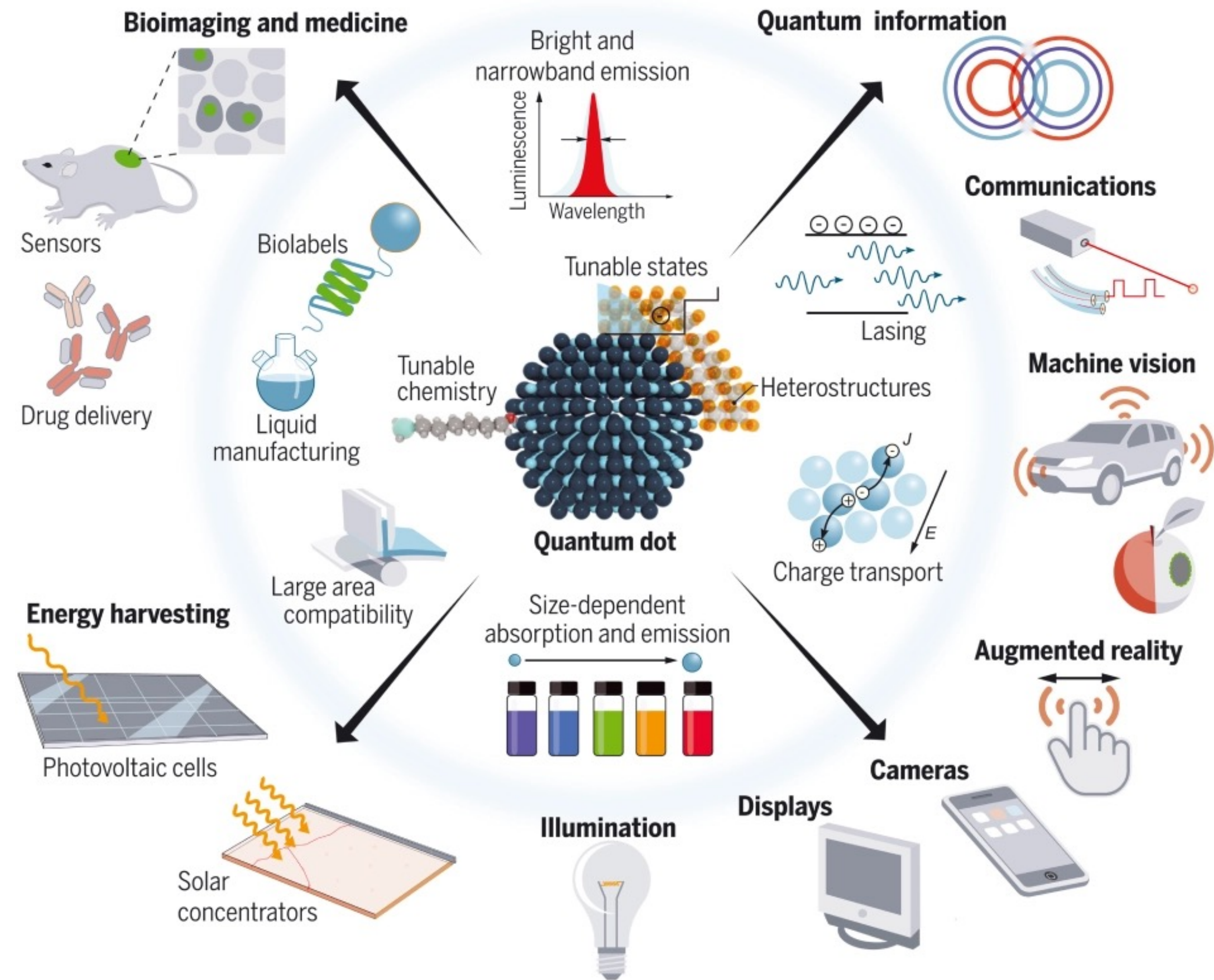
Shell materials: ZnS, CdS, ZnSe

→ Passivate the surface to improve stability and tune electronic interactions

Core materials: CdSe, PbS, InP, CdTe

→ determines emission color

Diverse Applications of Quantum Dots + 2023 Nobel Prize



2023 Nobel Prize in Chemistry Discovery & Synthesis of Quantum Dots



III. Niklas Elmehed © Nobel Prize Outreach
Moungi G. Bawendi



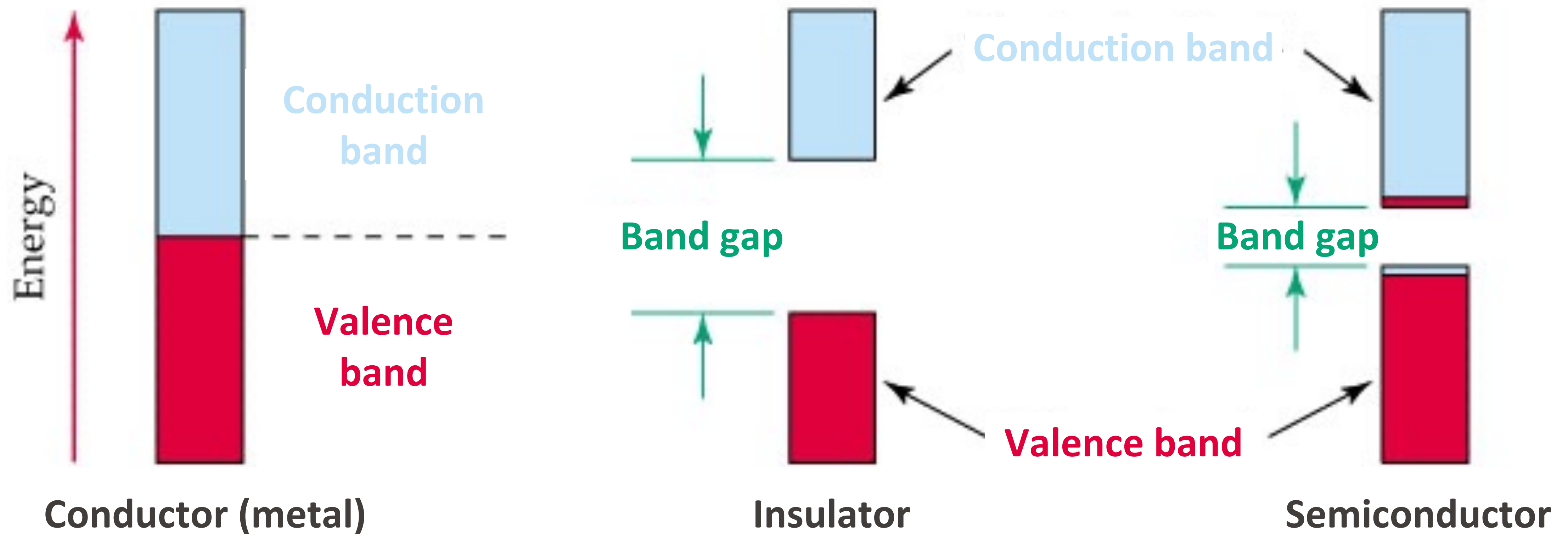
III. Niklas Elmehed © Nobel Prize Outreach
Louis E. Brus



III. Niklas Elmehed © Nobel Prize Outreach
Alexei I. Ekimov

Source: science.org

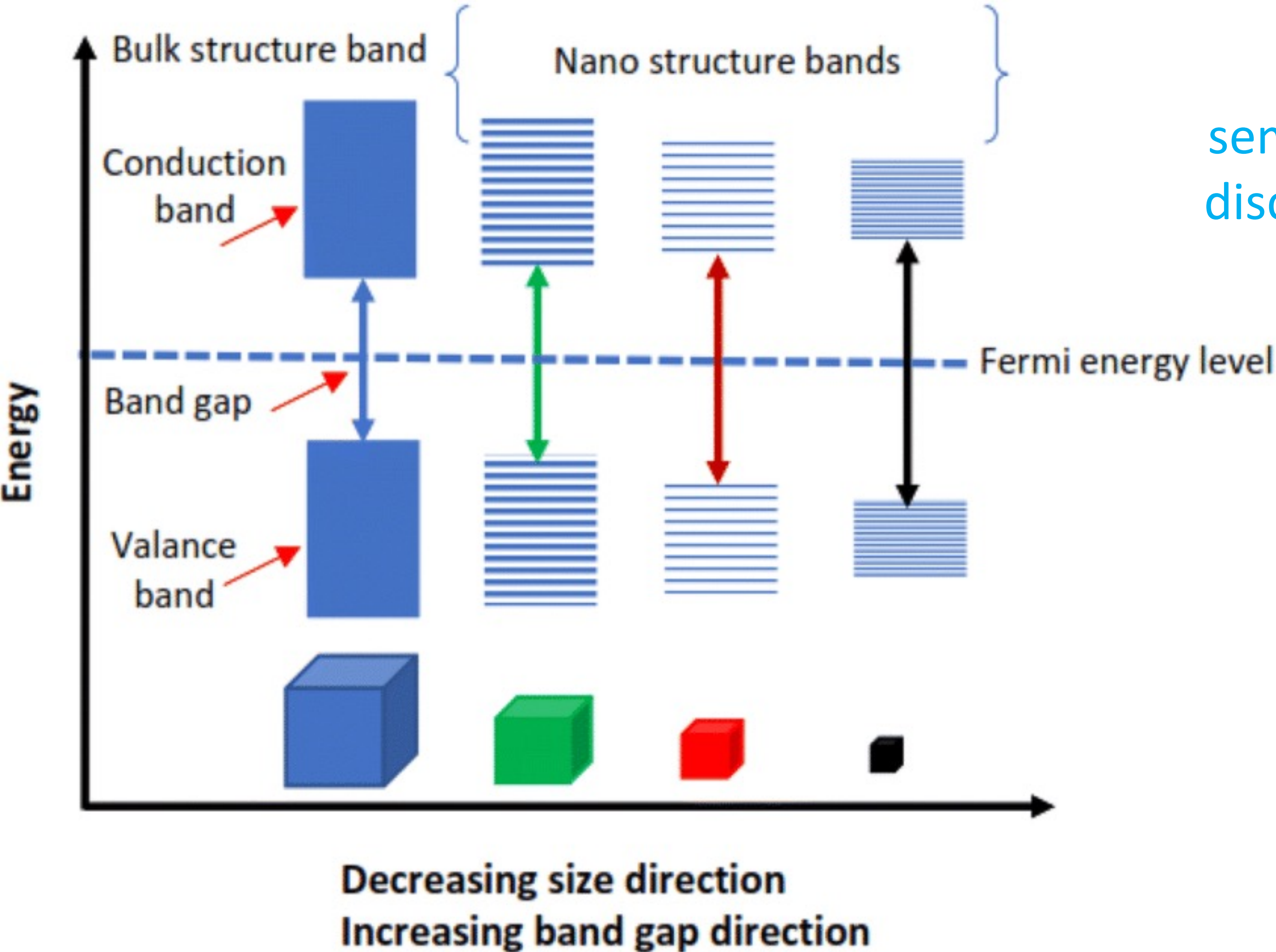
Semiconductors have Size-Dependent Band Gaps



Note: boxes represent broad energy ranges rather than sharp edges
– each band shows a range of energies where electrons can exist

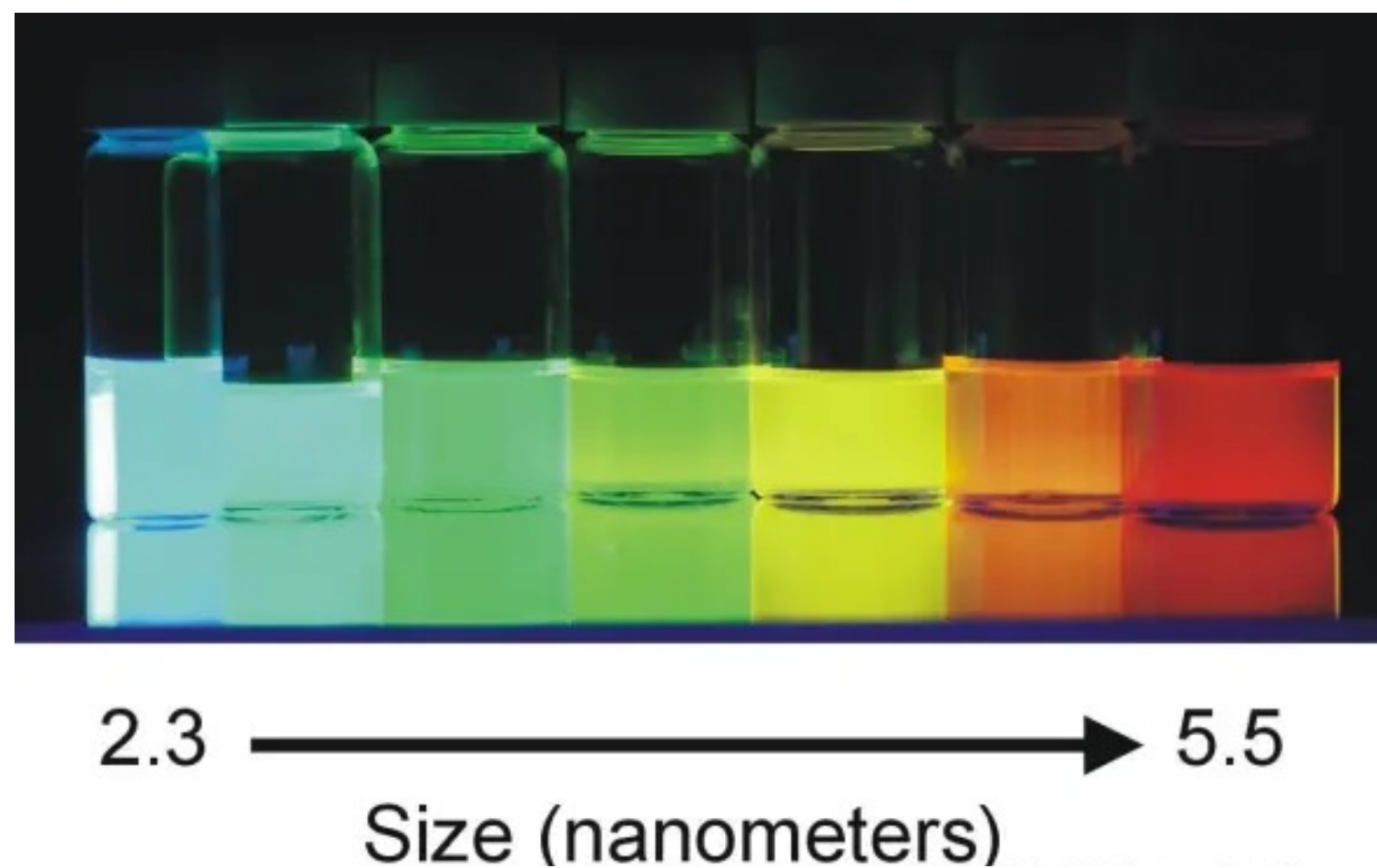
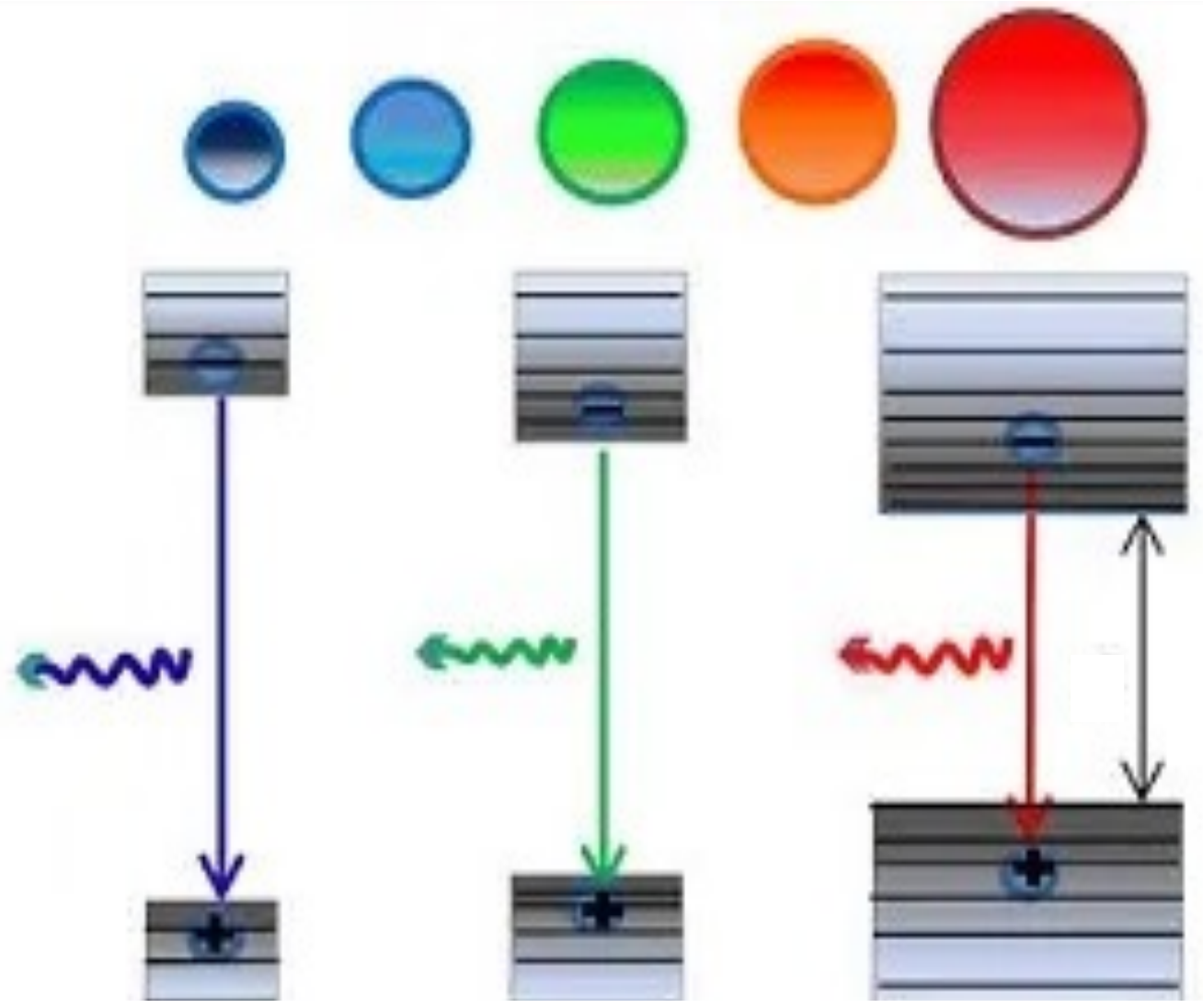
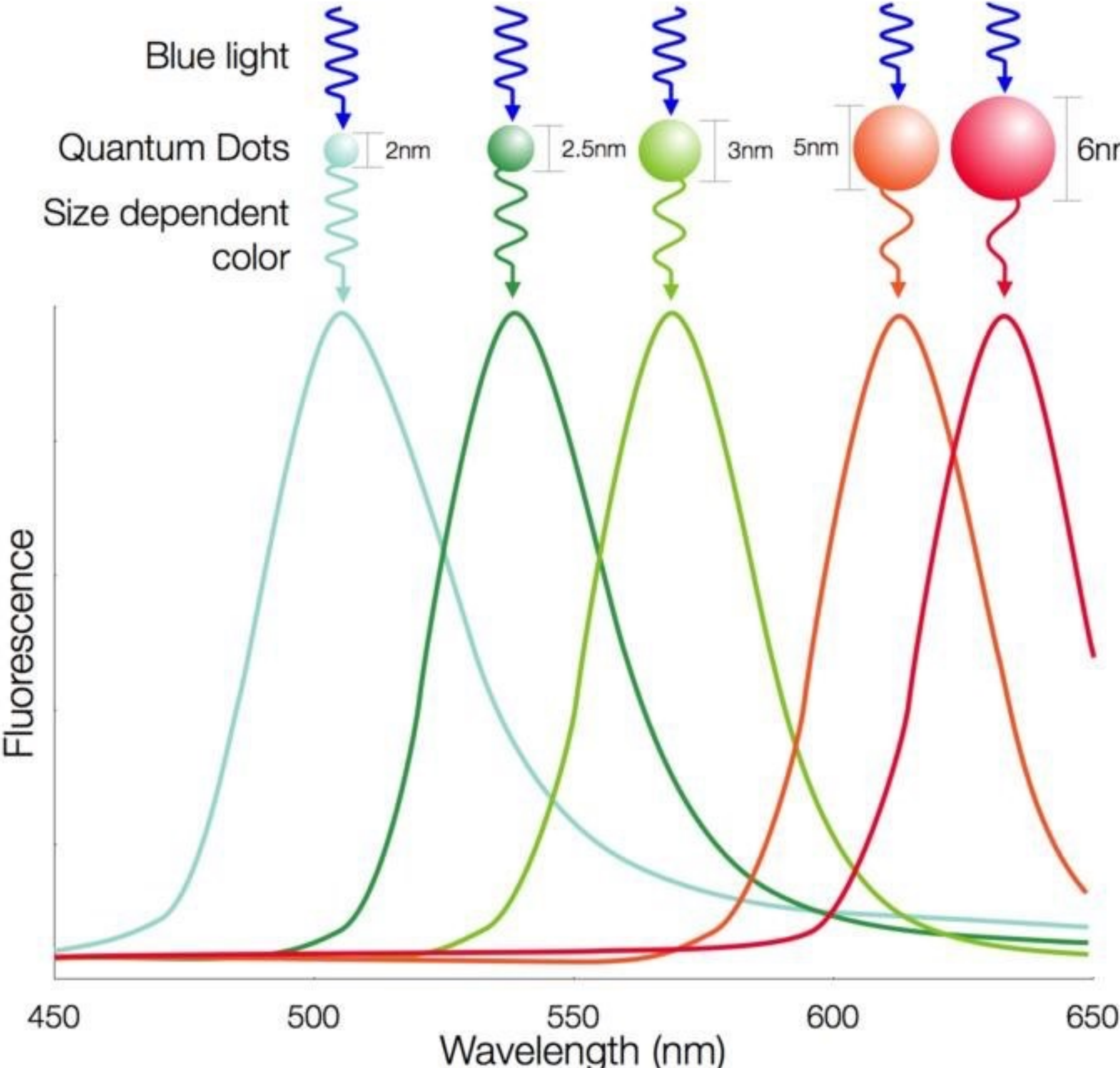
Semiconductors have Size-Dependent Band Gaps

Bulk semiconductor have continuous valence and conduction bands



Nanoscale semiconductors have discrete energy levels (quantized)

Quantum Dots Emit Different Light Colors Depending on Size



Mitra | 2018

Dubertret | 2004

Metal Nanoparticles: Size Controls Optical Properties

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



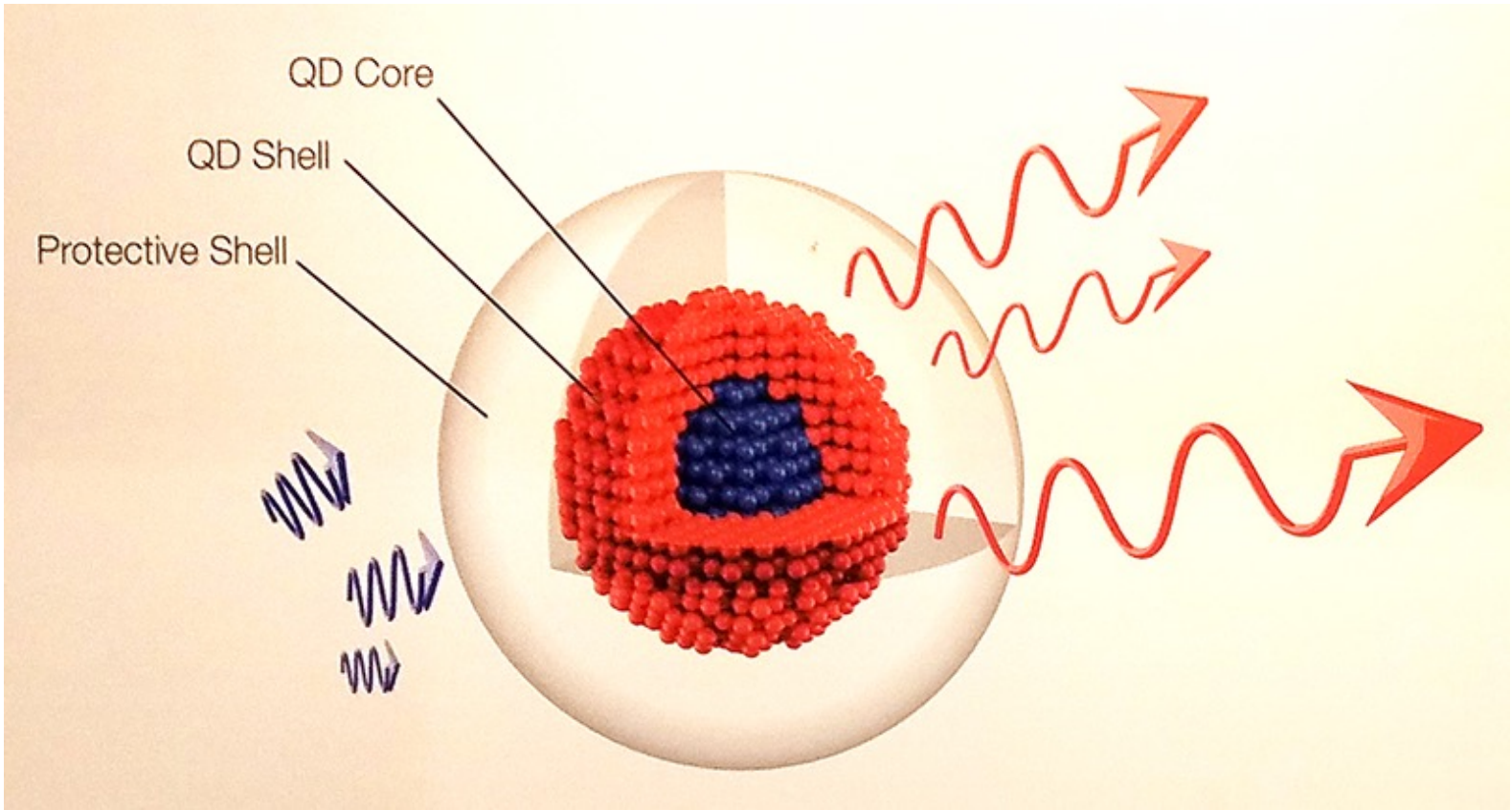
Bulk gold



Gold nanoparticles

How Different Nanoparticles Interact With Light

Semiconductors (Quantum dots)

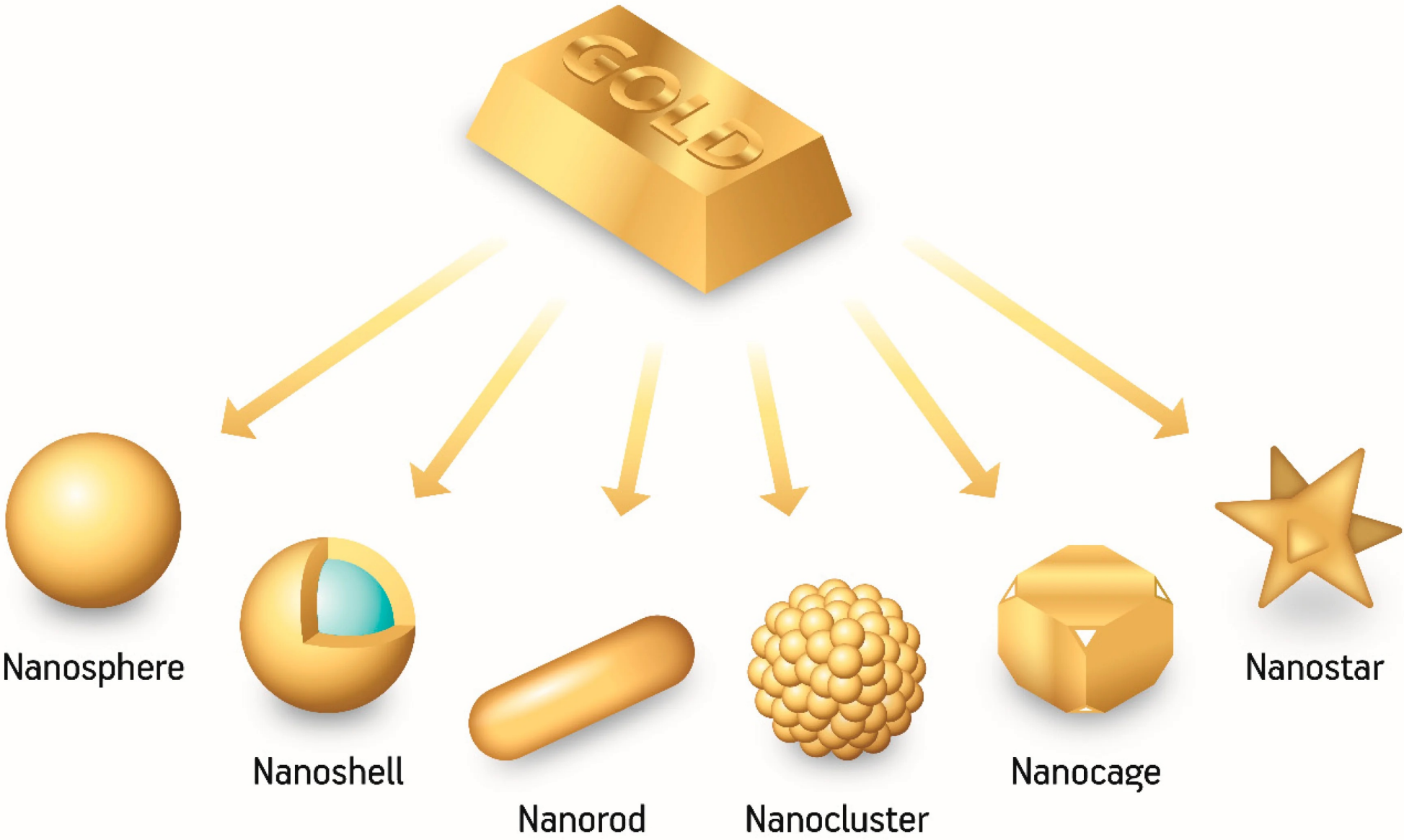


Electrons confined

Discrete energy levels

Size controls band gap → color

Metals (Gold, silver)



Electrons move collectively

Plasmon oscillations

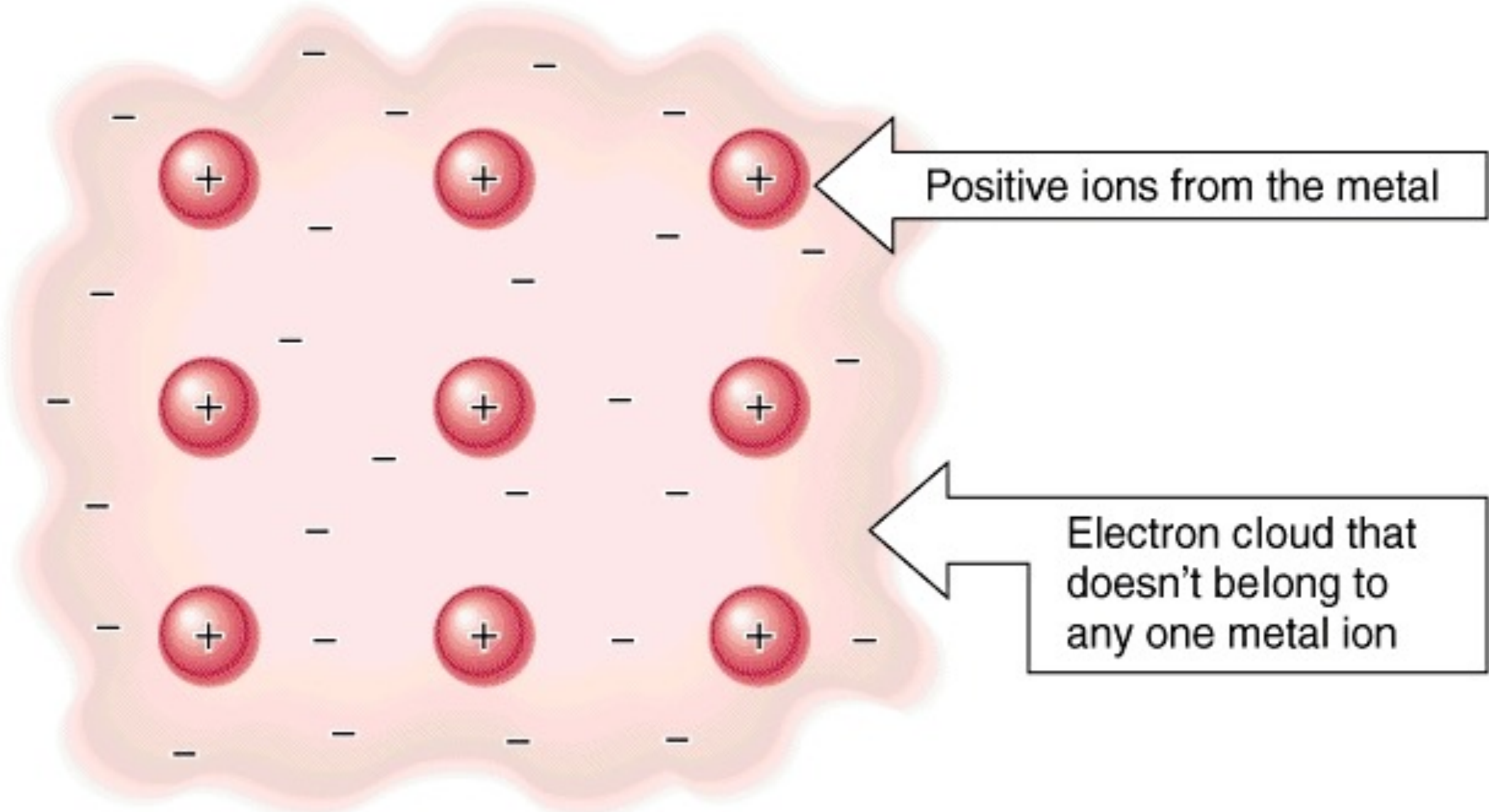
Size/shape controls resonance → color

Key Takeaways

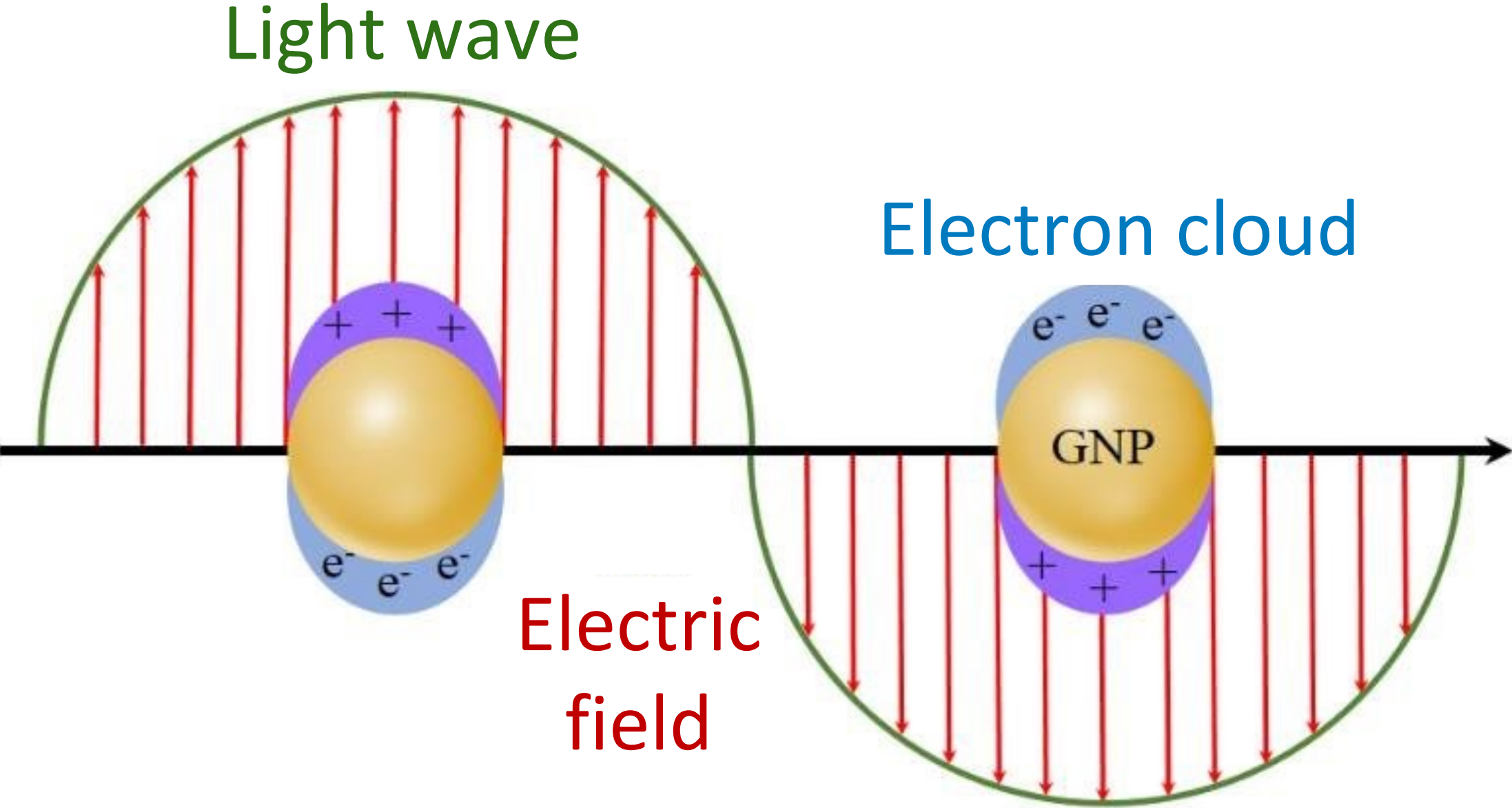
- At nanoscale dimensions, almost every atom becomes a surface atom
- Properties change at the nanoscale due to high fraction of surface atoms and the quantum confinement effect
 - Semiconductors (quantum dots) have size-dependent band gaps
 - Quantum dots vs. metal nanoparticles

Physical Mechanism that Enables Tunable Colors: Plasmons

The Free Electron Sea



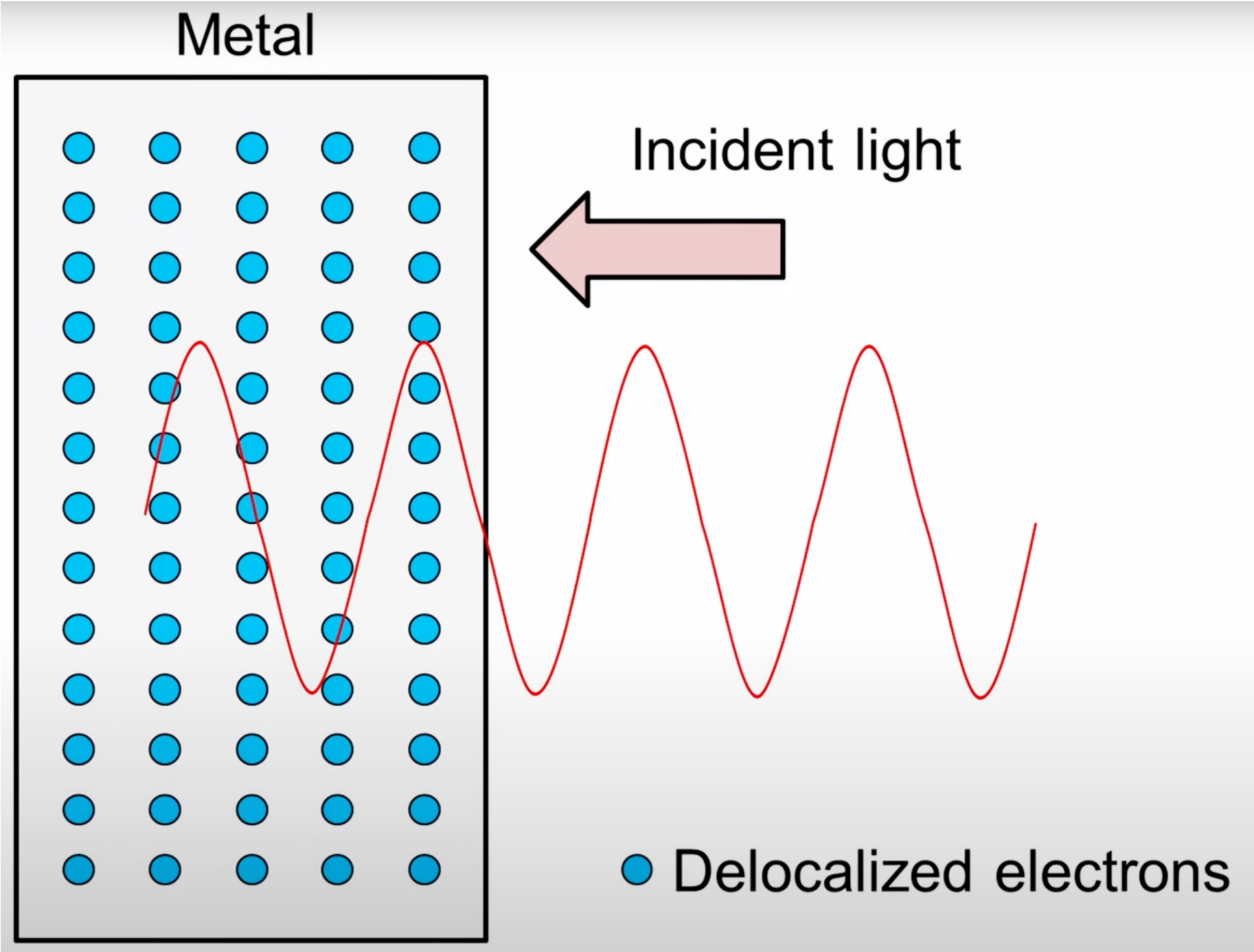
Light as an oscillating electromagnetic field



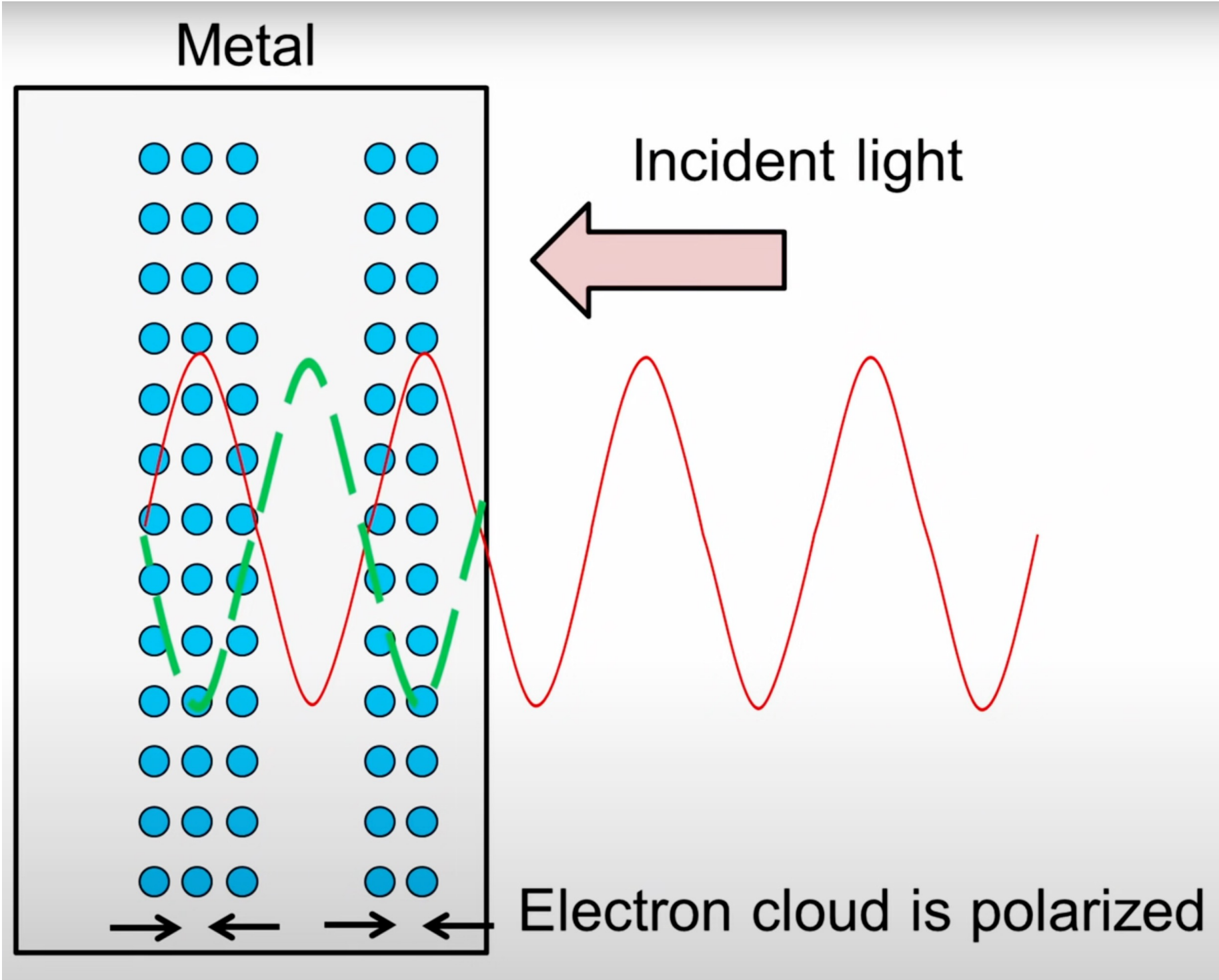
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Electrons in metal are affected by the electromagnetic field from light incident to surface

From Light to Plasmons: Collective Electron Motion in Metals

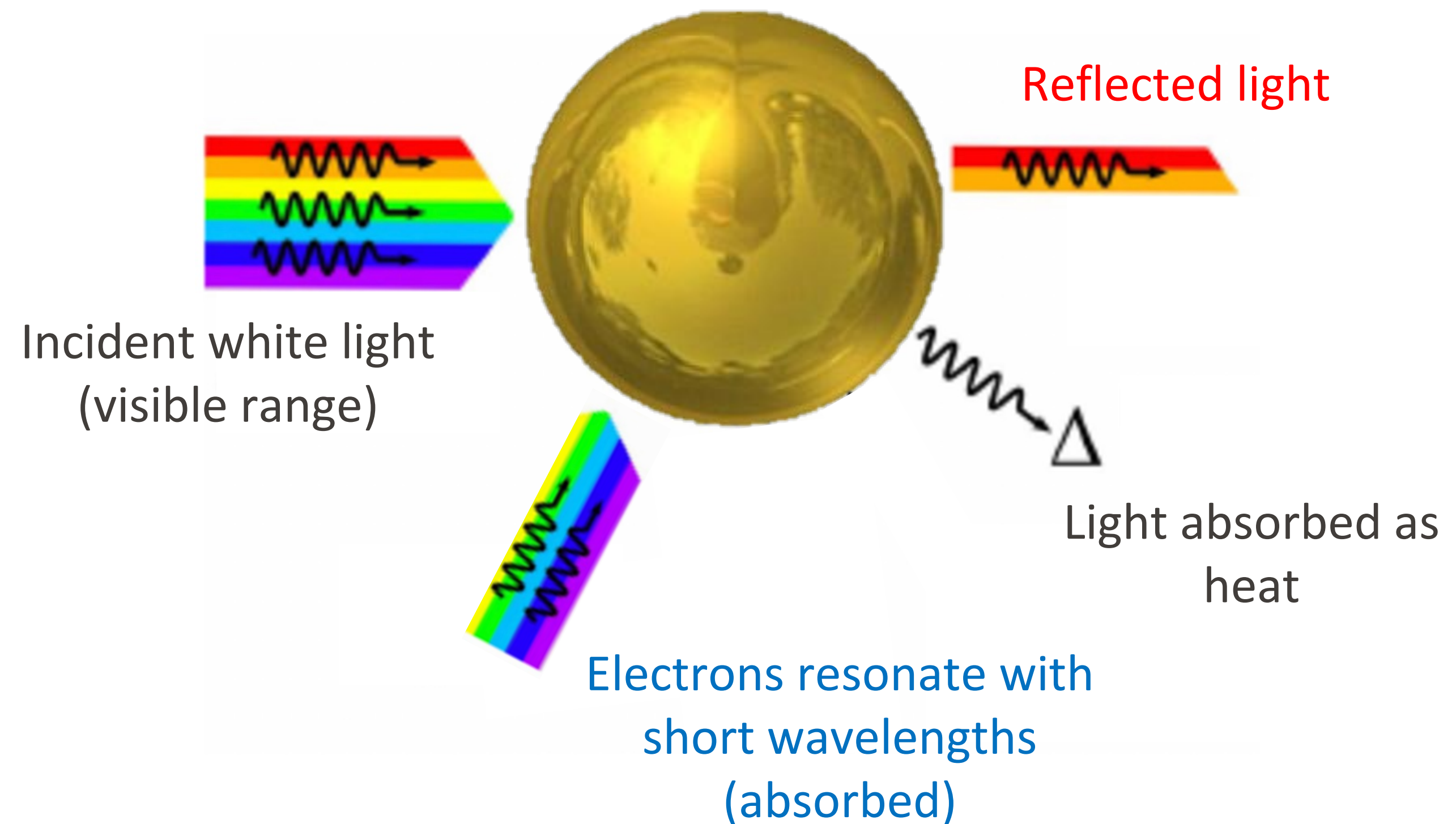
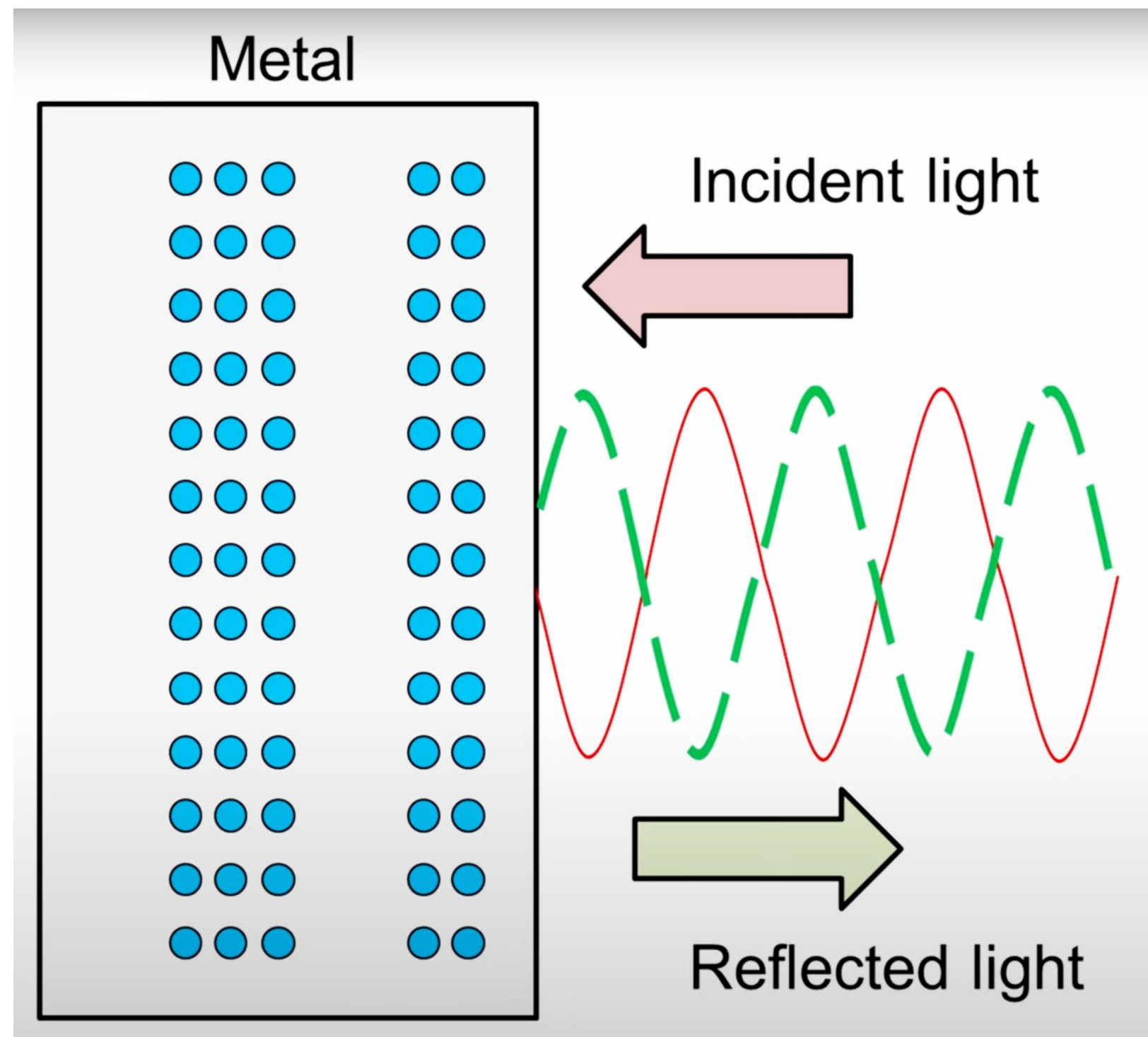


Electric field of incident light excites free electrons on metal surface



When all electrons oscillate collectively at the resonance frequency, they move as a polarized cloud = **plasmon**

How Do Electron Oscillations Lead to Different Colors?

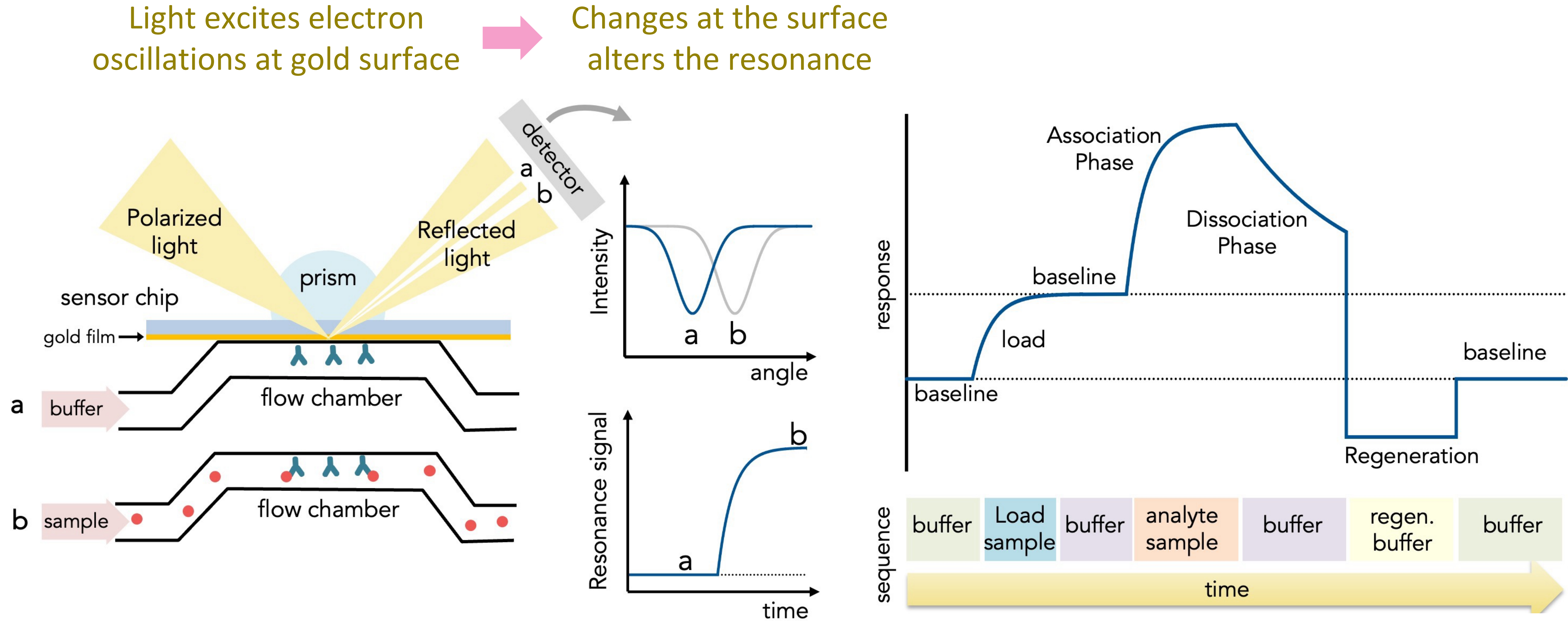


At **resonance frequency**, incident light energy transferred to oscillating electron cloud (**plasmon excitation**)

This is the frequency where nanoparticle most efficiently absorbs energy from incident light

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

Plasmons are the Basis of Surface Plasmon Resonance (SPR)



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

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

Resonance scatters
green wavelengths



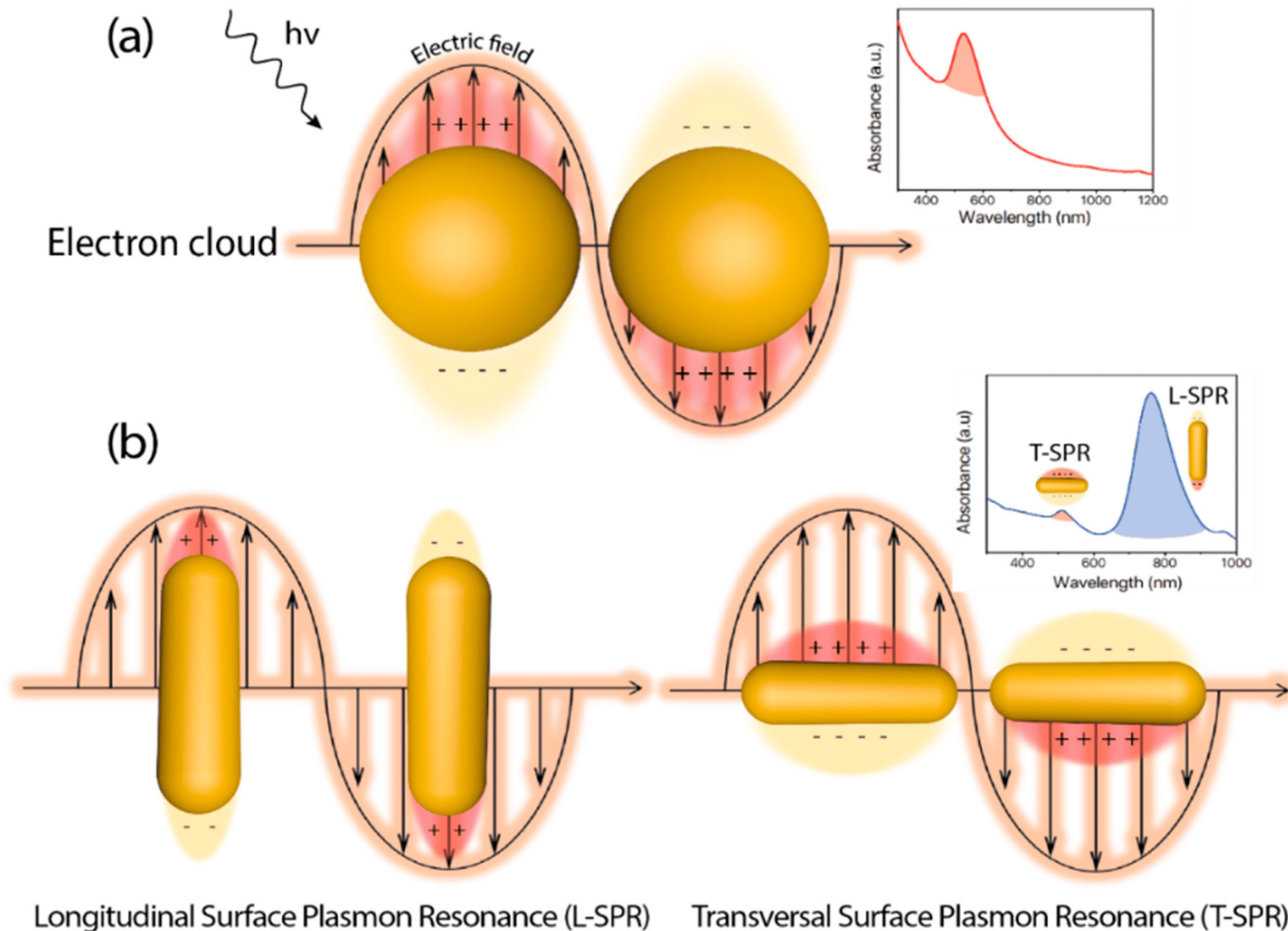
Lit from front
(reflection)

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



Lit from behind
(transmission)

Broader Color Range with Asymmetric Nanostructures



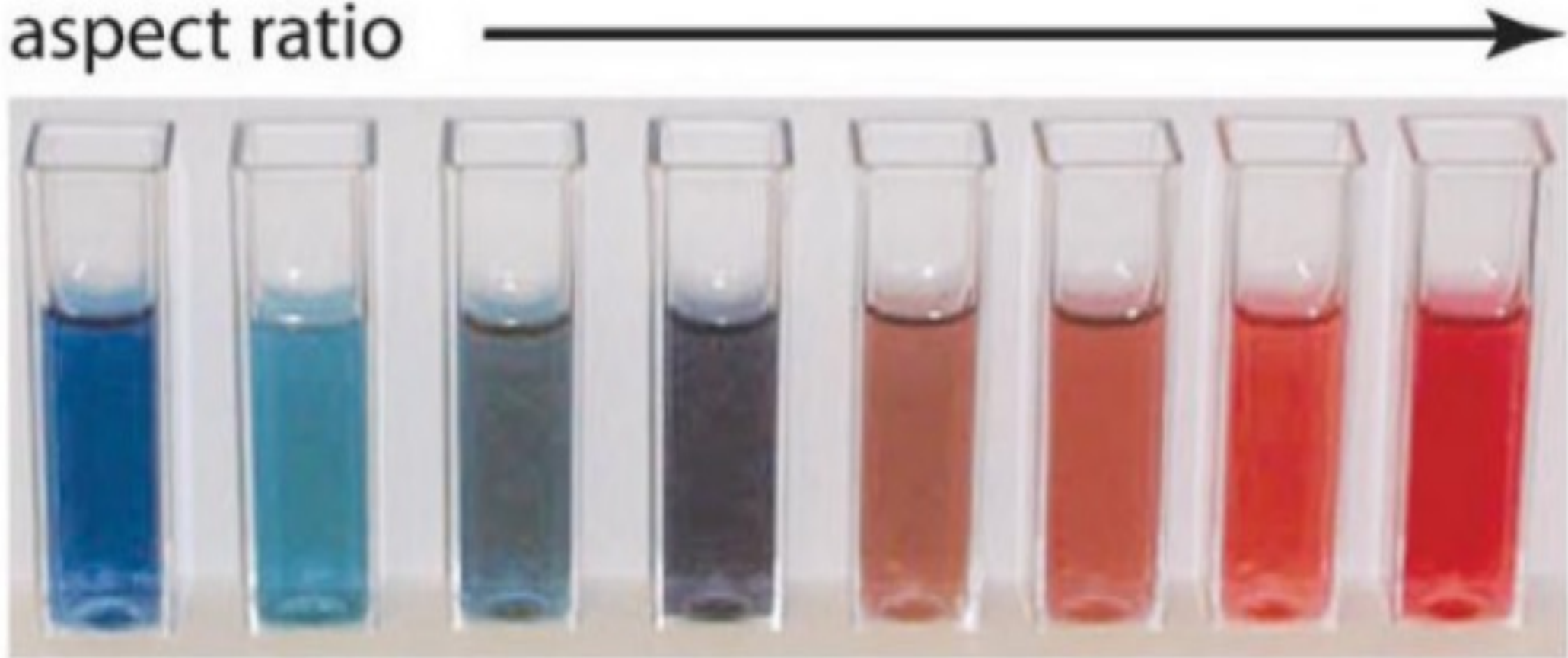
While nanoparticles are symmetric, **nanorods** are anisotropic (different resonant frequencies depending on aspect ratio leading to multiple plasmon resonances)

Broader Color Range with Asymmetric Nanostructures

Nanorods



50 nm



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

Nanoshells

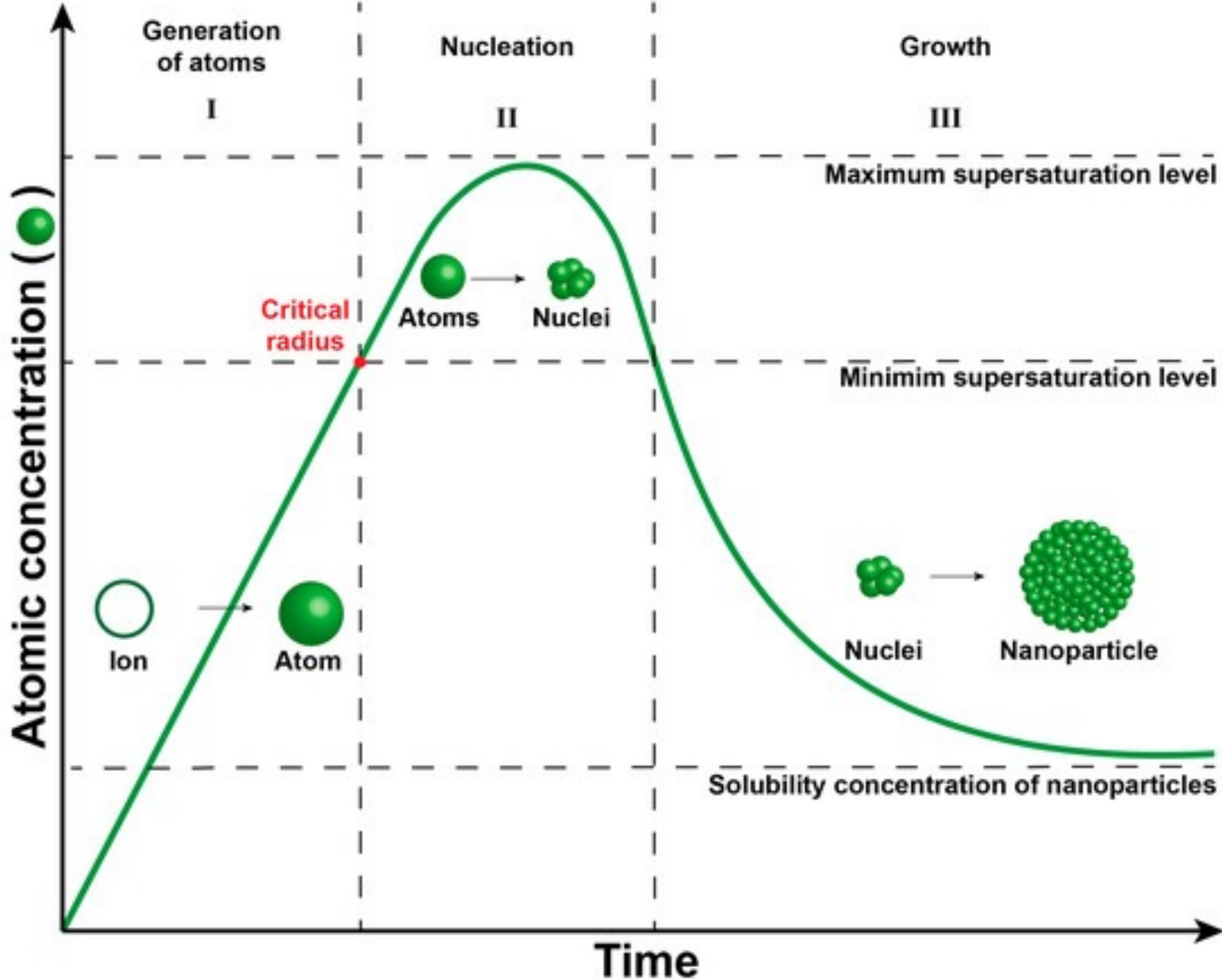


140 nm



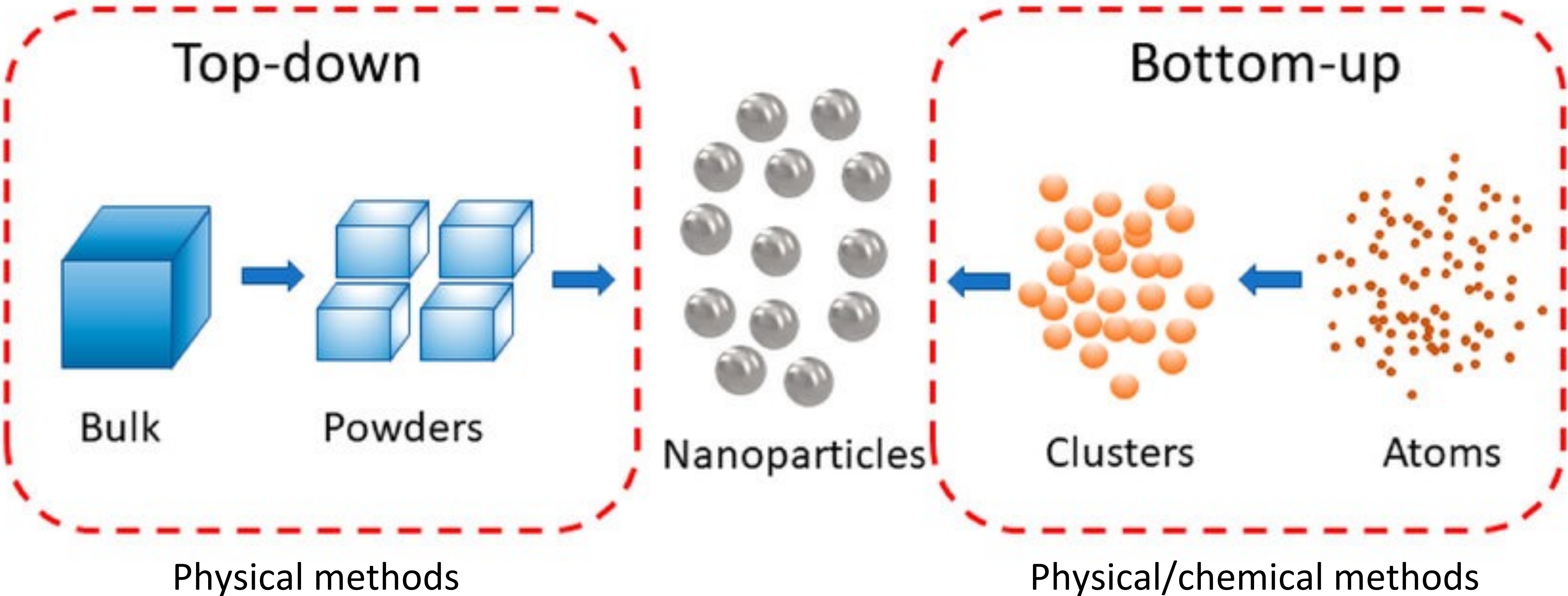
Nanoshells have inner and outer plasmon modes with tunable optical properties based on shell thickness

Nanoparticle Formation Stages – Nucleation vs. Growth



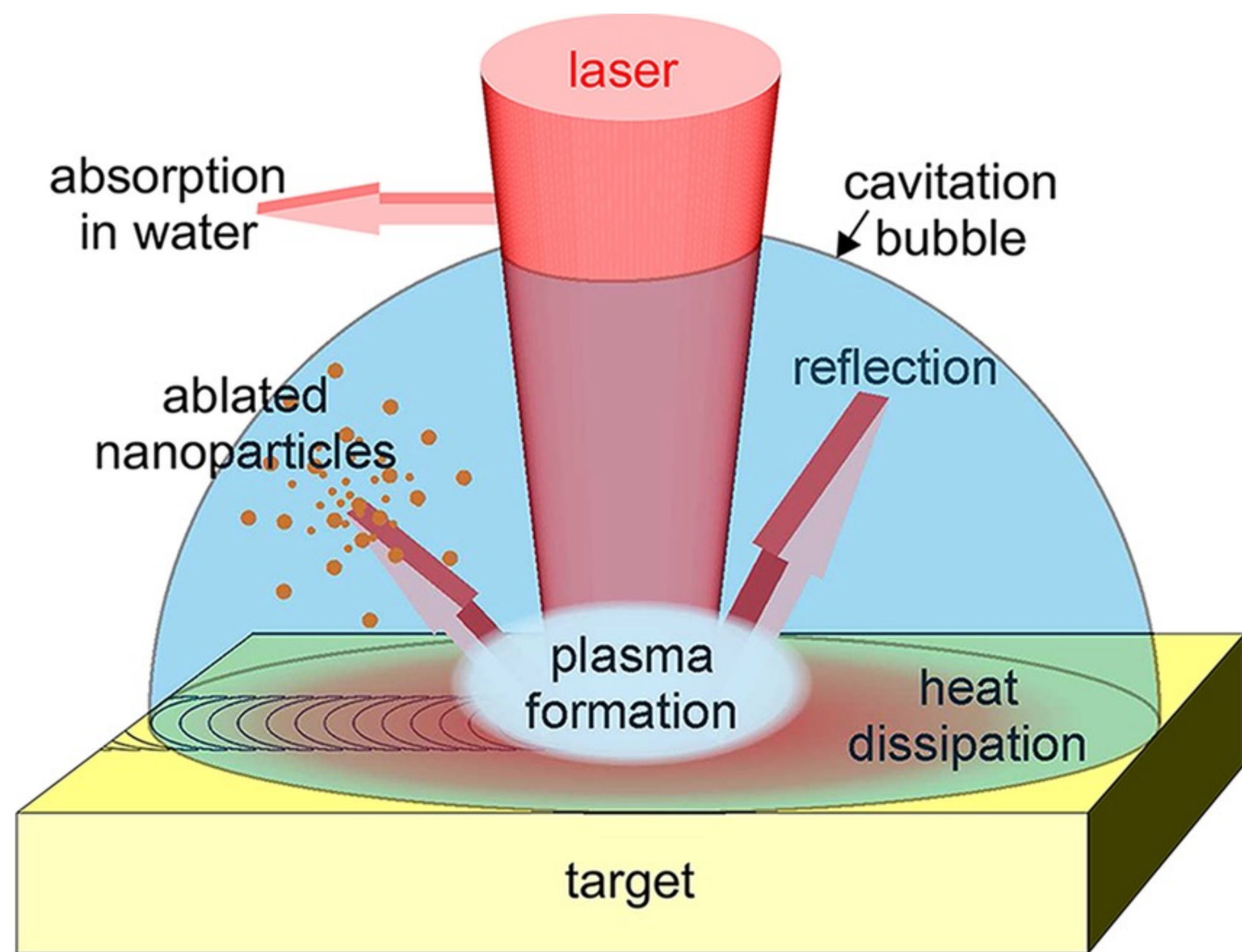
How to Synthesize Gold Nanoparticles?

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



How to Synthesize Gold Nanoparticles?

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



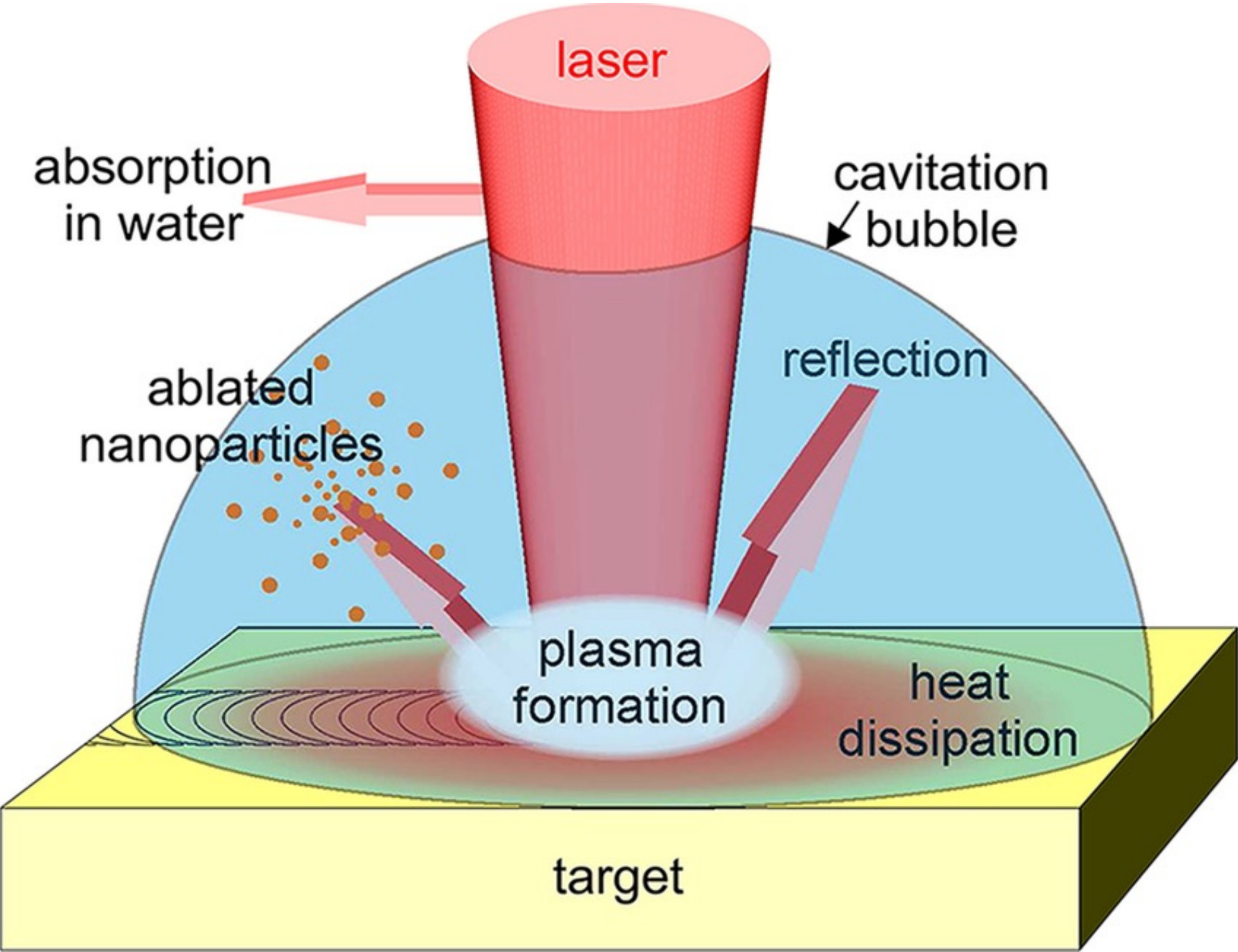
Physical methods

Laser ablation

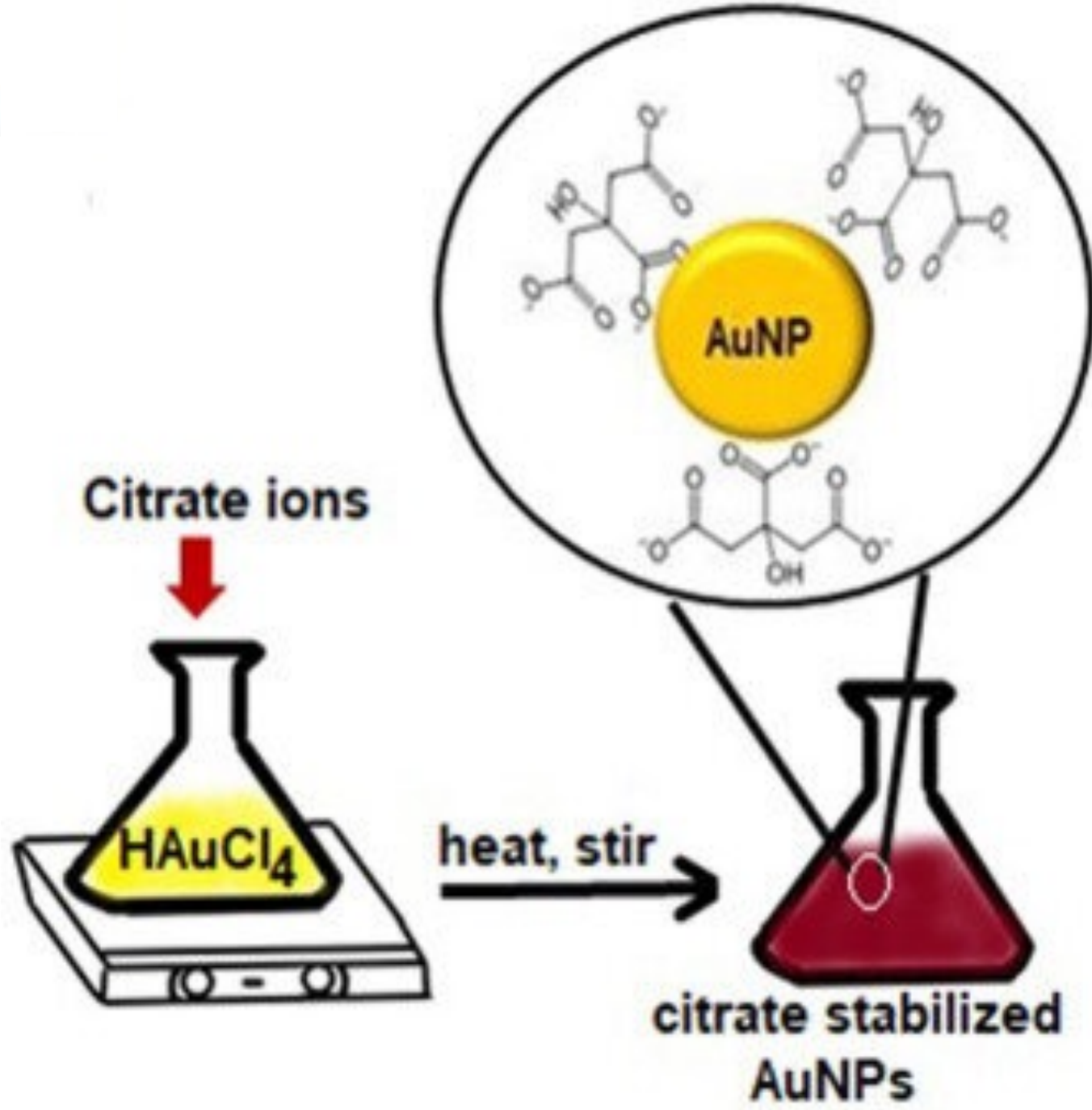


How to Synthesize Gold Nanoparticles?

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



Physical methods
Laser ablation



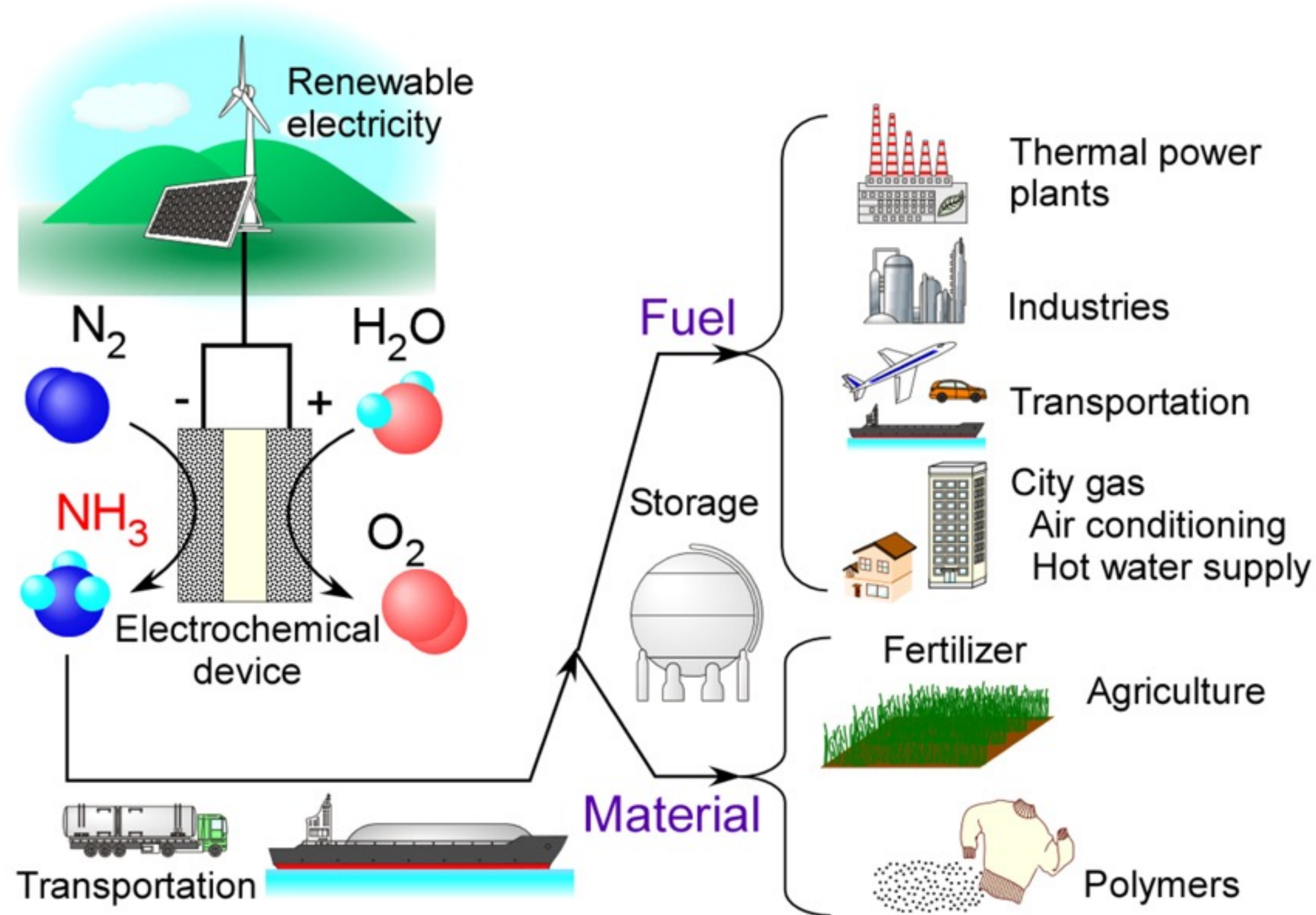
Physical/chemical methods
Turkevich method (citrate reduction)

Key Takeaways

- Electrons excited by light oscillate collectively to create plasmons
- Size and shape of metal nanoparticles defined by the absorbed wavelengths
 - Plasmons are the basis for SPR
 - Nanoparticles nucleate then grow to a finite size
- Nanoparticles can be synthesized from the top-down or bottom-up

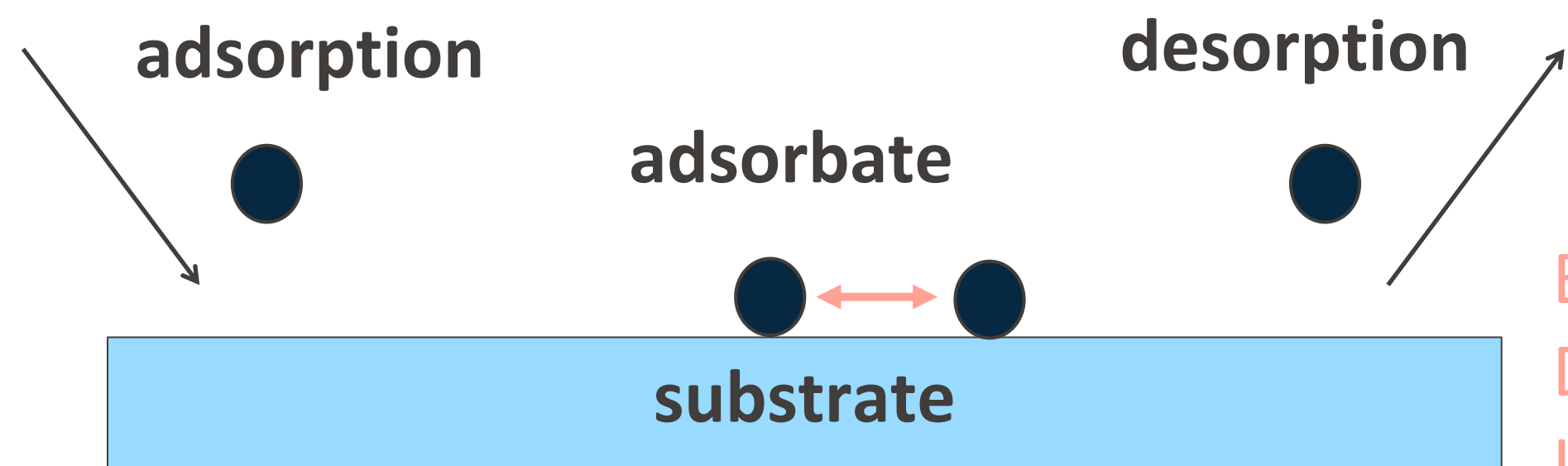
Importance of Catalysis: Sustainable Ammonia Synthesis

Catalysis is the increase in rate of a chemical reaction due to an added substance known as a **catalyst**. Catalysts are not consumed by the reaction and remain unchanged after it.



Catalysis is a surface phenomenon

Different Interactions on Surfaces Influence Catalysis



Interaction between adsorbate and surface depends on coverage (θ):

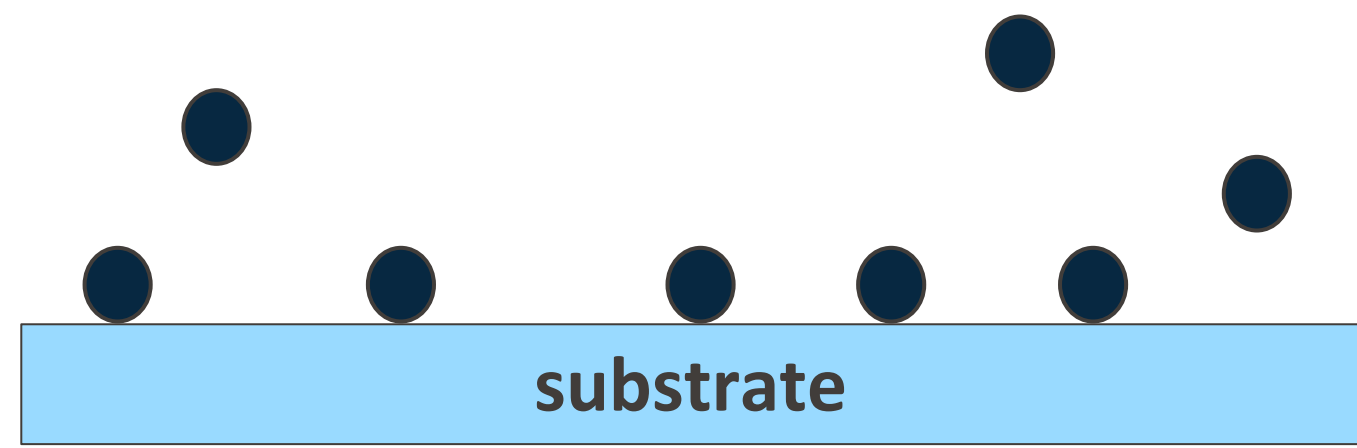
$$\theta = \frac{\text{Number of occupied adsorption sites}}{\text{Number of adsorption sites present}}$$

- Electrostatic interactions
- Direct adsorbate interactions
- Local induced surface perturbations

- $\theta = 0$ clean surface
- $\theta = 1$ monolayer

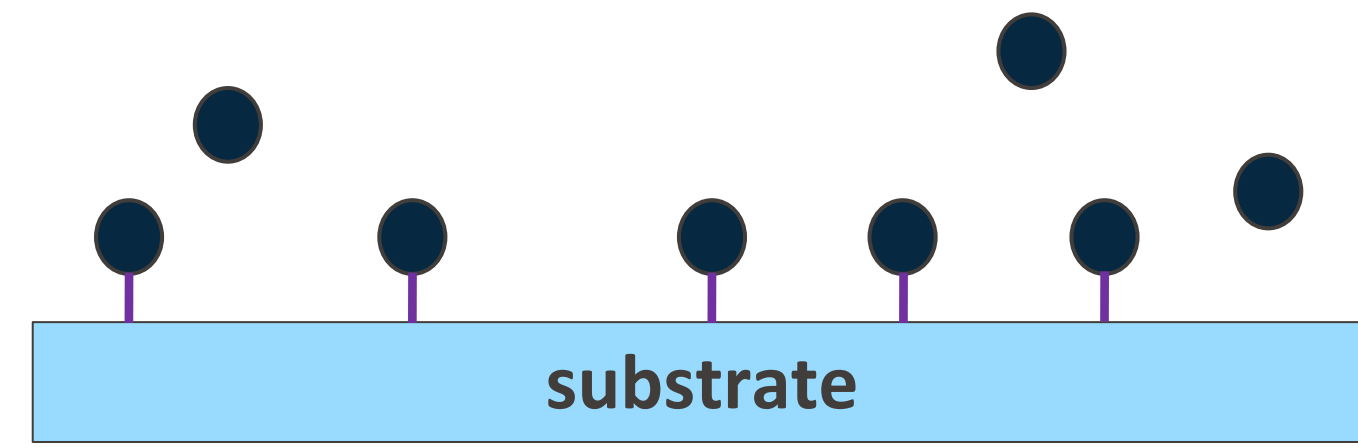
Adsorption = Physisorption

Electrostatic interaction (charge transfer)
 non-specific and weak
 multilayer growth possible

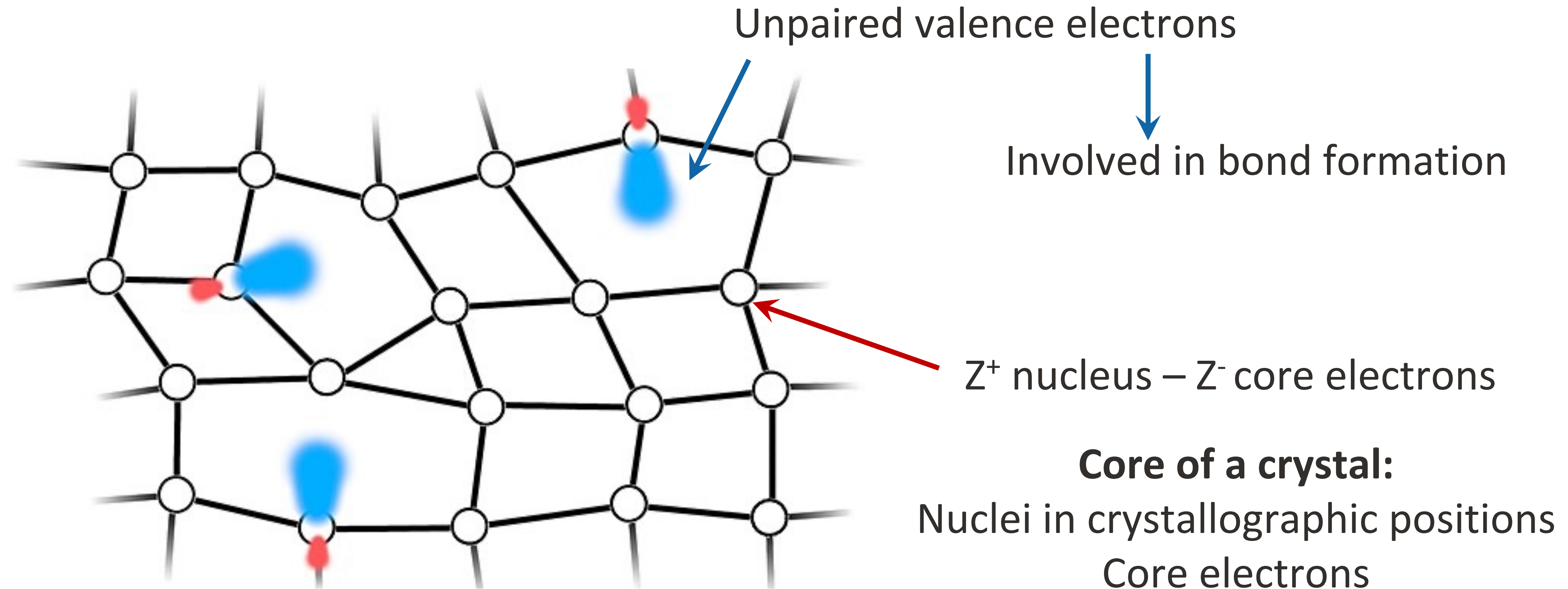


Absorption = Chemisorption

Geometrically defined interaction
 Chemical bond between adsorbate and substrate
 maximum coverage is 1 monolayer ($\theta = 1$)

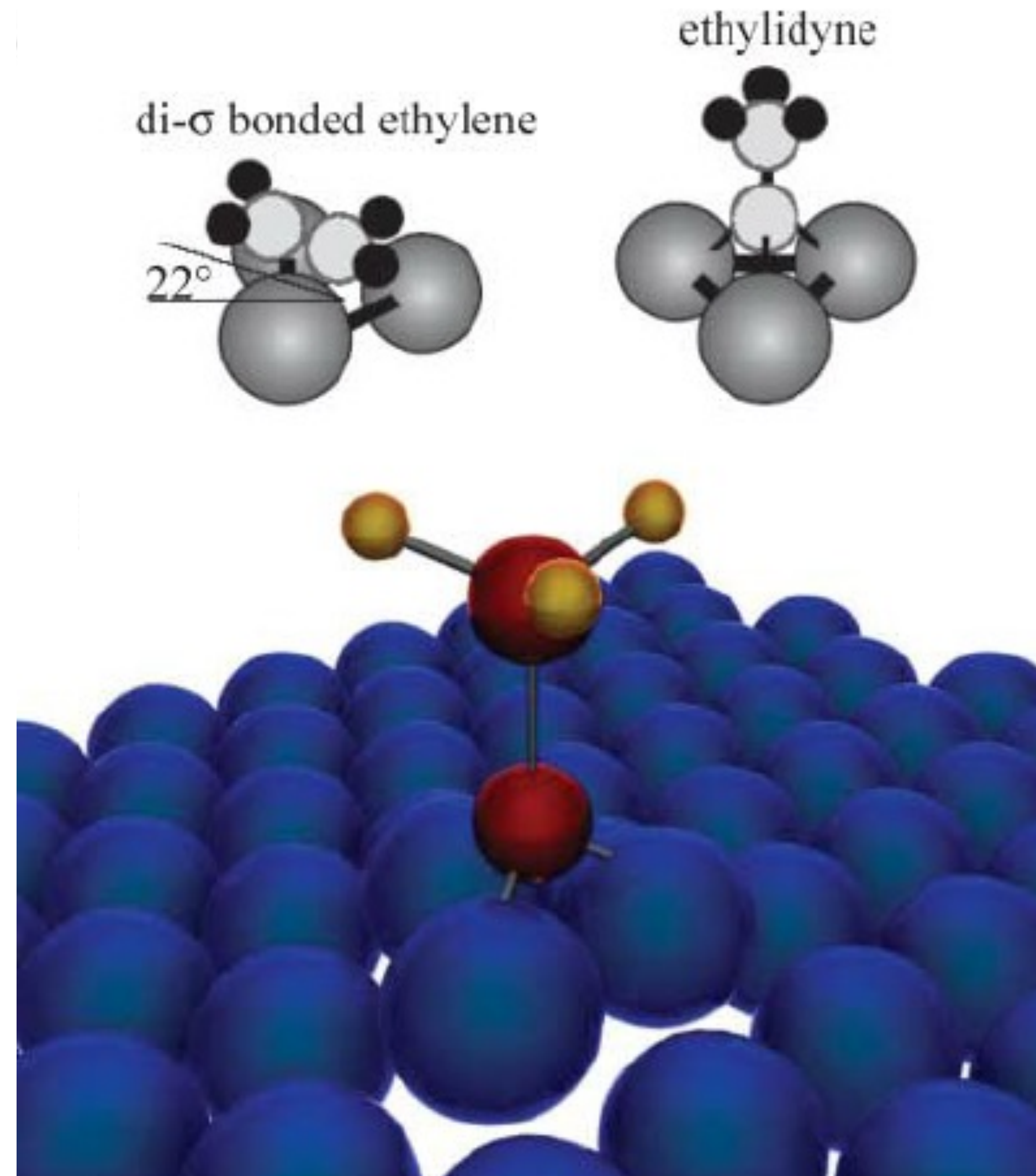


Why Surfaces are Reactive: Intrinsically Dipolar



Since they are dipolar → form bond → driver for absorption

Chemical Bonds of Molecules Rely on Symmetry and Geometry

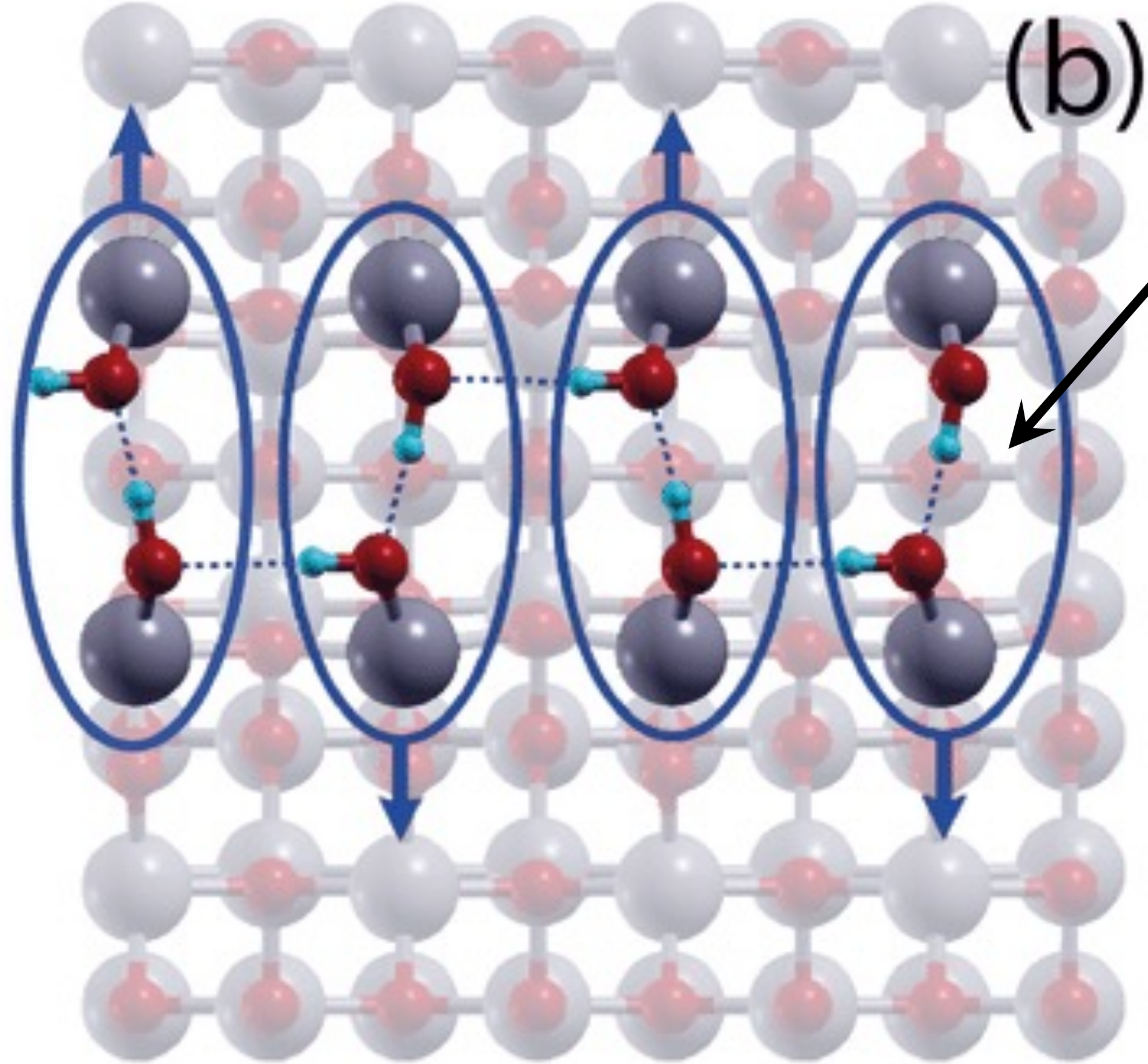
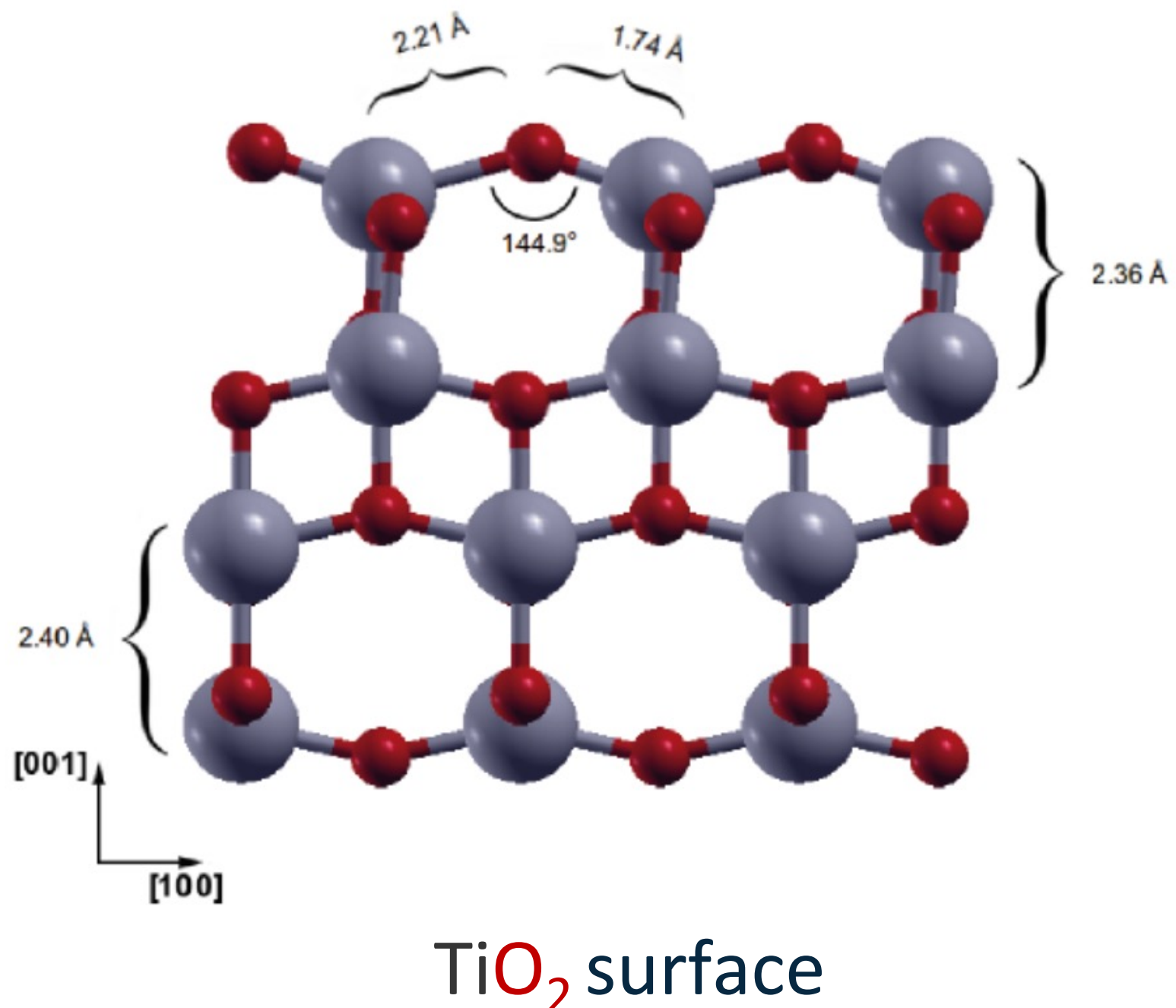


Pt (111)

The way a molecule sits on the surface (orientation, symmetry, bonding configuration) influences catalytic reactions

Reconstruction of “Soft” Surfaces Due to Absorption

Adsorbates can induce surface reconstructions – reshape surface and alter electronic structure

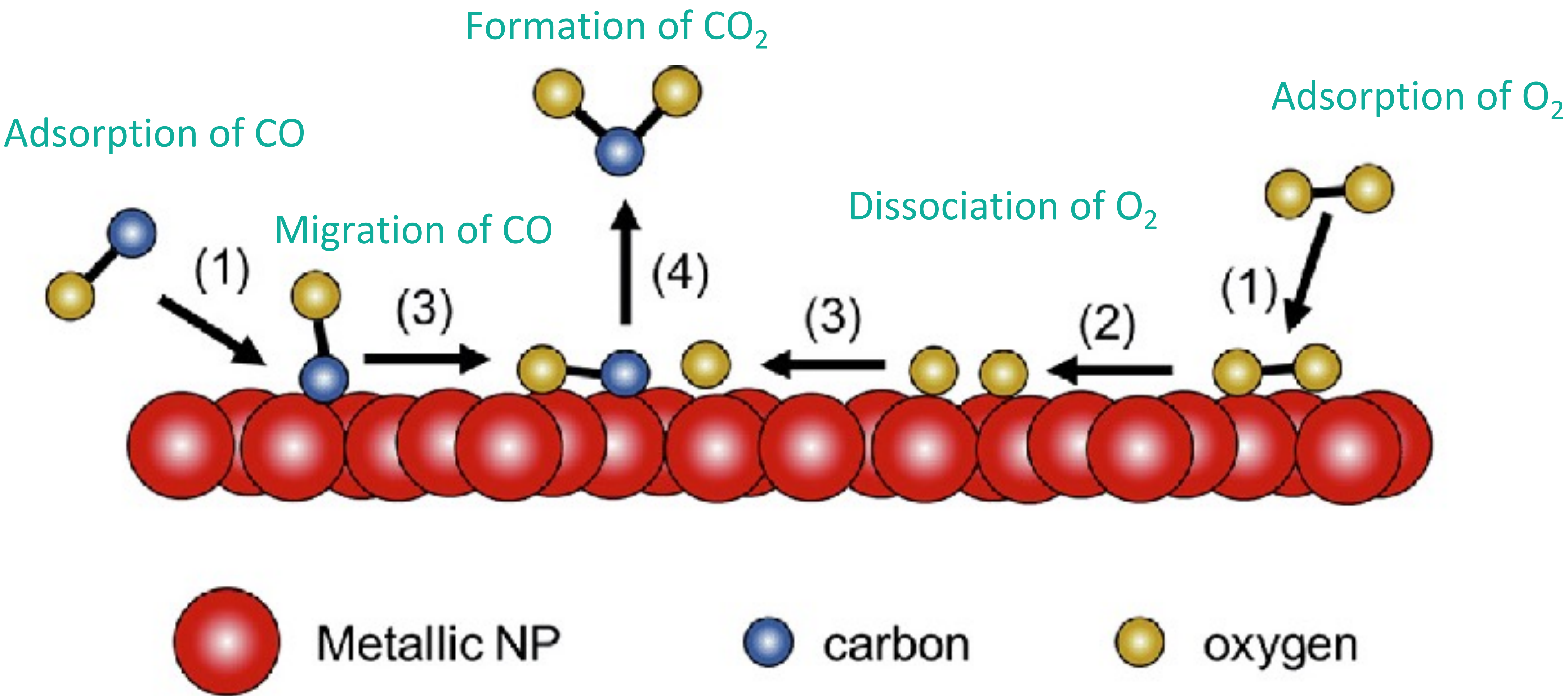


Absorb on surface and pull the surface based on intermolecular forces

H₂O-induced reconstruction

Interaction different from facet to facet (ledge vs. kink. vs. terrace)

How Surfaces Serve as Catalysts: Adsorption + Dissociation

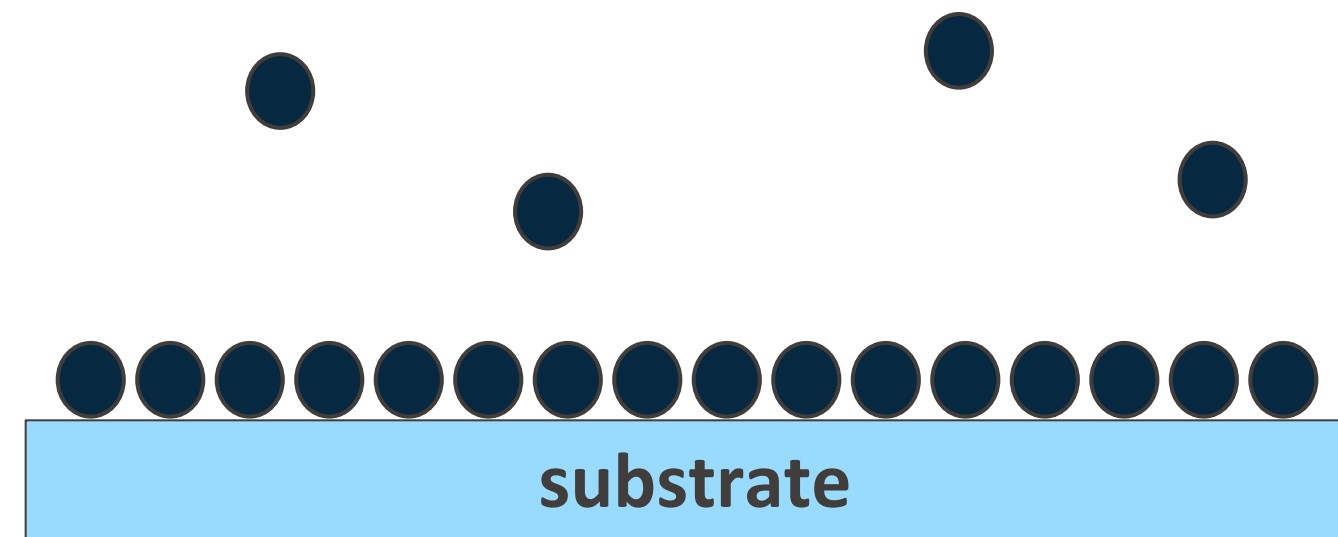


How can Surfaces Serve as Catalysts?

1. Locally enhance the concentration of reactants

Physisorption

Van der Waals interactions between adsorbate and substrate (non-specific and weak)



$$C_R^{\text{Surface}} \gg C_R^{\text{Solution}}$$

$$P(t) = K_a \times C_R$$

Rate of product formation over time (mol L⁻¹ s⁻¹)

Rate of adsorption (s⁻¹)

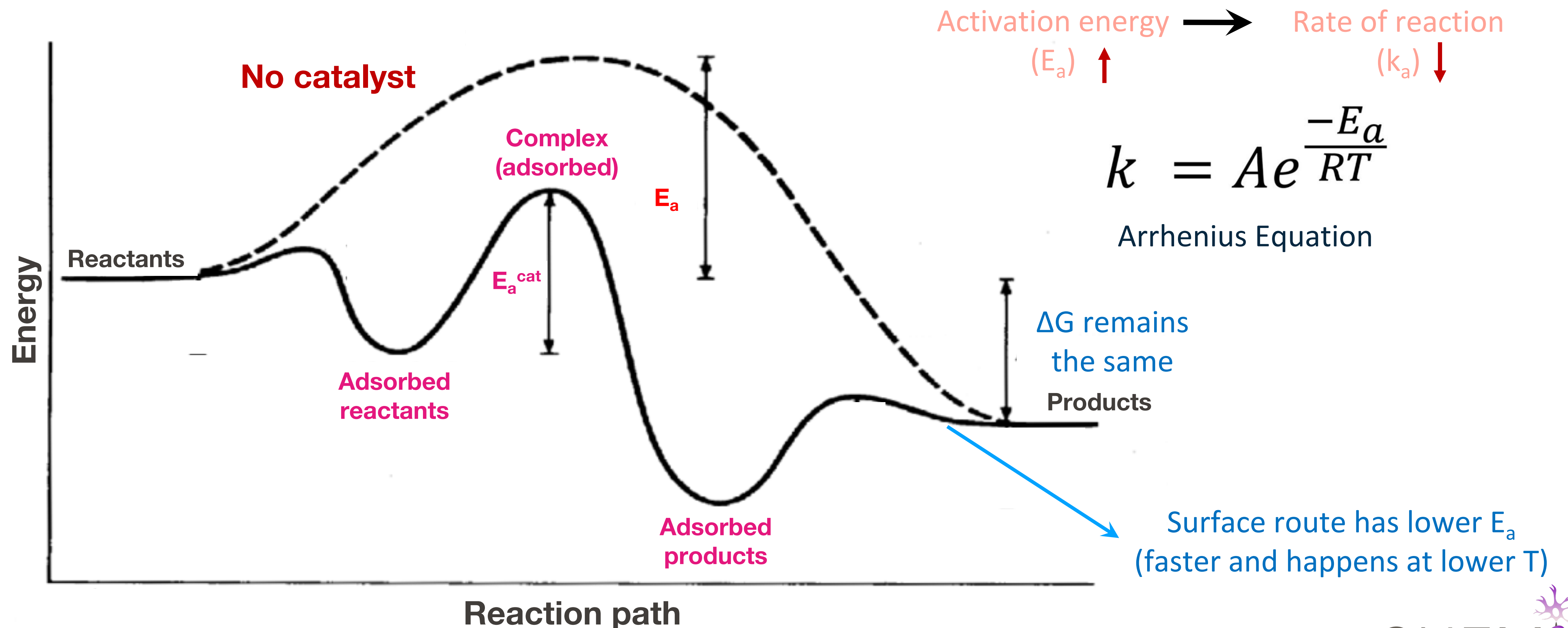
Concentration of reactant (mol L⁻¹)

Adsorption increases encounter frequency

How can Surfaces Serve as Catalysts?

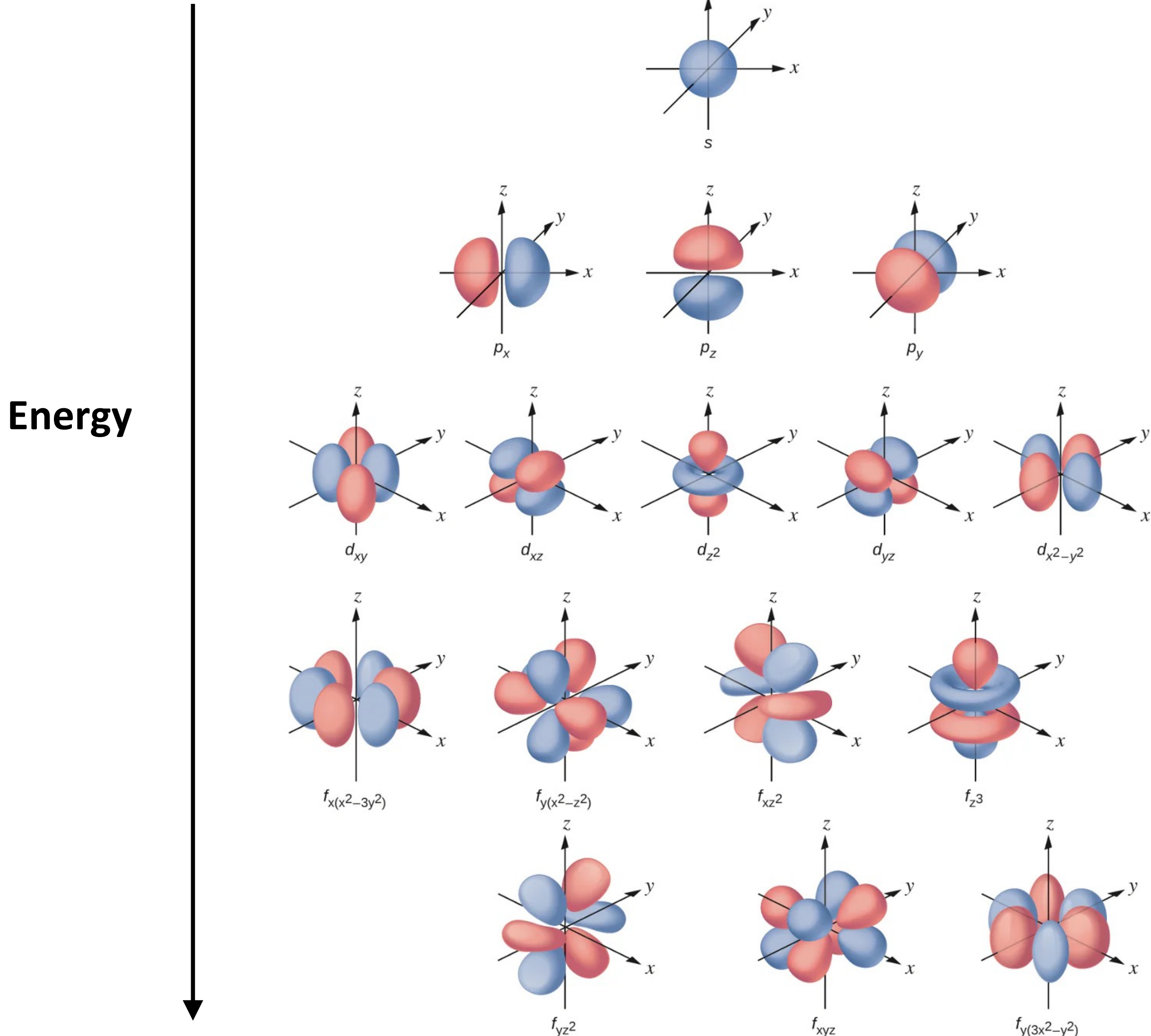
2. Surface bonds can change the energy landscape of the reaction, lowering activation energy

Rate of catalysed reaction: function of E_a , T , number of active sites on catalyst surface, surface concentration of reagents



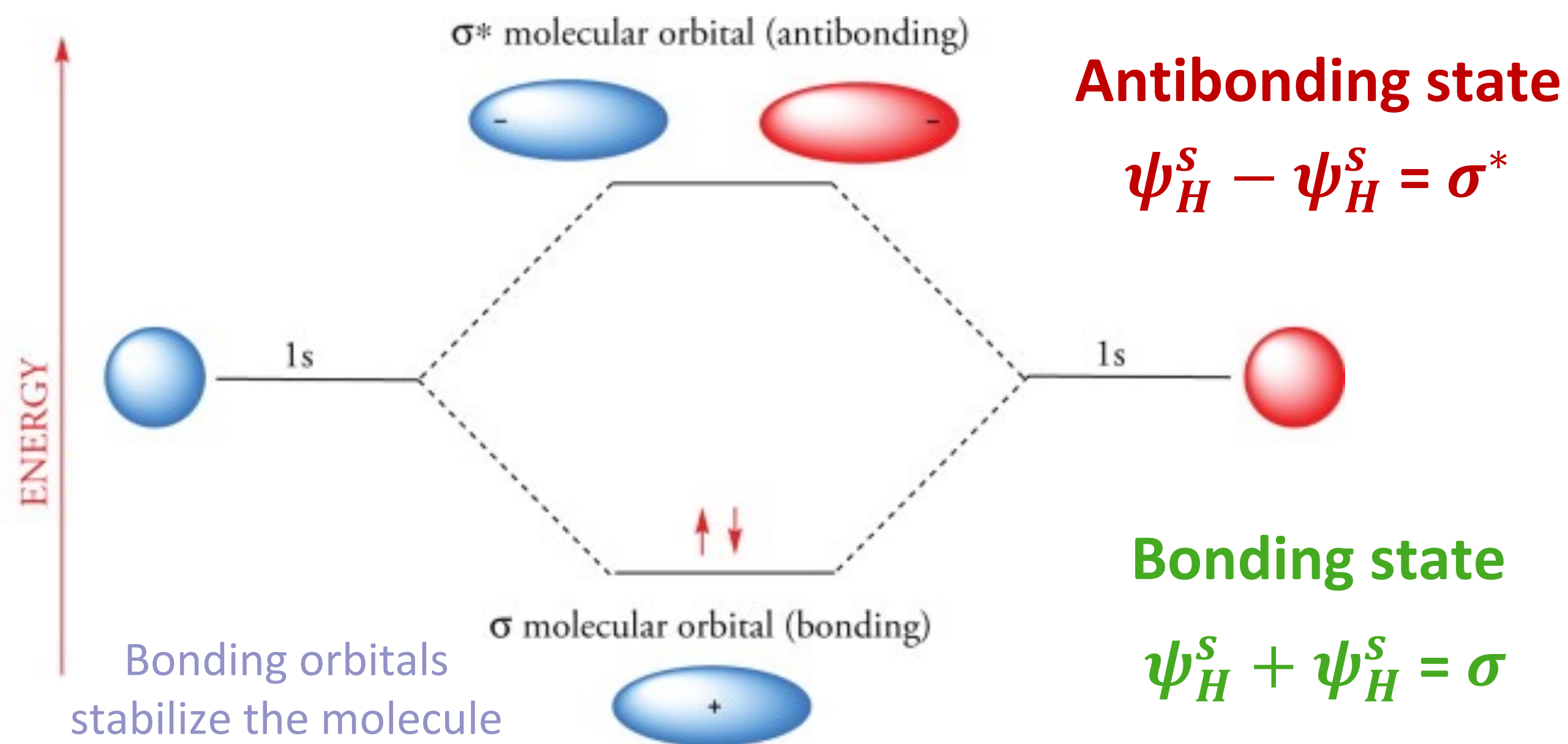
Electronic Configuration and Molecular Orbitals

Orbital: region in an atom or molecule where there is high probability of finding an electron



Catalysis depends on how surface orbitals interact with molecular orbitals

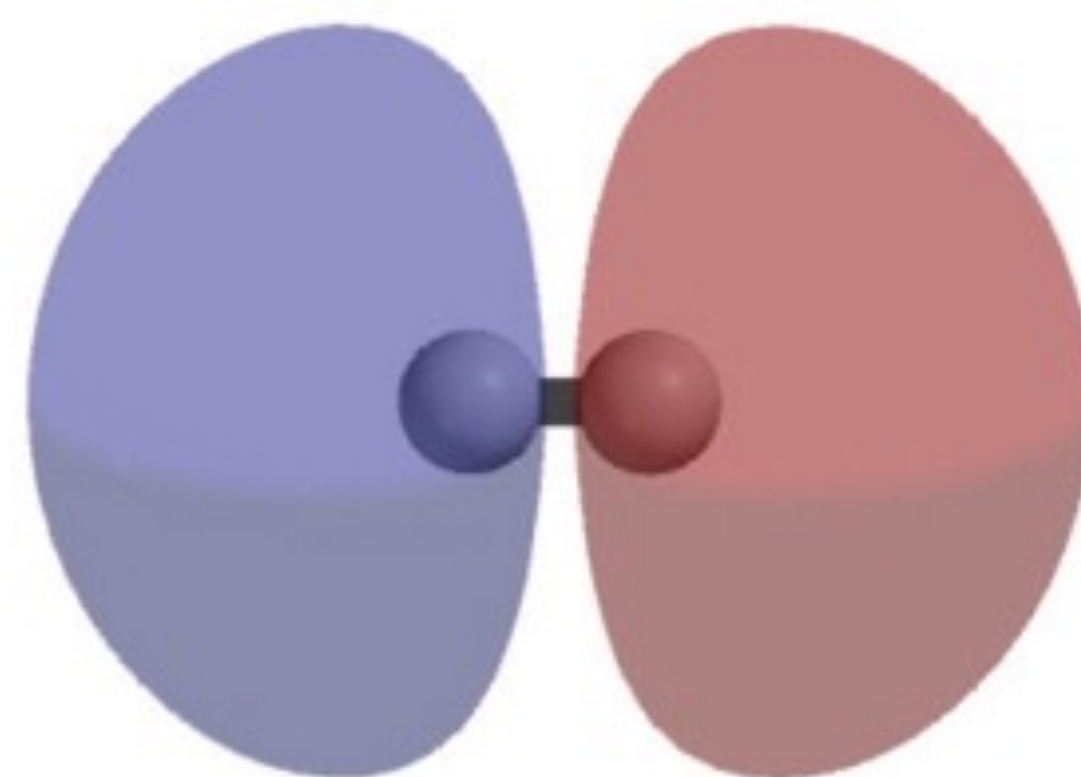
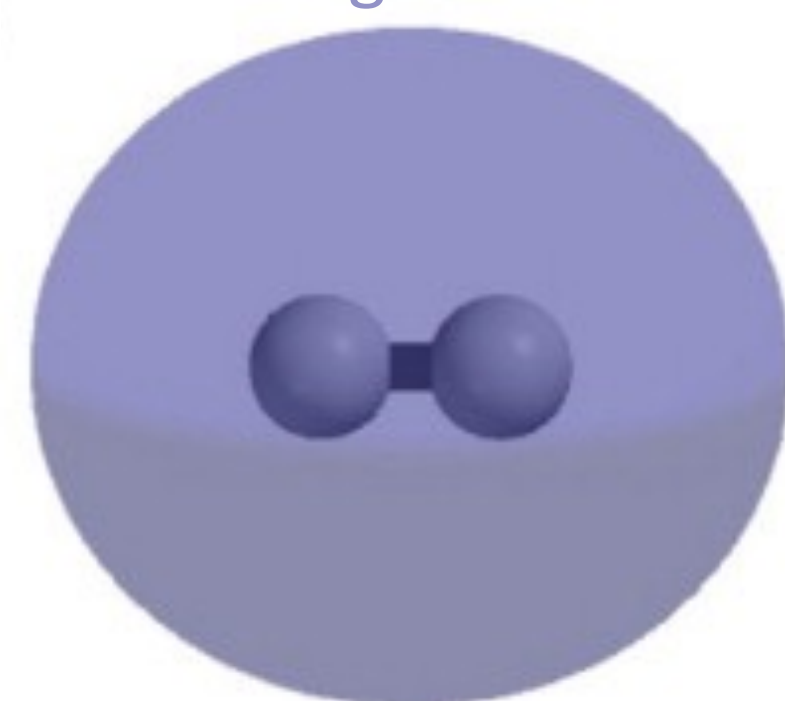
Molecular Orbital Diagrams and Bond Order



*Don't forget the Pauli exclusion principle

$$\text{Bond Order} = \frac{\# \text{ Bonding } e^- - \# \text{ Antibonding } e^-}{2}$$

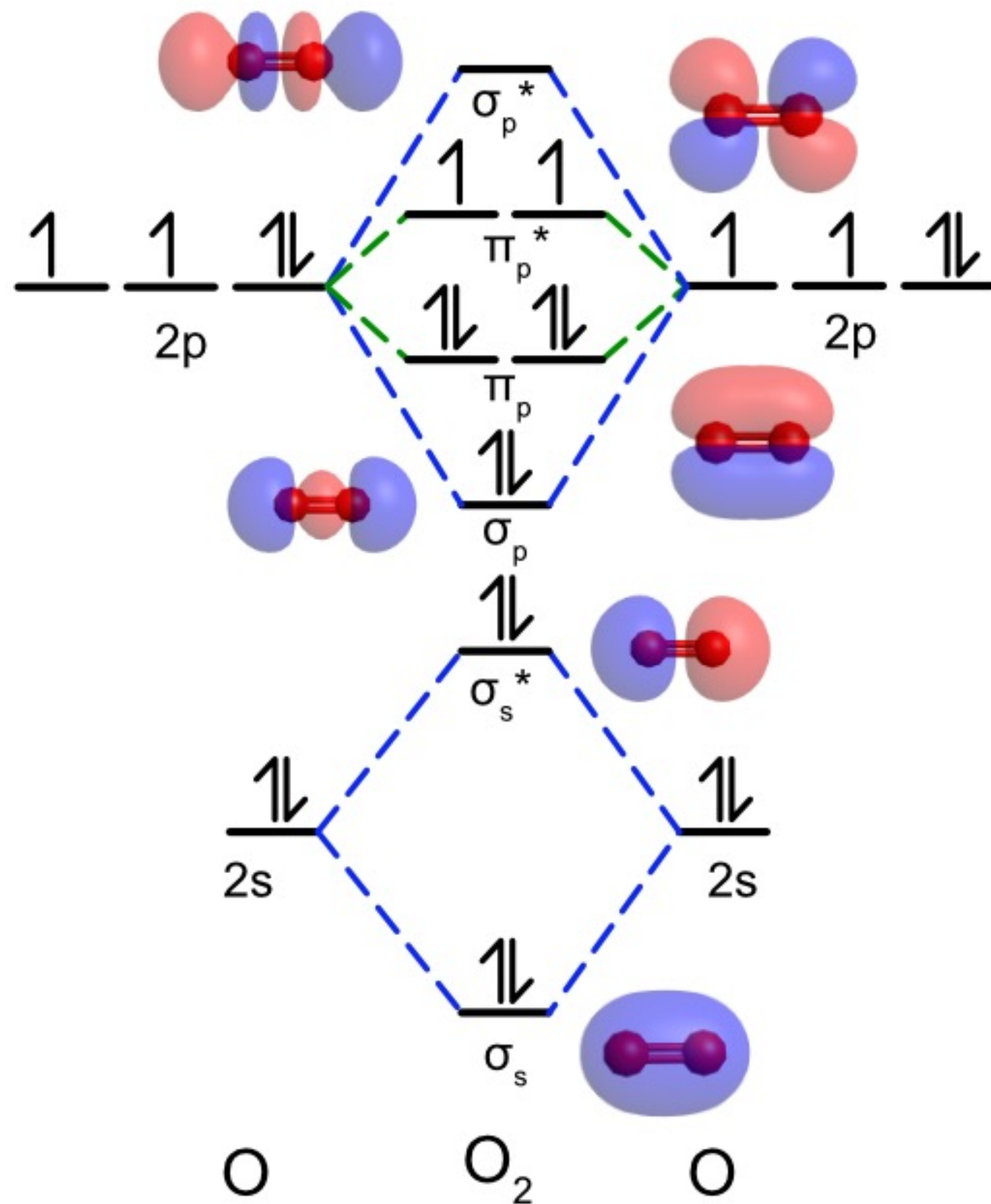
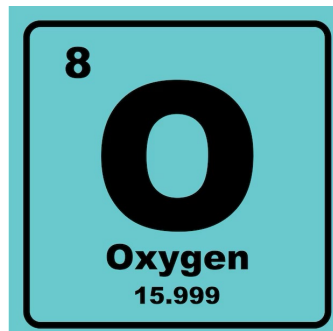
$$\text{Bond Order} = \frac{2 - 0}{2} = 1$$



Antibonding orbitals have electron density that pulls nuclei apart, destabilizing the molecule = weaker bonds

H - H

Molecular Orbital Diagrams and Bond Order



$$\text{Bond Order} = \frac{\# \text{ Bonding } e^- - \# \text{ Antibonding } e^-}{2}$$

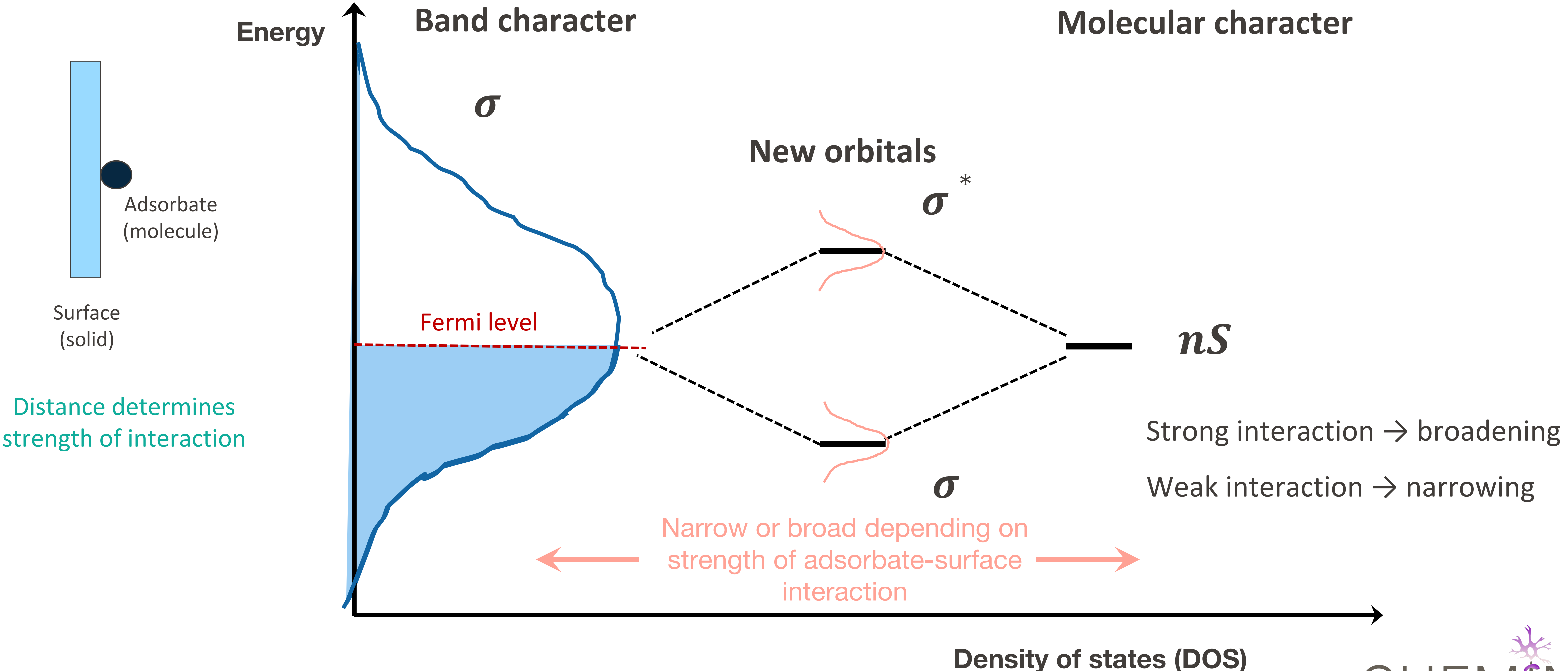
$$\text{Bond Order} = \frac{10 - 6}{2} = 2$$

$$O = O$$

Surfaces can stabilize antibonding orbitals,
lowering the barrier for bond cleavage

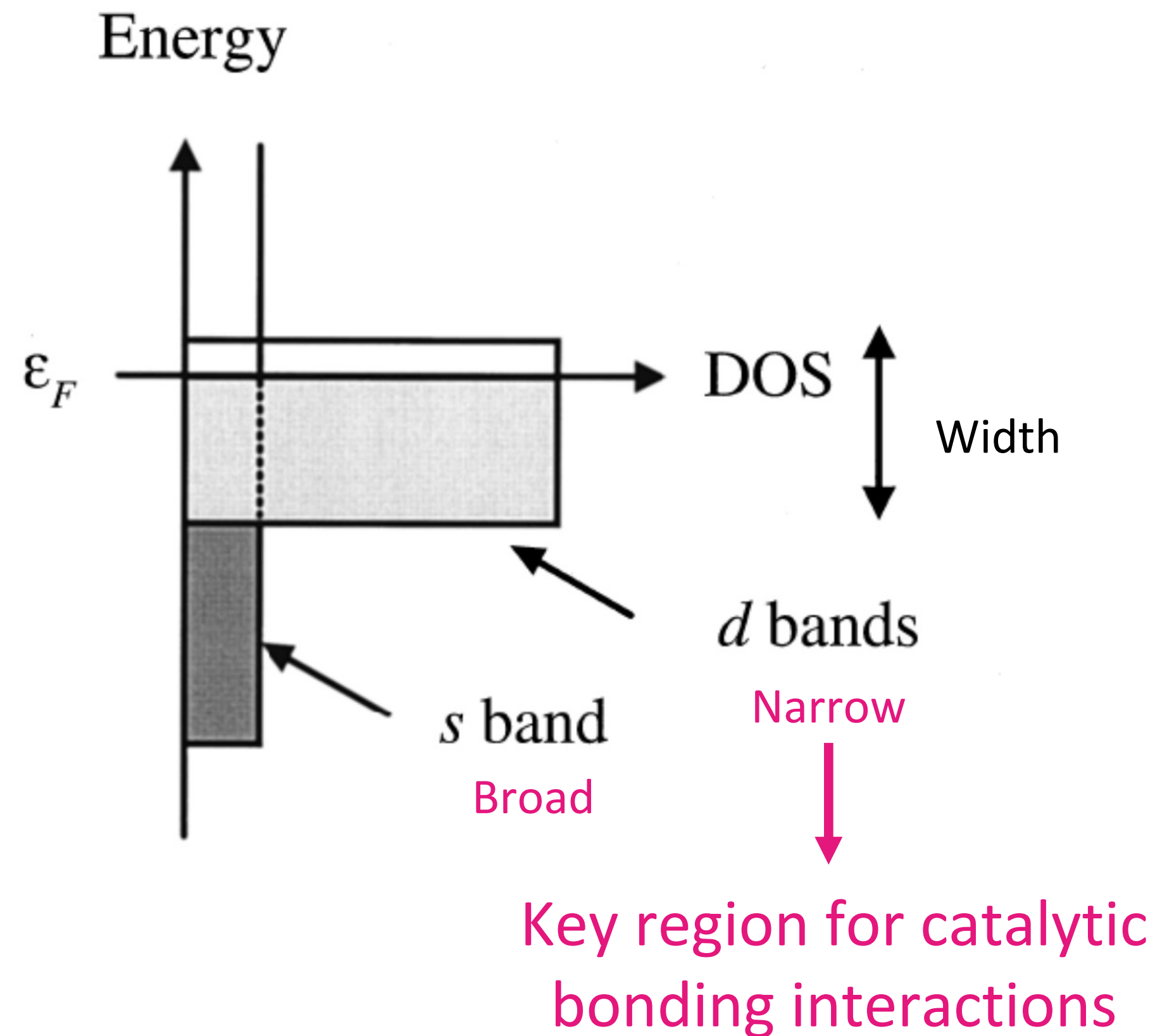
Bonding at Surfaces = Orbital Mixing

Surface bond = Molecular orbital between band of surface + orbitals of adsorbate

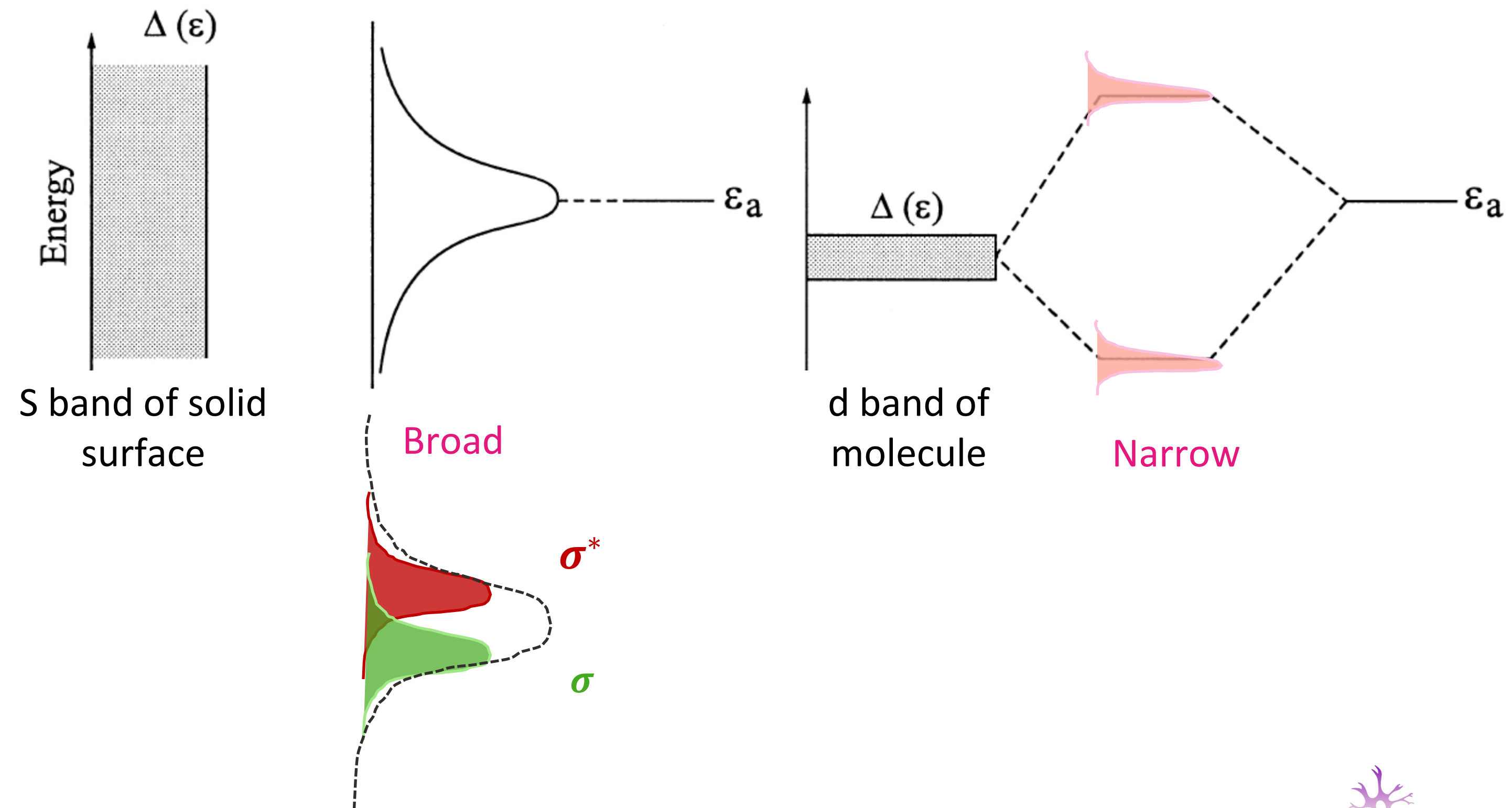


Bonding at Surfaces – Density of States (DOS) of Transition Metals

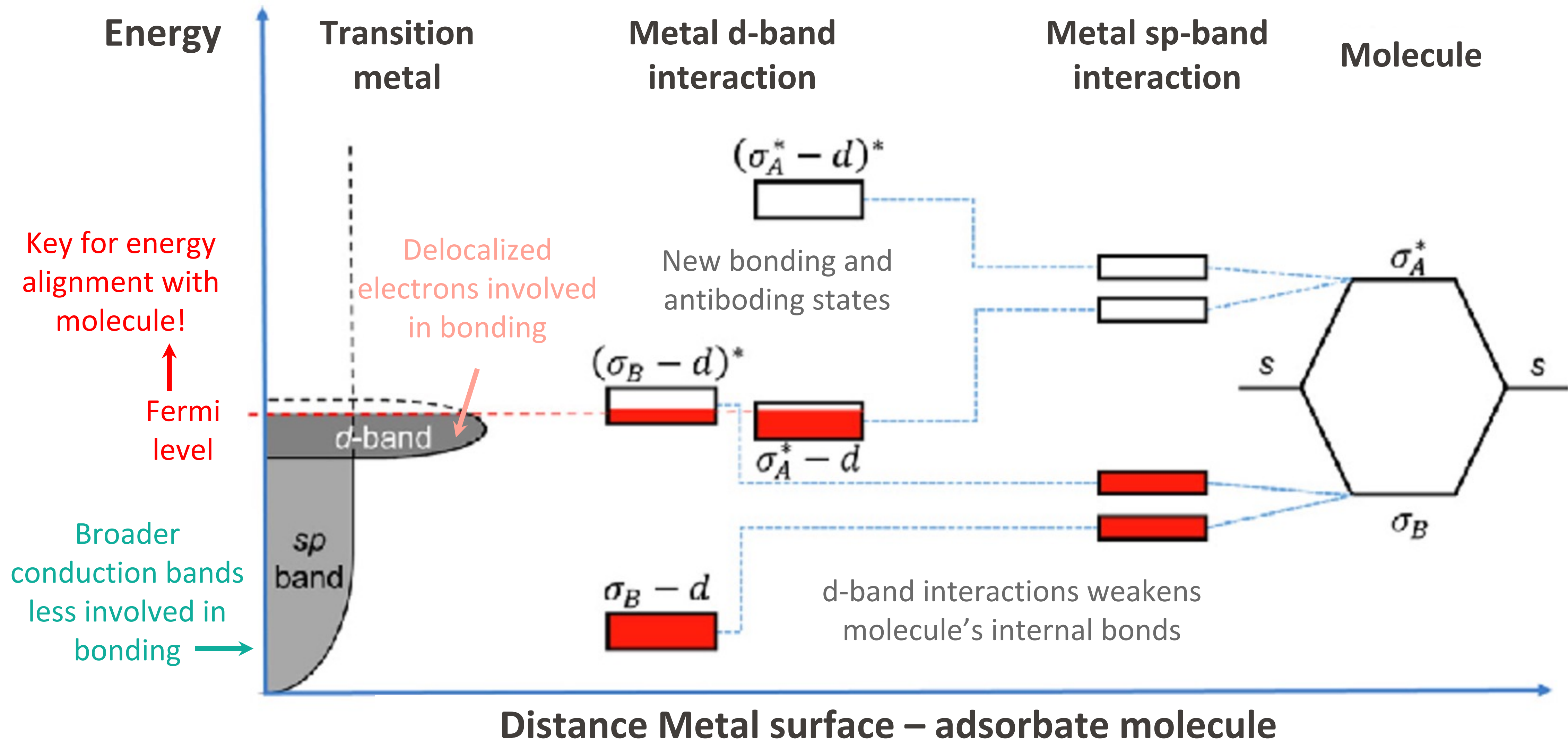
Transition metals have **d-bands** that play a critical role in catalysis by interacting with molecular orbitals



Mixing molecular orbital with **s-band** of solid surface



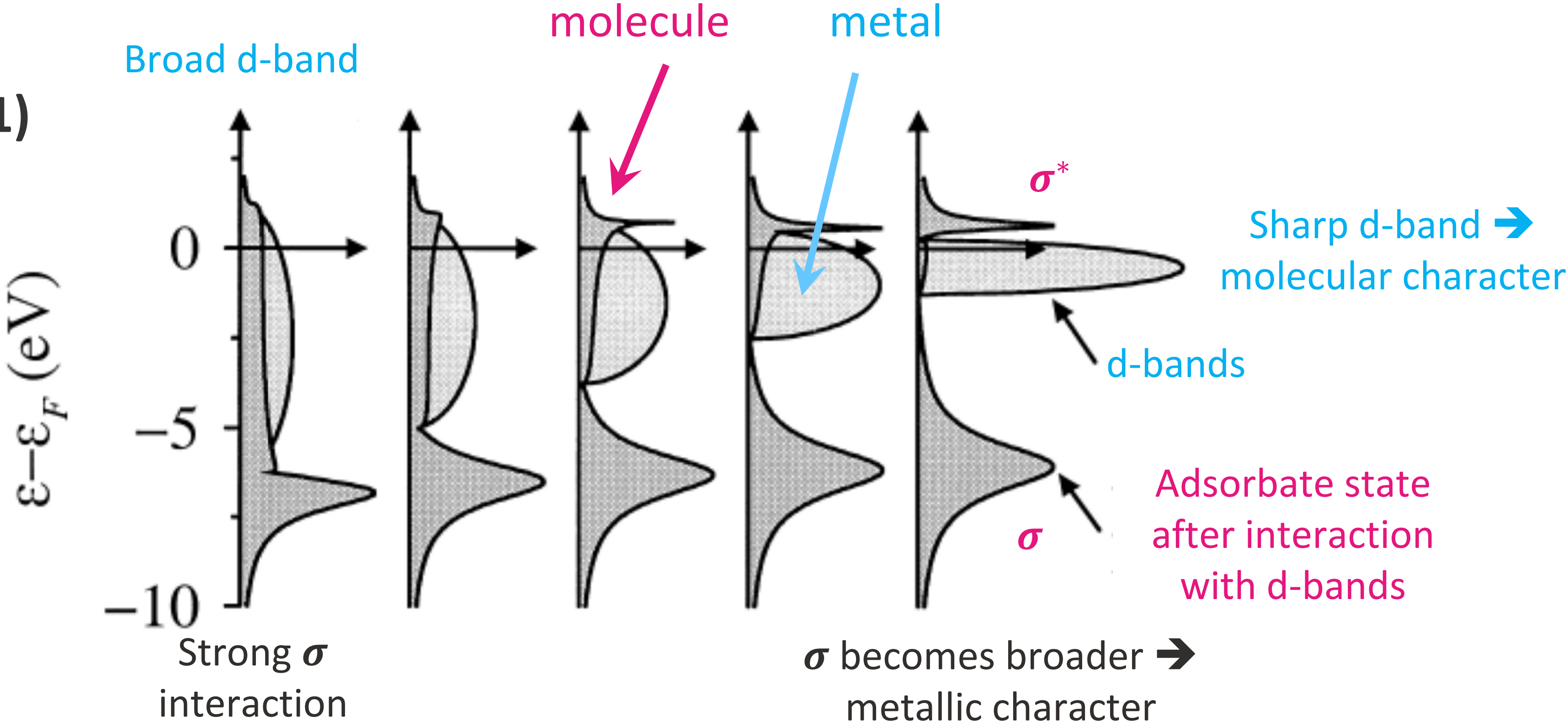
Molecular Orbital Interactions on Transition Metal Surfaces



Strength of Bonding on Surfaces

Adsorption strength depends on orbital overlap—broad bands promote metallic character, while sharp bands retain molecular character

Oxygen on Pt(111)



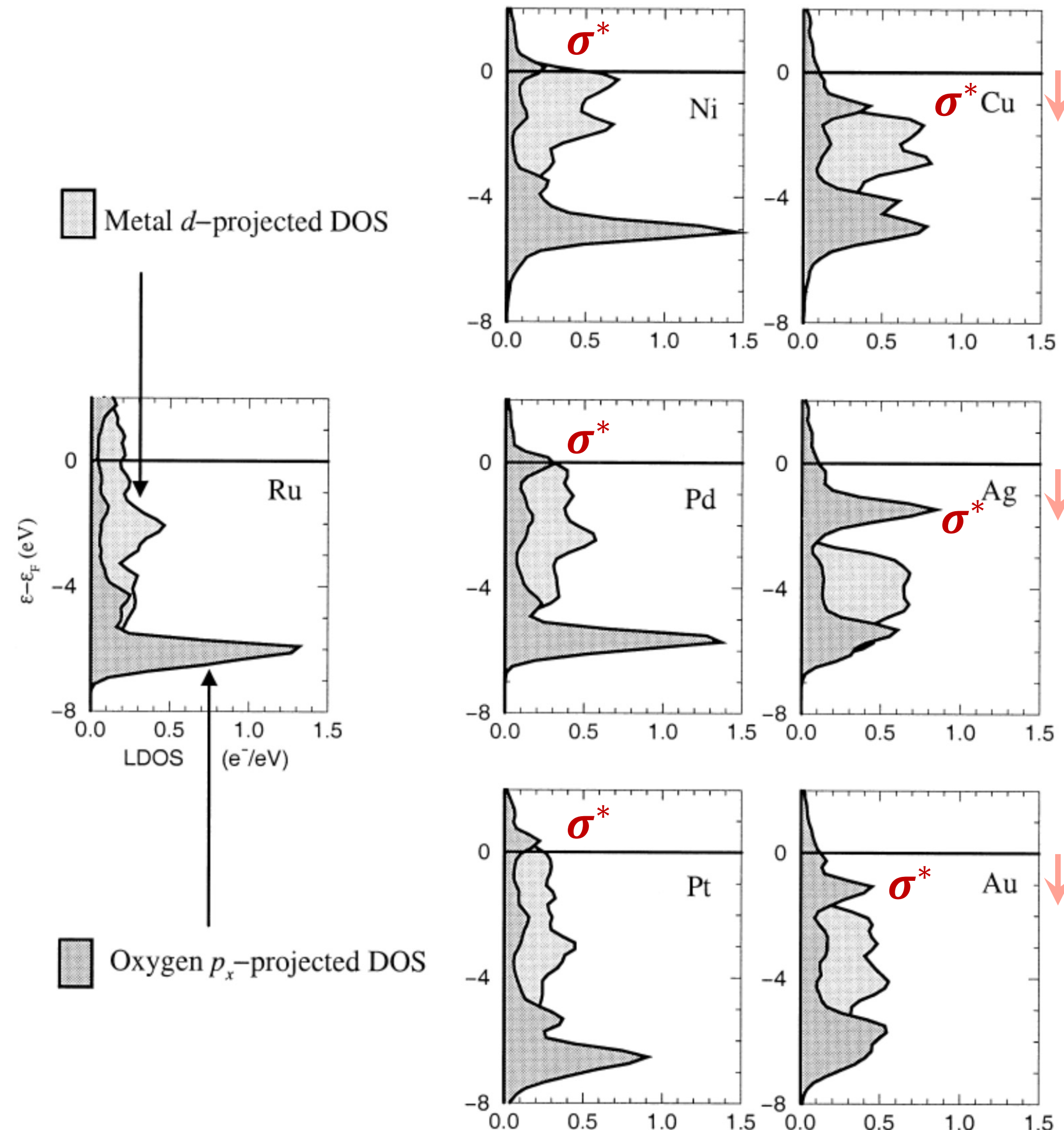
Weak chemisorption

Strong chemisorption

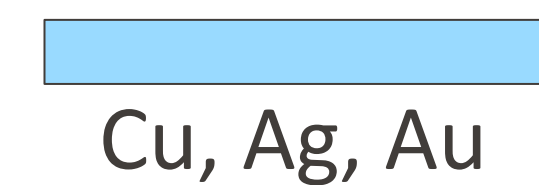
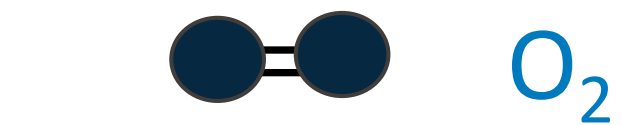
Facilitating Dissociation via Antibonding Orbitals

Strong adsorption is defined as clear peak of σ^* above the Fermi level

If σ^* orbital remains unpopulated, O–O bond remains strong



Filled σ^* weakens O–O bond, promoting dissociation

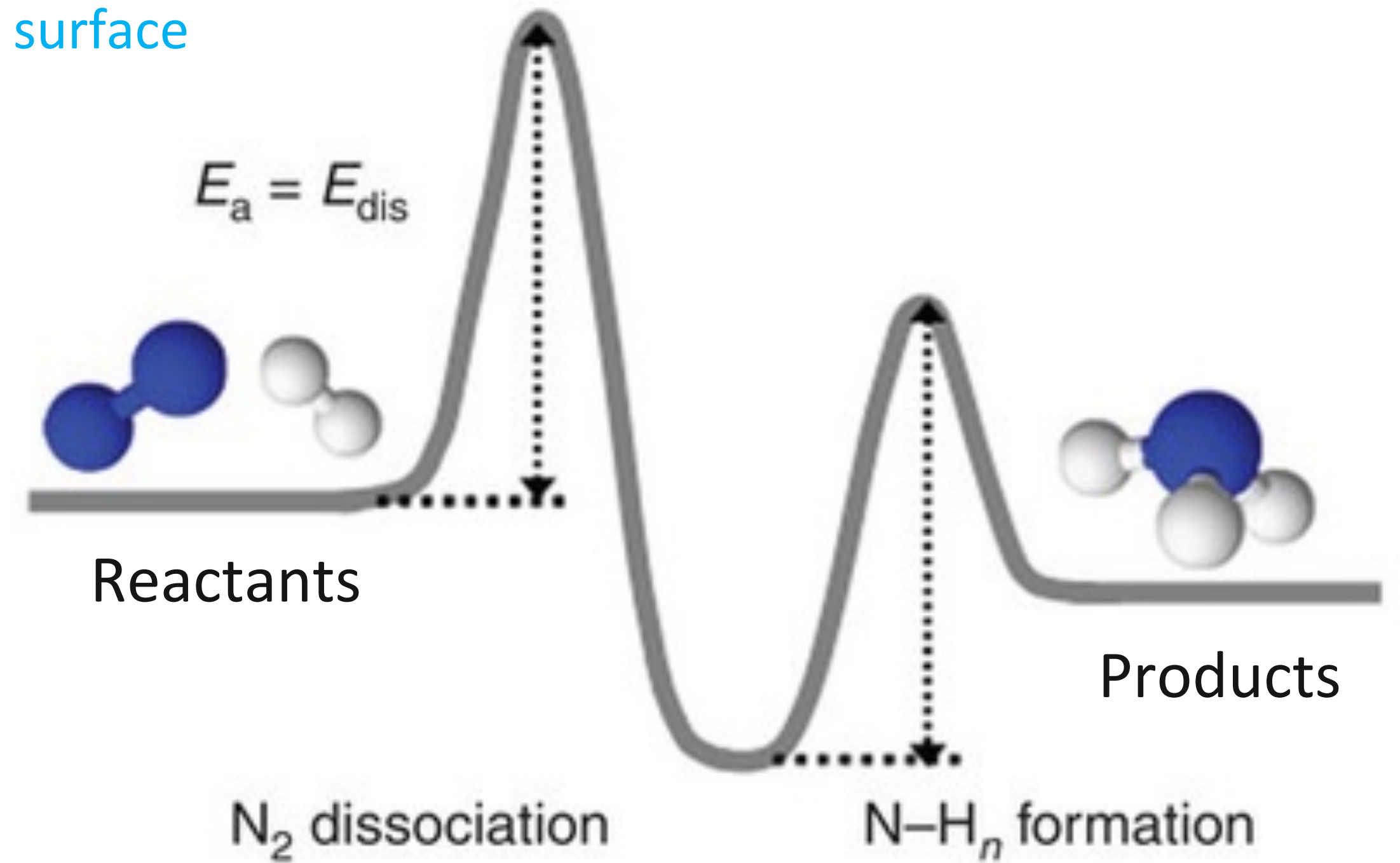
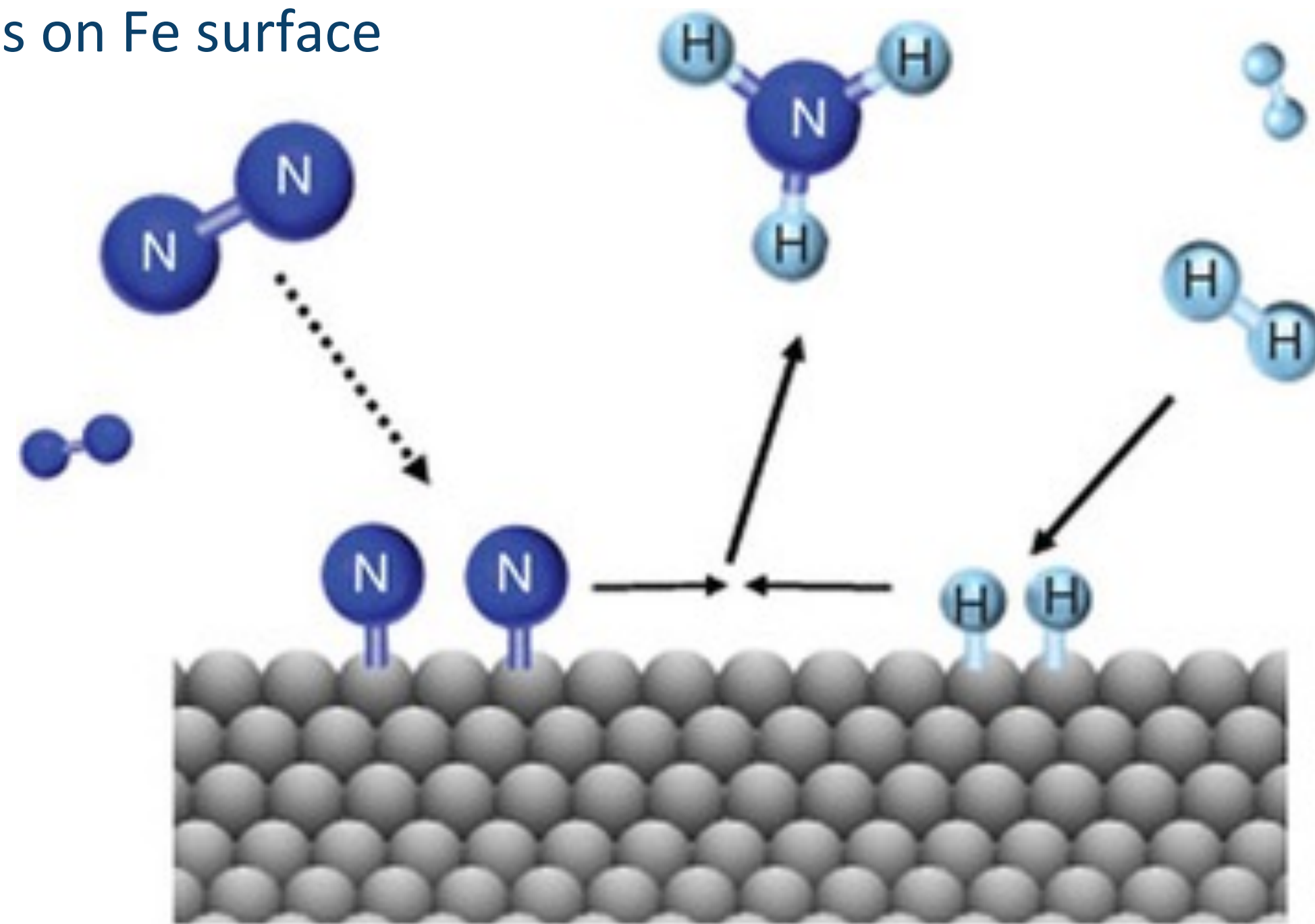


Example of Important Catalyzed Reaction: Ammonia Synthesis

Adsorption of N_2 gas on Fe surface

Ammonia desorption

Adsorption of H_2 gas on Fe surface



Fe catalyst provides active surface that adsorbs molecules, weakening their bonds

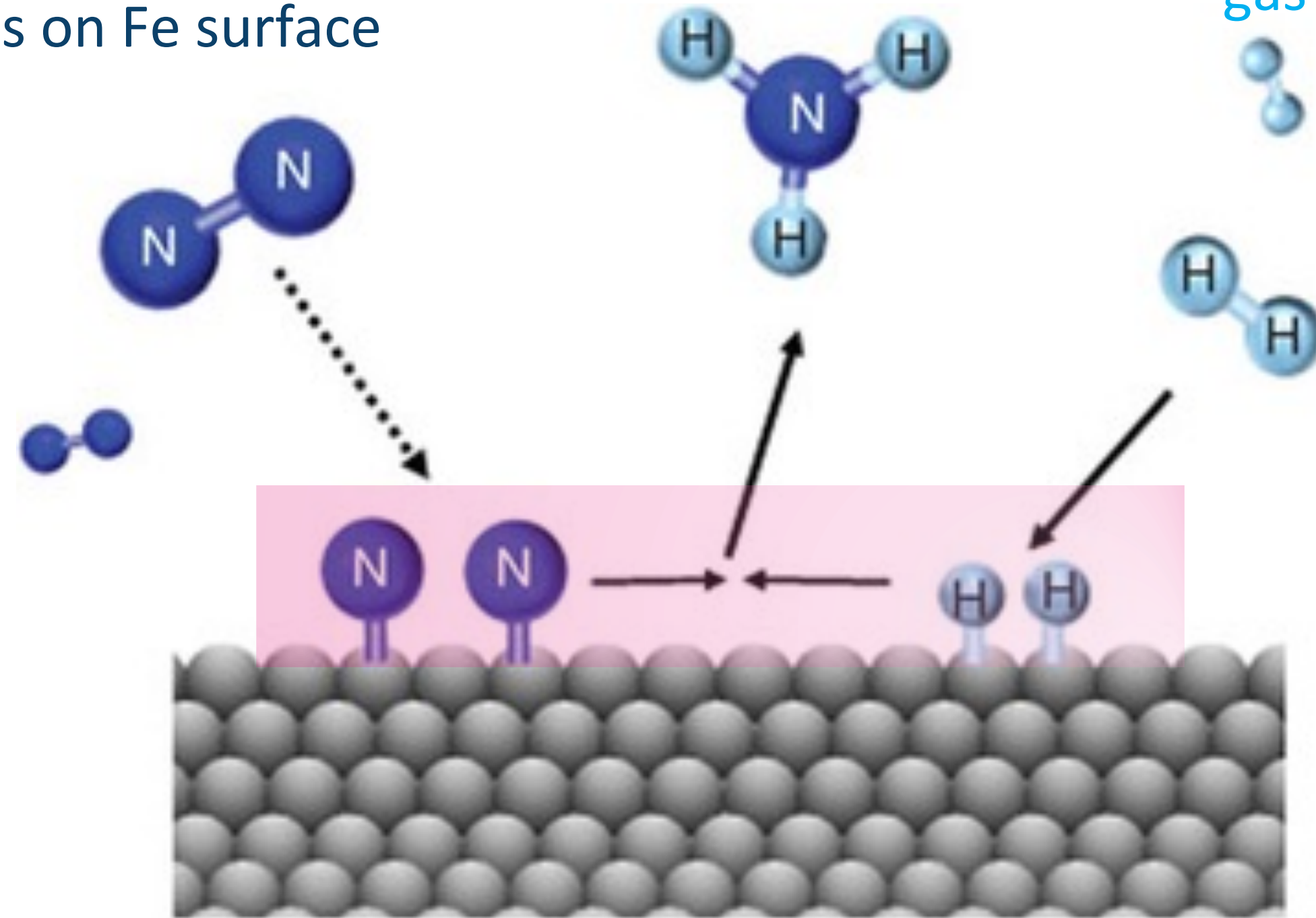
Nitrogen atoms easier to dissociate from the surface

Example of Important Catalyzed Reaction: Ammonia Synthesis

Adsorption of N_2 gas on Fe surface

Ammonia desorption

Adsorption of H_2 gas on Fe surface



Fe catalyst provides active surface that adsorbs molecules, weakening their bonds

Nitrogen atoms easier to dissociate from the surface

CO

Dissociated molecule (D)						Molecule (M)			
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	3d
		D			D		M		
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	4d
			D		M		M		
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	5d
			D+M			M	M		

N_2

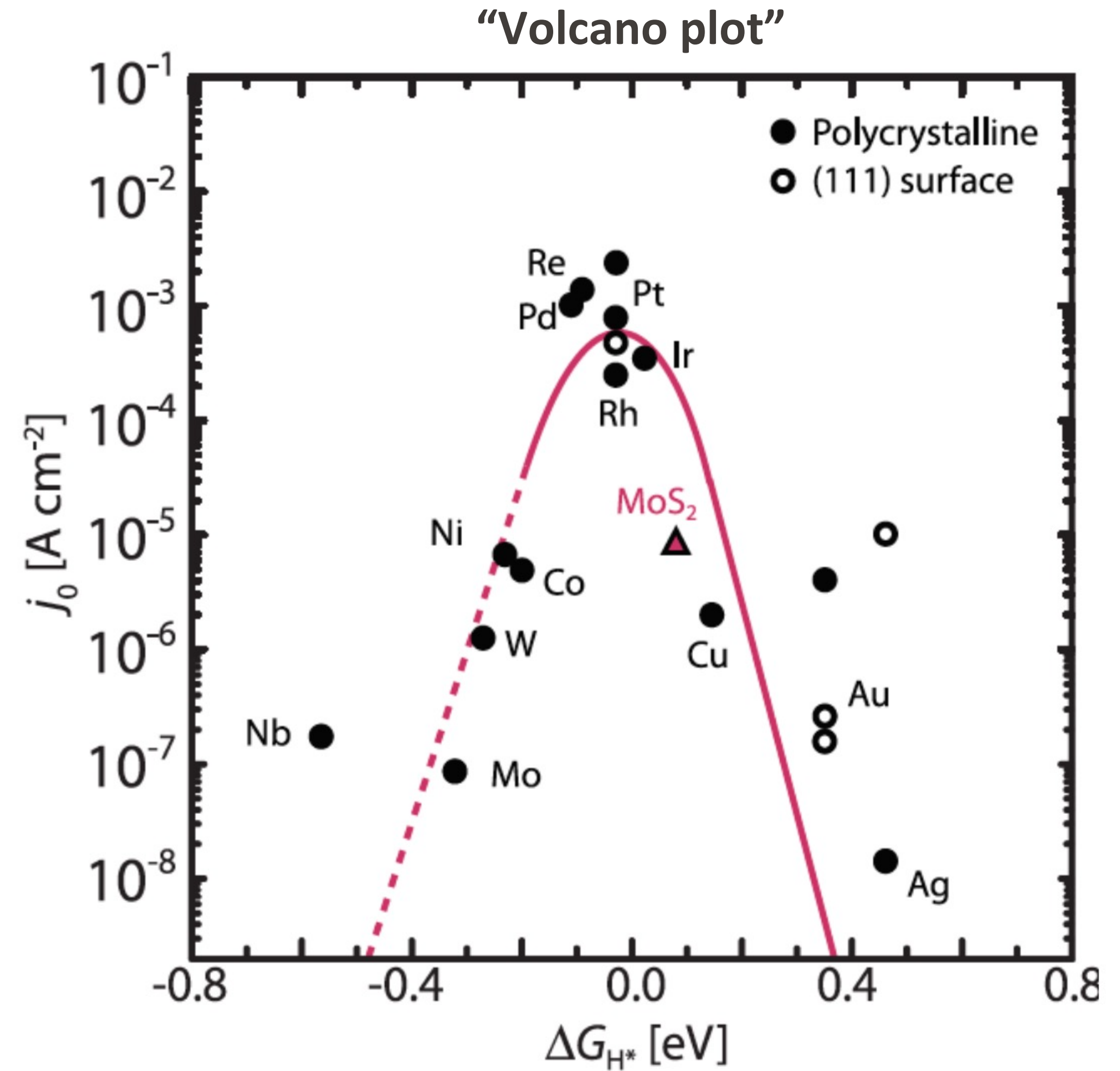
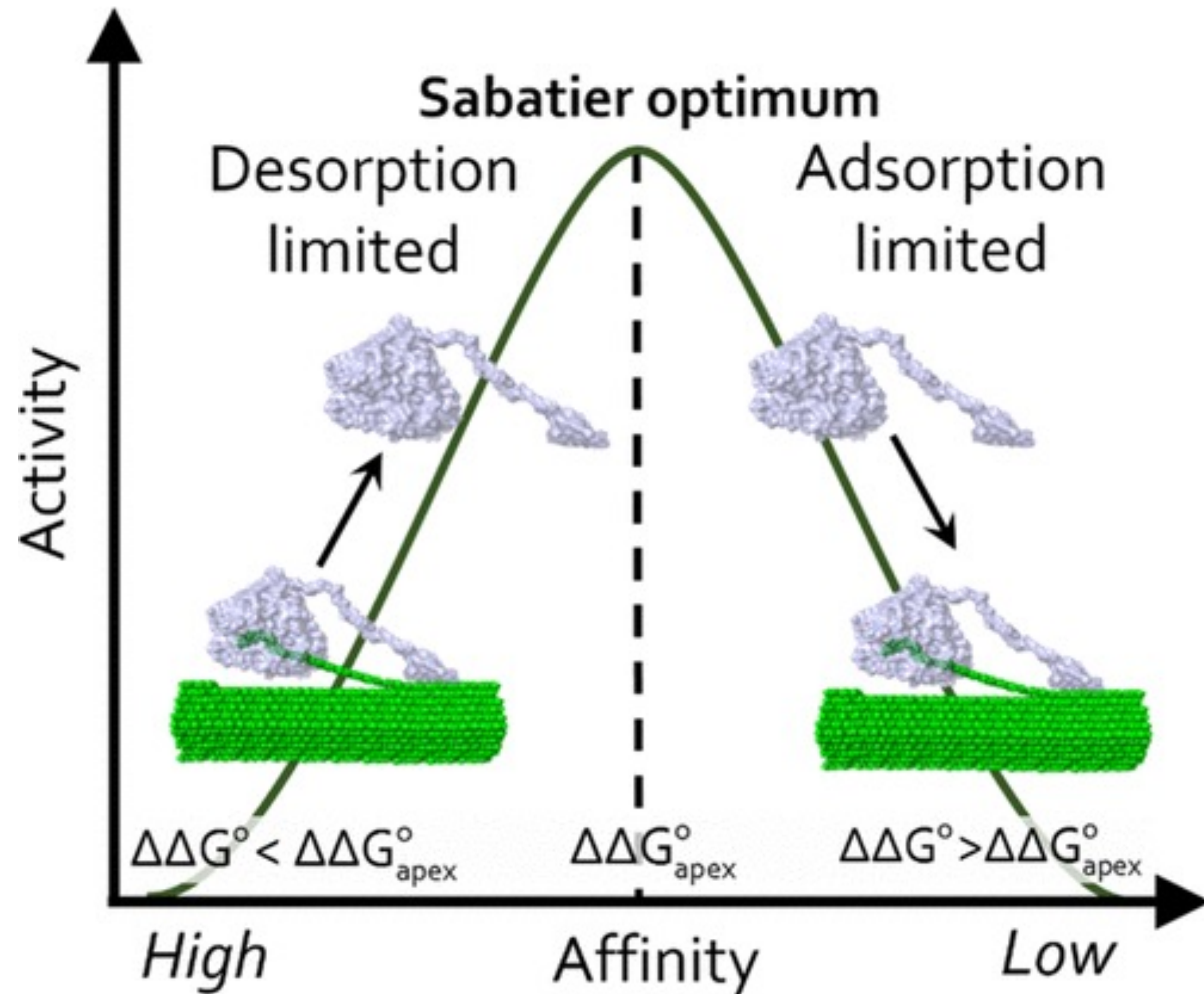
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	3d
		(D)	(D)		D				
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	4d
			(D)						
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	5d
		(D)	D						

NO

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	3d
							D+M		
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	4d
					M		M		
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	5d
						D+M	M		

Not every metal can activate a molecule – only those with the right d-band alignment can weaken bonds

Balance Between Adsorbing Strongly But not too Strongly

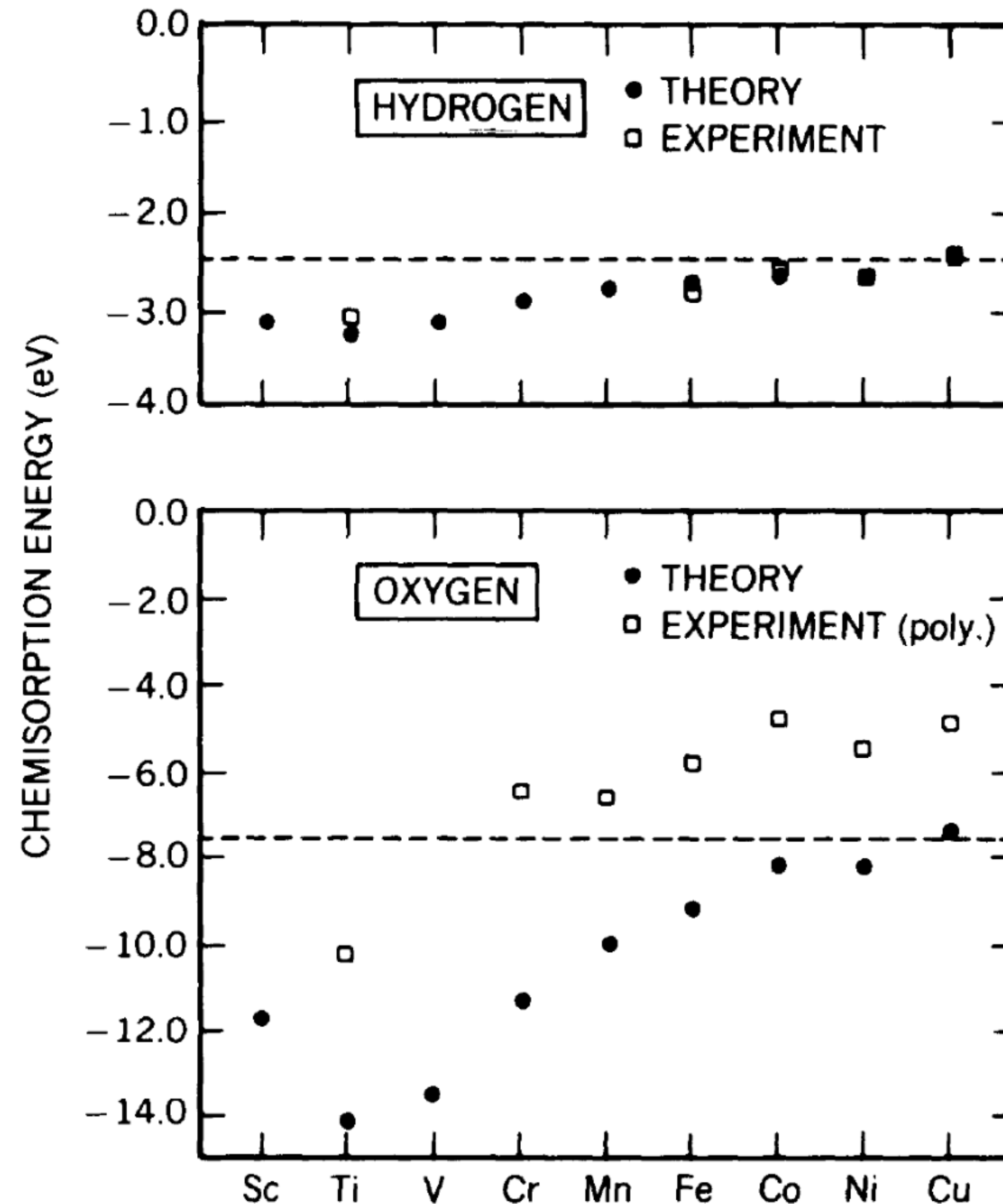


Different Adsorption Energy from Gas to Gas/Metal to Metal

Hydrogen adsorption does not cause major surface reconstructions

Oxygen adsorption often induces reconstruction of metal surface (e.g. formation of oxide layers)

Hard to account for theoretically



Hydrogen primarily interacts with metal surfaces through 1s orbital

Simply bonding interaction with metal's conduction (s or d) bands

Oxygen interacts with metal surfaces through 2p orbitals

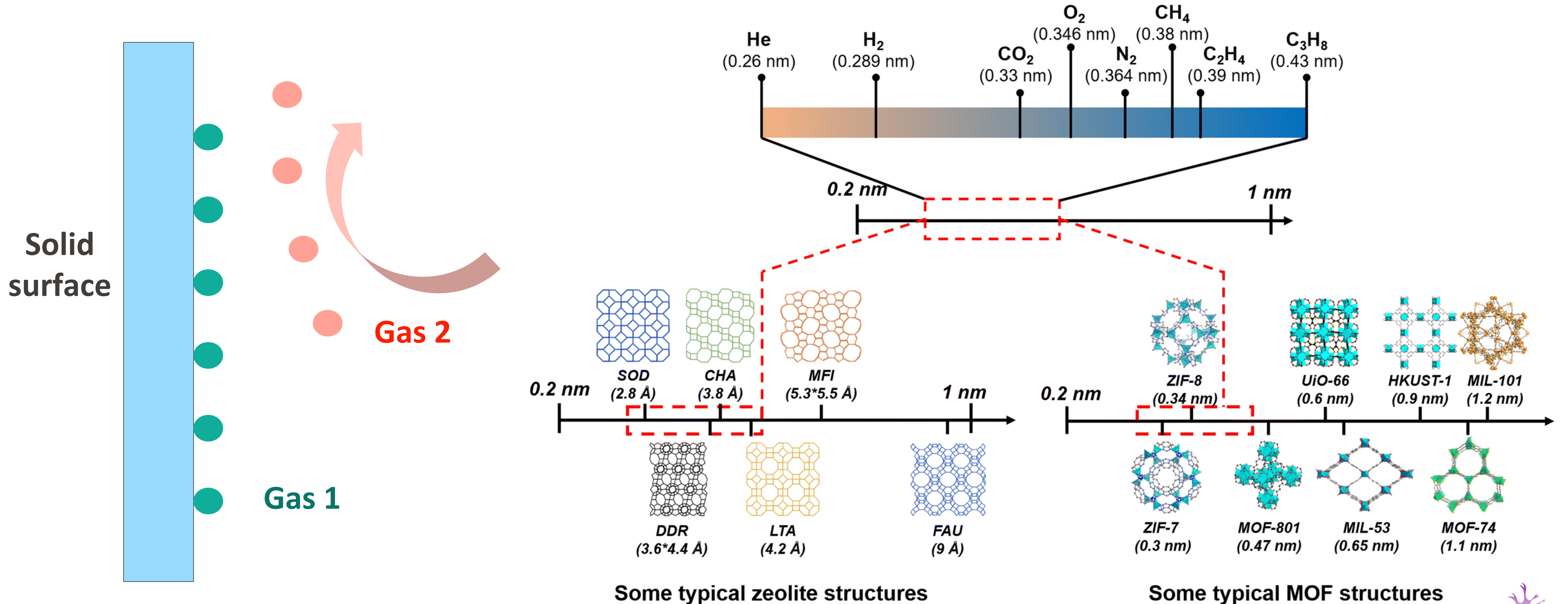
Overlap with metal d-bands (strong covalent bonding)

Important Application: Gas Separation for Sustainability

Different molecules absorbing differently on different surfaces based on:

- Formation of specific bonds
- d-band of the material

Need materials with high surface area:volume ratio (Porous structures)



Catalysis Performance Metrics: Activity and Turnover Frequency

Specific activity: When the reaction rate is normalized to the surface area of the active component in the catalyst

Turnover frequency (TOF): Number of times a single active site on catalyst converts a reactant into a product per second

Provides measure of catalyst's efficiency → higher TOF means more active catalyst

$$\text{TOF} = \frac{r}{N_{\text{active}}}$$

(s⁻¹)

Reaction rate (mol s⁻¹)

Number of active sites on catalyst (mol)

ACS Catalysis

Viewpoint

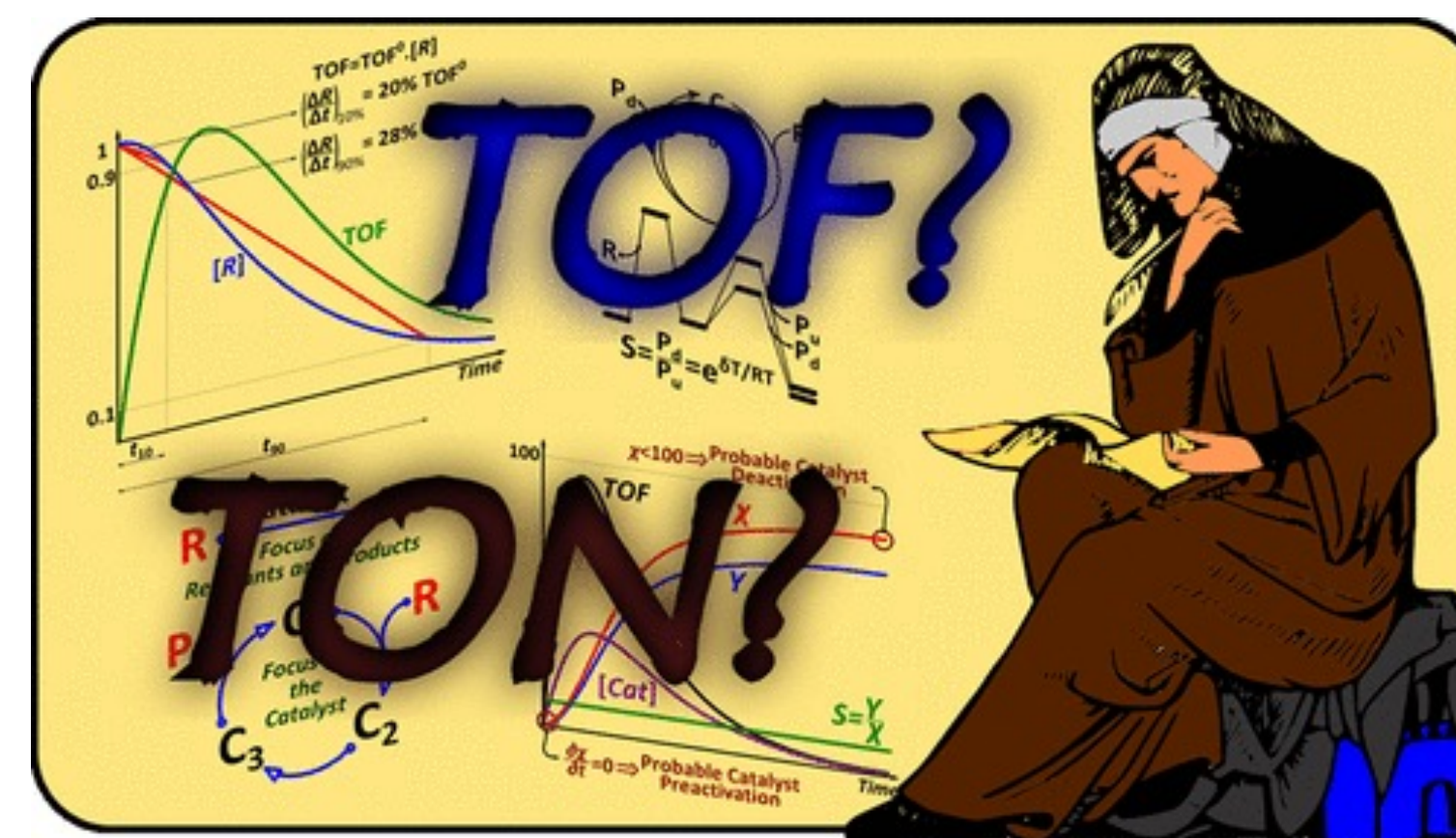
pubs.acs.org/acscatalysis

“Turning Over” Definitions in Catalytic Cycles

Sebastian Kozuch*[†] and Jan M. L. Martin^{†,‡}

[†]Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Rehovot, Israel

[‡]Center for Advanced Scientific Computing and Modeling (CASCAM), Department of Chemistry, University of North Texas, Denton, Texas 76203, United States



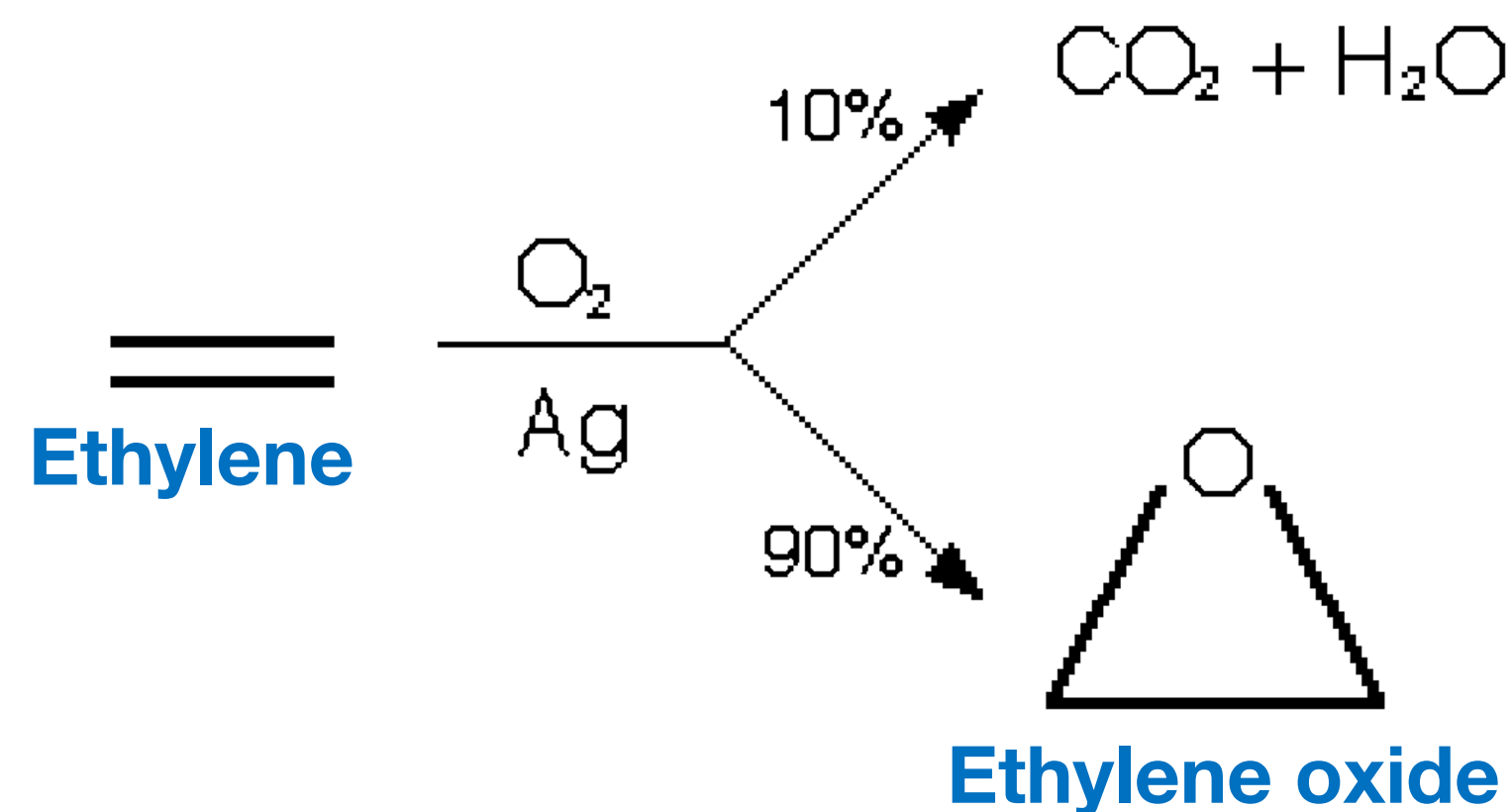
Catalysis Performance Metrics: Selectivity

Selectivity completely depends on the catalyst surface chemistry

By changing a catalyst, completely different products can be obtained

$$\text{Selectivity} = \frac{\text{Formation rate of a particular product}}{\text{Formation rate of all products}}$$

Two oxidation paths for ethylene:



90% of the ethylene molecules are converted into ethylene oxide

Commercial ethylene oxide procedure runs with 90% selectivity

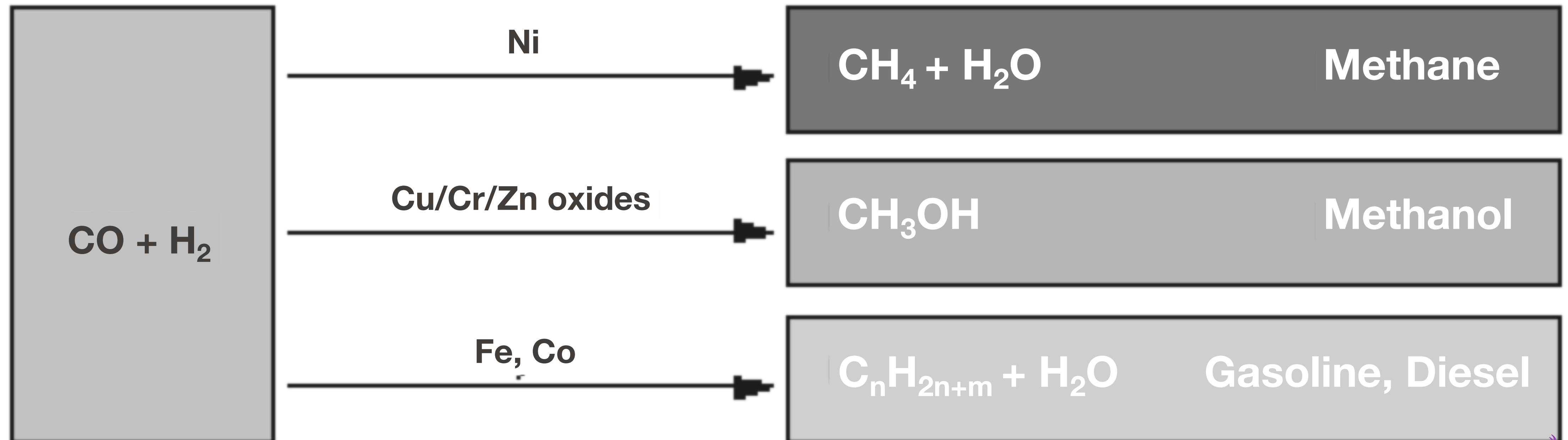


Same Reactants, Different Products – Catalysts Control Pathway

Selectivity completely depends on the catalyst surface chemistry

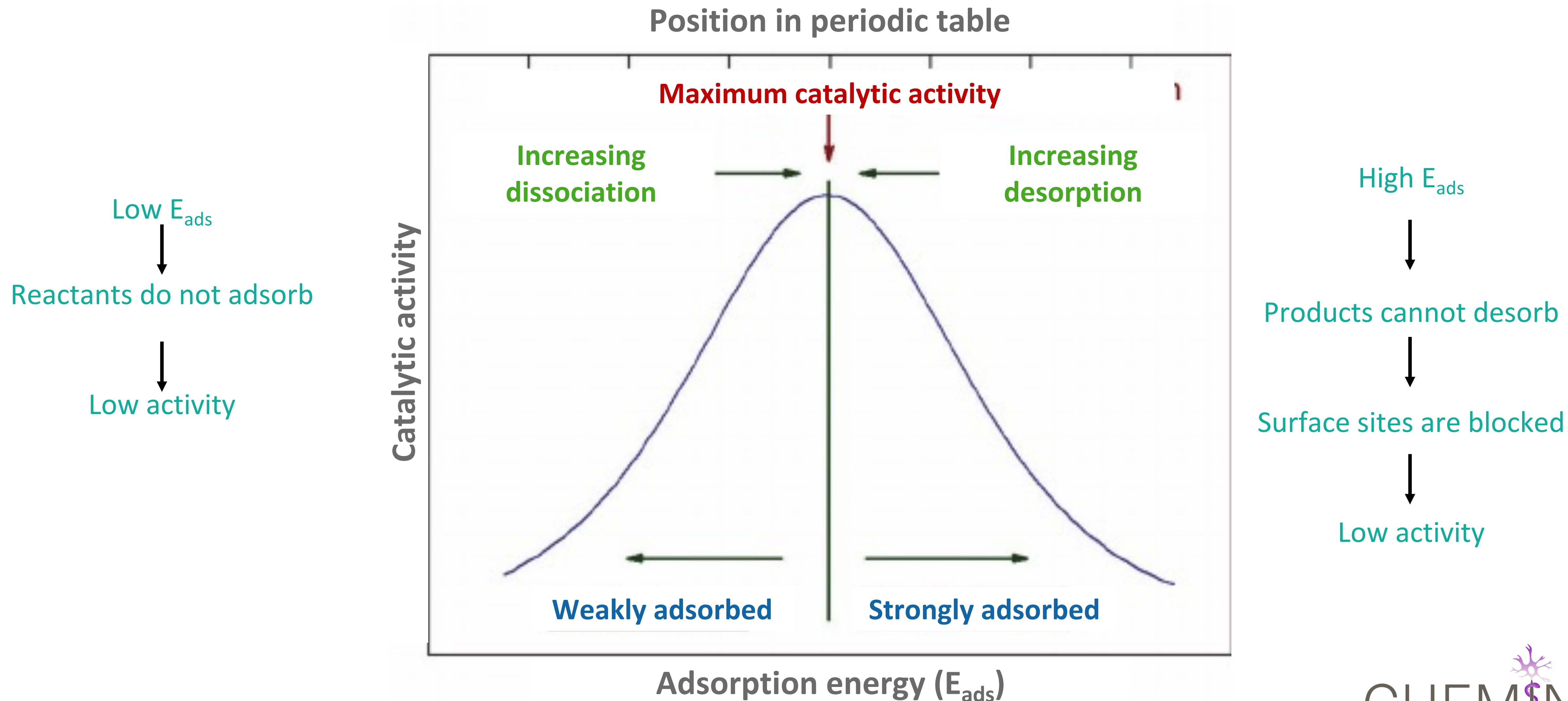
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Catalysis Optimization – Trade-Offs of Adsorption Energy

Adsorption Energy (E_{ads}): energy change when a molecule binds to the catalyst surface



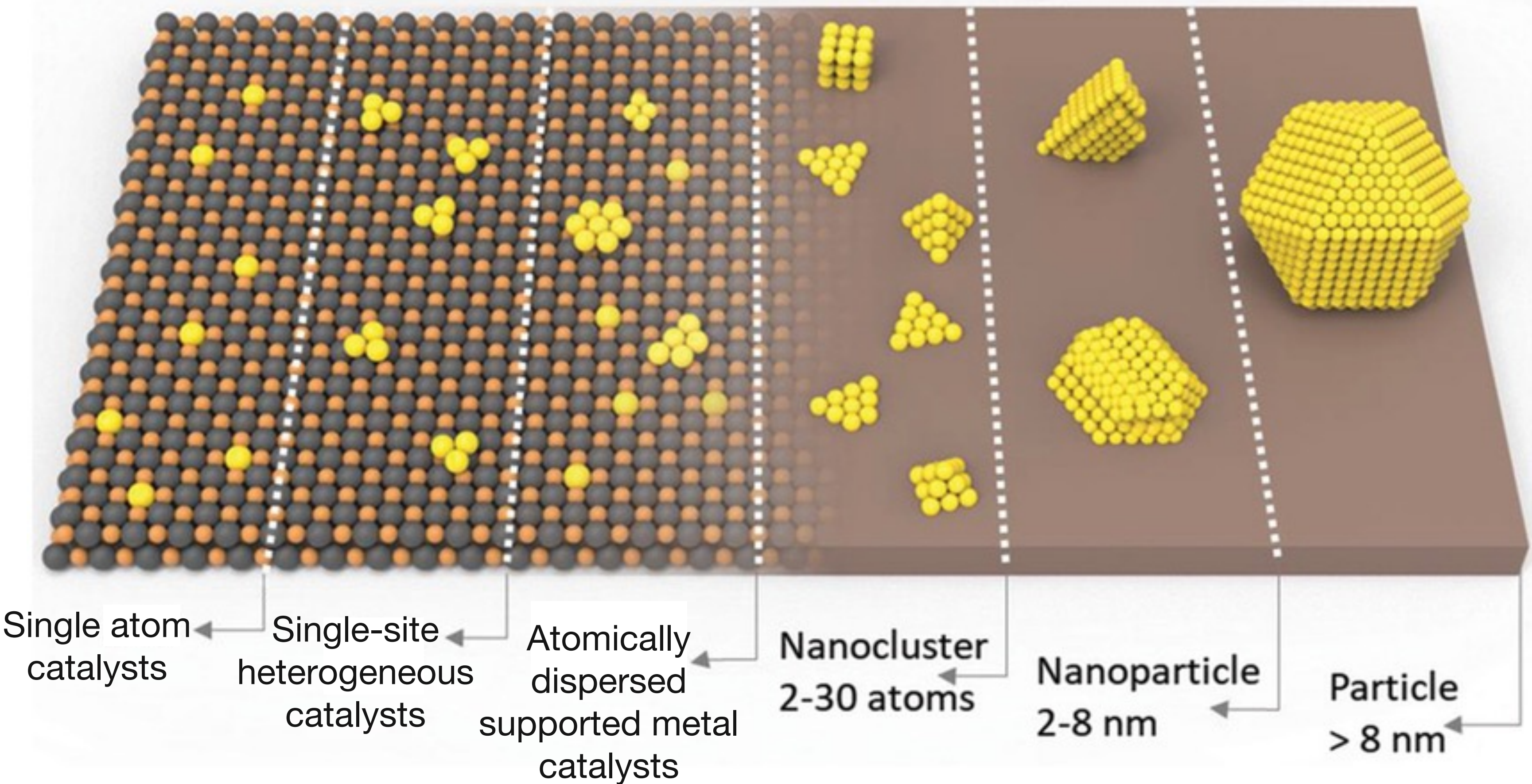
Nanostructuring for Increased Active Sites at the Nanoscale

Increased surface:volume ratio

Higher density of defects, edges, corners, or steps → active sites

More active sites exposed → more interactions

At the nanoscale, electronic structure of materials can be tuned to optimize E_{ads}



Specific shapes can lead to greater selectivity

Alloying Catalysts to Fine-Tune Adsorption

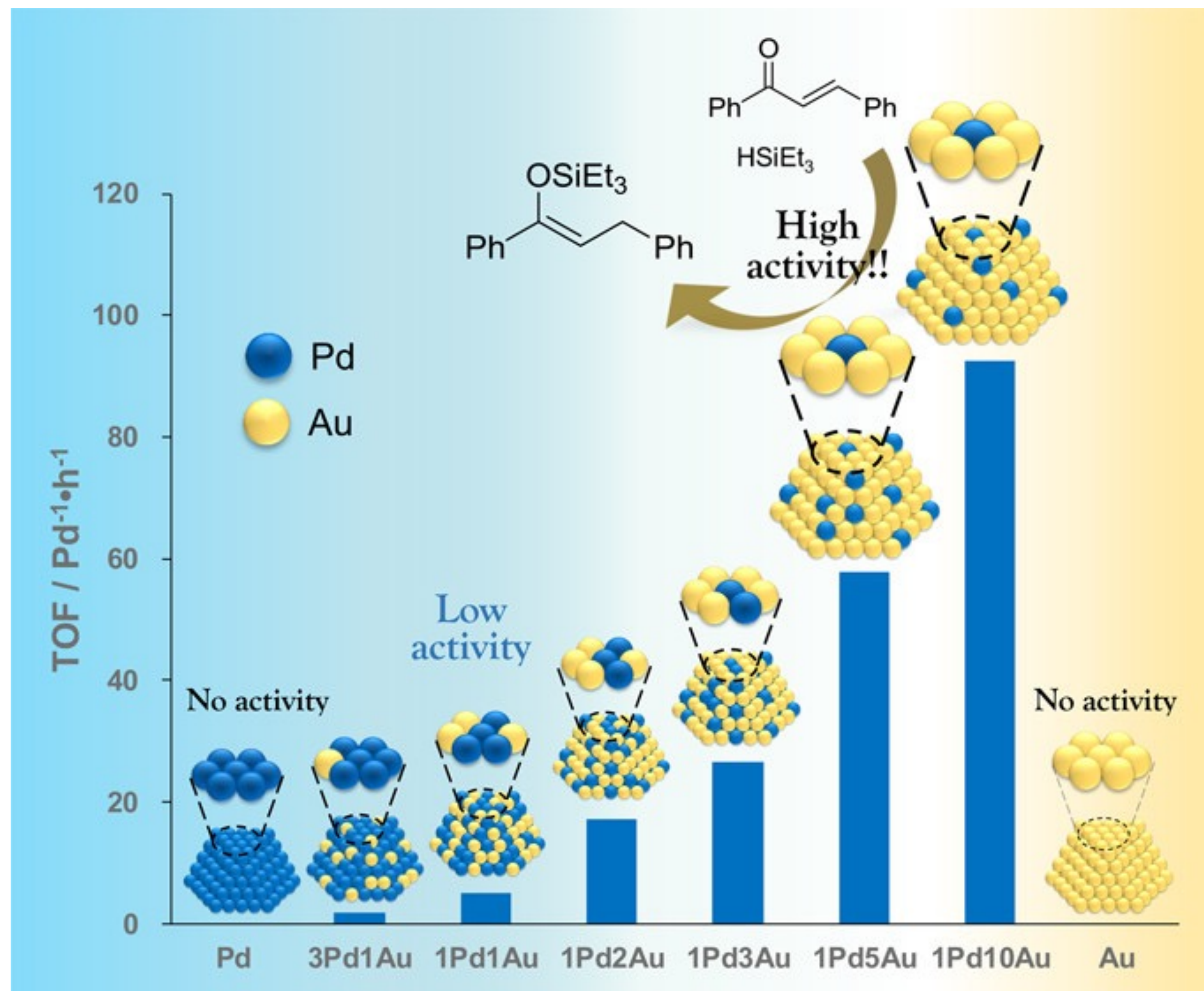
Alloying: combining metals to modify the surface's electronic structure

Introducing Au changes the electronic structure of Pd

Pd has a high d-band center (closer to E_F)
(high E_{ads} \rightarrow low TOF)

When alloyed with Au, d-band center of Pd shifts downwards \rightarrow lowers E_{ads}

Incorporation of Au into Pd lattice introduces strain \rightarrow fine-tune surface reactivity



Key Takeaways

- Catalysis is fundamentally a surface phenomenon
- The strength of adsorption is governed by orbital mixing (MO theory)
 - Effective catalysts strike a balance – Sabatier principle
- Catalyst performance depends on both activity and selectivity
 - Surface engineering can enhance catalytic activity

Summary of Today's Class

- At the nanoscale, materials behave differently – quantum dots and metal nanoparticles
- Plasmons arise from coherent oscillation of free electrons
- Bonding at surfaces is governed by the electronic structure of surfaces
- Catalysis occurs through orbital mixing between adsorbate molecules and surfaces
- Optical catalytic activity requires the right adsorption strength
- Nanostructuring and alloying allows us to fine-tune materials for catalytic performance

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