Review Session

Today we recapped the 4 weeks' worth of course material on applications of surfaces & interfaces. These questions are to help you prepare for your oral exams. My recommendation is that you get into a group of two or more and discuss how best to answer these questions – even trying a "mock oral exam" in a group. Good luck preparing for exams and happy holidays!

Part 1: Surface Science

Surfaces in a laboratory become contaminated almost immediately after cleaning. Explain:

1. Why is the contamination process slowed down in ultrahigh vacuum (UHV)? What kind of pressures constitute "UHV"?
   In UHV, the number of gas molecules in the environment is drastically reduced, resulting in fewer collisions of gas molecules with the surface. Contaminants (*e.g.*, water vapor, hydrocarbons) that would normally adsorb onto the surface are present in significantly lower concentrations, which slows the rate of contamination. UHV is defined as a pressure range between 10^{-8} to 10^{-12} Torr. In these conditions, the molecular density is on the order of 10^{5} atoms/cm^{3}, enabling experiments on clean surfaces with minimal contamination over extended time periods.

2. What factors (beyond pressure) influence contamination rates in both environments?
   Factors Influencing Contamination Rates:
   - **Surface Energy:** High-energy surfaces (*e.g.*, metals) attract contaminants more quickly due to stronger adsorption forces.
   - **Temperature:** Higher temperatures increase molecular motion, potentially enhancing adsorption kinetics but may also facilitate desorption.
   - **Gas Composition:** We observed that different gases chemisorb differently to surfaces during our catalysis section
   - **Surface Morphology:** Rough surfaces provide more adsorption sites compared to smooth surfaces, accelerating contamination.

Part 2: Surface Characterization Techniques

A new nanostructured gold surface has been fabricated for biosensor applications. You want to investigate the following properties of the surface. For each, choose the most suitable technique and justify your choice:

1. Surface topography (roughness and nanostructures).
2. Chemical composition of adsorbed molecules on the surface.
3. Real-time monitoring of molecular adsorption on the surface.
4. Orientation or structural arrangement of molecules on the surface.

1. Surface Topography: Atomic Force Microscopy (AFM)
   AFM provides nanoscale 3D imaging of surface roughness and nanostructures, making it ideal for topographical studies.

2. Chemical Composition of Adsorbed Molecules: X-ray Photoelectron Spectroscopy (XPS)

XPS can identify elemental composition and chemical states of surface species within a few nanometers of the surface.

3. Real-Time Monitoring of Molecular Adsorption: Quartz Crystal Microbalance (QCM)
   QCM detects mass changes in real-time with nanogram sensitivity, making it highly effective for studying adsorption dynamics.

4. Molecular Orientation or Arrangement: Scanning Tunneling Microscopy (STM)
   STM provides atomic-scale imaging and insight into the orientation and arrangement of molecules on conductive surfaces.

Part 3: Nanoscience and Plasmonics
Gold nanoparticles are used for biosensing applications such as the lateral flow assay for the COVID-19 rapid test. Based on the concepts covered in class:

1. Explain how **plasmon resonance** is generated and why gold nanoparticles exhibit distinct colors.
   When gold nanoparticles are irradiated with light, their conduction electrons resonate collectively in response to the electromagnetic field, creating a phenomenon known as surface plasmon resonance.

   The specific wavelength of light absorbed during this resonance depends on the size, shape, and surrounding environment of the nanoparticles. For example:
   - Small spherical nanoparticles (~20 nm): Absorb blue-green light, reflecting red, hence appearing red.
   - Larger or aggregated particles: Shift resonance to longer wavelengths, appearing purple or blue.

   This unique optical property makes them ideal for biosensing, where the particles can be visualized (*i.e.,* as red lines on the COVID-19 rapid test).

2. How can asymmetric nanostructures (e.g., nanorods or nanoshells) extend the range of plasmonic responses for specific applications?
   Nanorods: Nanorods have two axes (longitudinal and transverse), allowing for two distinct plasmon resonance modes:
   - Longitudinal mode (along the long axis): Resonates at longer wavelengths (red to near-infrared).
   - Transverse mode (short axis): Resonates at shorter wavelengths (visible range).

   This dual resonance enables tunable optical properties for applications in multiplexed biosensing or photothermal therapy.

   Nanoshells: Nanoshells consist of a dielectric core surrounded by a thin gold layer. The plasmonic response depends on:
   - Core size
   - Shell thickness

By adjusting these dimensions, the resonance can be tuned across the visible to infrared spectrum, making them useful for imaging or therapeutic applications in biological systems.

Part 4: Biosensors

Design a biosensor for lactate using an enzymatic reaction (driven by lactate oxidase). Describe the reaction and the transduction mechanism for an electrochemical signal. What kind of biosensor is this?

Reaction:

- Lactate + O_2 → Pyruvate + H_2O_2

Signal transduction:

- H_2O_2 is oxidized at an electrode: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
- Amperometric sensor measures current generated, which is proportional to lactate concentration.

Part 5: Catalysis

Sketch a volcano plot for a hypothetical reaction. Explain how changing the catalyst alters the activation energy and predict the optimal adsorption energy.

- **Volcano Plot:**
  - X-axis: Adsorption energy.
  - Y-axis: Catalytic activity.
  - Optimal point: Balance between strong and weak adsorption (moderate binding).
- **Key Concepts:**
  - Weak adsorption: Reactants desorb too quickly, limiting reaction.
  - Strong adsorption: Product desorption slows, blocking active sites.