Week 1

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1.1 Nanomaterials

1/3:

- Contact Dr. Shevchenko at eshevchenko@anl.gov or eshevchenko@uchicago.edu.
- How to make nano.
  - Top-down approach: Start with large, end with nano. Includes nanofabrication.
  - Bottom-up approach: Solution-based approach.
    - Scalable and cheap.
    - Use an inorganic core with a coating.
- What nanoparticles look like.
  - Differences in size, size distribution, shape, chemical composition, and structures.
  - Different sizes (like atoms) and different shapes (like bacteria and viri).
- Ancient nanoscience.
  - The Lycurgus cup.
    - A 4th-century Roman glass cage cup.
    - Currently housed at the British Museum.
    - Contains $\sim 70\,\text{nm}$ gold/silver nanoparticles.
    - When front-lit, it appears green (light is scattered by larger NPs).
    - When back-lit, it appears red (light is absorbed by NPs).
  - Hair dye.
    - 2000 years ago from Greco-Roman times.
    - Made of lead oxide (PbO), slaked lime ($Ca(OH)_2$), and water (H_2O).
    - The lead oxide combines with sulfur-rich peptides in the hair to make $\sim 5\,\text{nm}$ PbS NPs.
- Applications of nanoparticles: Catalysis.
  - Refining of petroleum (transformation of crude oil into gasoline, jet fuel, diesel oil, and fuel oils).
  - Converter of automobile exhaust (reduction of nitrogen oxides [NO_x] to N_2 and O_2; oxidation of CO to CO_2; oxidation of unburnt hydrocarbons to $CO_2 + H_2O$).
  - Hydrogenation of CO (synthesis of fuels such as methane or methanol).
  - Selective oxidation of hydrocarbons (synthetic fibers, plastics, and fine chemicals).
- Methods of NP analysis: XRD, TEM, XANES, and XPS.

- Applications of nanoparticles: Displays.
  - Semiconductor nanoparticles (e.g., solutions of CdSe or InP nanoparticles) emit different colors.
  - Sony has announced that it will embed quantum dots in its latest flat-screen TV.
  - QLEDs can be made out of CdSe, CdS, InP coatings with silica, perovskite (CsPbX where X = $\text{Cl}, \text{Br}, \text{I}$), and cesium lead halide salts.
- Milestones in the synthesis of nanomaterials (a subjective and incomplete POV).
  - Alexei Ekimov (late 1970s-1981, USSR): $CuCl_x$ and CdSe in molten glass matrix (fluorescence, gradient colors).
  - Alexander Afros (1982): Theoretical description of size effect.
  - Louis Brus (1983, Bell Labs, US): CdS in solution.
  - Paul Alivisatos (UChicago) and Moungi Bawendi (MIT).
  - Moungi Bawendi et al. (1993): Synthesis of monodisperse CdSe nanoparticles — a big one!
  - Philippe Guyot-Sionnest (1996): Synthesis of core/shell nanoparticles.
  - Paul Alivisatos (1997 and 2003): Synthesis of nanorods and tetrapods.
  - Chris Murray and Shouheng Sun (2000): Synthesis of magnetic FePt nanoparticles.
  - Benoit Dubert (2007, France): Synthesis of CdSe nanoplates (more stable, emission is polarized and directional).
  - Maksym Kovalenko (2015): Synthesis of perovskites.
  - Mostafe El-Sayed, Catherine Murphy, Peidong Yang, and Yunan Xia: Synthesis of Au and Ag nanoparticles.
- Synthesis of nanoparticles.
  - The 1993 Bawendi paper.
  - The innovation was the synthesis of NPs in organic solvents, still widely used today.
- LaMer model.
  - Precursors under go nucleation, focusing, and "nano"-Ostwald ripening.
  - Key idea: Separation of nucleation and growth in time.
- Nanomaterials: State-of-the-art.
  - The chemistry behind QD synthesis is rather simple compared to what is used by organic or coordination chemists, but the field sometimes lacks depth and chemical understanding.
  - Indeed, only a fraction of reported results have been reproduced, and only a fraction of those have been understood and optimized.
  - This is a big problem for AI/ML approaches.
  - During the next 5-10 years, nanomaterials synthesis will progress mostly through systematic mechanistic studies.
- Synthesis of nanocrystals without Ostwald Ripening.
  - The nanocrystals form and grow during 0.1-1 minute after the start of the reaction.
  - Annealing at high temperatures (250-280 °C) is required to improve crystallinity.
  - No change in particle size takes place upon the annealing.
  - Tune particle size with nucleation, since growth proceeds until all monomer is consumed — fast nucleation leads to many particles, which can only grow so large; slow nucleation leads to a few particles which can grow very large (conservation of end volume).

- Synthesis with "artificial molecules."
  - Rearrangement, addition, substitution, and elimination.
- Hollow nanocrystals: Kirkendal Effect at Nanoscale.
  - Uniform spherical cobalt nanocrystals can be synthesized by rapid pyrolysis of cobalt carbonyl in hot solvent.
  - Hollow nanocrystals form after sulfidation reaction.
- Kirkendal effect.

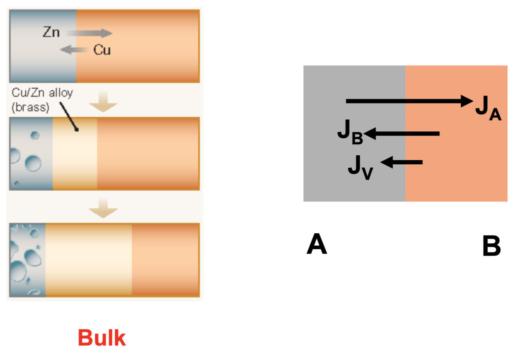

Figure 1.1: Kirkendal effect.

  - Occurs when the diffusion rates of two species are different.
  - When vacancies become supersaturated, they condense into voids in the fast diffusion species side.
  - The Kirkendall voids result in weak bonding and lead to brittle fracture at the bonding interface.
- Top-down approaches for the synthesis of MoS_2.

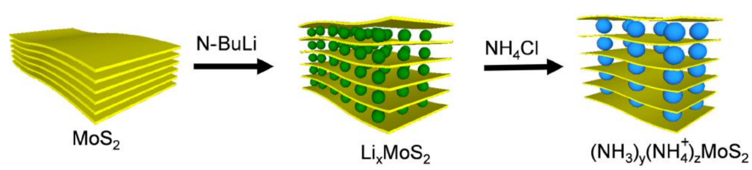

Figure 1.2: Top-down synthesis of MoS_2.

  - This is the synthesis of interlayer expanded (IE) MoS_2 through chemical intercalation of Li and the following exchange with NH_3 and NH_4.
  - Each MoS_2 layer is composed of an atomic layer of Mo sandwiched between atomic layers of S through strong ionic/covalent bonds. Weak van der Waals forces link individual MoS_2 layers with an interlayer spacing of 0.615 nm.
  - Procedure.
    - Electron-donating species, e.g., alkali metals, Lewis bases, and organolithium compounds can intercalate between layers.
    - Alkali metals can after that be evaporated or react with water.
    - **Exfoliation** with ultrasound (mechanical exfoliation).
  - Useful characterization methods: TEM, XRD, XPS.
- **Exfoliation**: The complete separation of the layers of a material.

- Bottom-up approaches for the synthesis of MoS_2.
  - Chemical synthesis of interlayer expanded (IE) MoS_2.
  - Chemical Vapor Deposition (CVD).
- MXene = 2D metal and surface chemistry.
  - Applicatoins to supercapacitors, batteries, conductors, catalysts, and composites.
  - Most made out of Ti_3AlC_2.
- MXenes: Solution processed 2D transition metal carbides and nitrides.
  - Scanning electron microscopy (SEM) and HRTEM images shown.
  - Etching and delamination phases.
- MXenes: Variable termination groups.
  - Ask in OH??
- MXenes are solution processable 2D transition metal carbides and nitrides.
  - Lists various experimentally synthesized structures.
- What can and cannot be synthesized in solution?
  - Current solution synthesis methodology can be applied to materials that crystallize below 400 °C. Many materials that require higher temperatures to form, e.g., nitrides, carbides, GaAs.
  - Higher temperatures: Gas phase and solid state synthesis, as well as synthesis in molten salts.
- Nanocrystals in molten salts.
  - QDs are synthesized at high T in molten salts.
  - There is typically a postpreparative treatment phase still in molten salts.
- Nanoparticles as building blocks to make new materials.
  - The idea behind nanoparticles is encapsulated by the synthesis of NaCl from Na° and $Cl_2{}^\circ$: Two substances with certain properties combine to form a new material with very different properties.
  - Assembly of atoms leads to new materials and new properties!
- Self-assembly of nanoparticles.
  - Can be multilayered (up to five).
- Crystals of nanocrystals.
  - Example: 3D crystals ($\sim$ 30 µm) have been assembled from 3.3 nm CdSe nanocrystals.
  - Example: 3D crystals ($\sim$ 10 µm) have been assembled from 6 nm $CoPt_3$ nanocrystals.
  - More conventional example: Crystals of quartz (made by atoms).
- Binary nanoparticle superlattices.
  - Natural opal vs. synthetic opals (very similar appearance and properties).
  - Formation of binary superlattices depends on the ratio of nanoparticle radii (γ), the concentration of nanoparticles, the size distribution of nanoparticles, the nature of the capping ligand, and the substrate.
  - Evaporating colloidal solutions of binary nanoparticle mixtures at 45 °C leads to the formation of binary nanoparticle superlattices.

- Periodic table of nanocrystals.
  - Different types of unit cells listed.
  - Examples include AlB_2, $MgZn_2$, Cu_3Au, Fe_4C, $CaCu_5$, and CaB_6.
- Directing of self-assembly of nanocrystals.
  - Various additives can be mixed in.
- Metal organic frameworks (MOFs).
  - MOFs (also called porous coordination polymers or PCPs) are two- or three-dimensional porous crystalline materials with infinite lattices synthesized from secondary building units (SBUs) — metal cations, salts, or clusters — and polydentate organic ligands with coordination type connections.
  - Common SBUs pictured.
  - From single-metal nodes to SBUs: More than 20,000 MOF structures have been reported so far.
  - Characterization methods: TEM, SEM, XRD, XANES, XPS, and electron paramagnetic resonance (EPR).
- Summary.
  - Structural information (XRD, ED).
  - Compositional information (XRD, ED, energy dispersive X-ray analysis [EDX], and X-ray fluorescence [XRF]).
  - Size and morphology of materials (TEM, SEM, and XRD).
  - Redox states of bulk and surface (XANES, XPS).
  - Important variables: Quality of synthesized materials, stability of materials during processes, and structure-property correlations.