Course Outline – Chemistry at the Nanometer Scale [H06A6A]

A. Introduction

- **Chapter 0: Introduction**
- **Chapter 1: Nanosafety**

B. Supramolecular Chemistry and Self-Assembly

- **Chapter 2: Supramolecular Chemistry (molecular recognition)**
  - Introduction
  - Molecular recognition
  - Preorganization
  - Intermolecular interactions involved in self-assembly
    - H-bonding
    - Metal-ligand
    - Pi-pi
    - Hydrophobic
- **Chapter 3: Self-Assembly (general)**
  - Supramolecular electronics
    - *Via* H-bonds and pi-pi interactions
  - H-bonded polymers
  - Non-infinite aggregates
- **Chapter 4: Self-Assembly (in water)**
  - Micelles
  - Vesicles
  - Shape-structure concept
  - A special application
- **Chapter 5: Self-Assembly (stabilization)**
  - Stabilization of:
    - Vesicles
    - Micelles
- **Chapter 6: Large Building Blocks**
- **Chapter 7: Liquid Crystals**
  - The basics
  - From simple to complex
  - Selected applications
- **Chapter 8: Bio-mineralization**
  - Templating mineral formation
  - From biominerals to functional materials
- **Chapter 9: Nanomotors**
  - Myosin-actin motor
  - Kinesin motor
  - Bacterial flagellar motor
  - F_1-ATPase motor
  - Synthetic motors
  - Applications
    - Catalysis
    - Electronics
    - Mechanics

C. Organization of Matter on Surfaces at the Nanometer Scale

- **Chapter 10: Scanning probe microscopy**
  - Intro
  - Scanning tunneling microscopy (STM)
  - Atomic force microscopy (AFM)

- **Chapter 11: Langmuir-Blodgett Films**
- **Chapter 12: Layer-by-Layer Deposition**
  - Monitoring layer build-up (*ex situ*)
    - UV-Vis
    - X-ray reflectometry
    - Quartz crystal microbalance (QCM)
  - Monitoring layer build-up (*in situ*)
    - Zeta potential
  - Post-preparation treatment
  - Multi-layer structure (zone model)
  - Polyelectrolytes
  - Spatially-graded composition LbL films
  - Crystal engineering: oriented *zeolite* films
  - Chemical reactions in films
  - Colloid coating
  - Formation of hollow particles
- **Chapter 13: Self-Assembled Monolayers (SAM) vs Covalent Grafting**
  - SAM end groups and substrates
  - Effect of substrate symmetry: Au vs. Ag
  - Head group effects on contact angle
  - Techniques for characterizing alkanethiol SAMs on Au
  - Methods/ligands for functionalizing SAM surfaces
  - Applications
    - Controlling/changing surface wettability, using:
      - Surface energy gradients
      - Light
      - Electrical stimulus
      - Electrical control
    - Bio-related applications of SAMs
    - Electrically contacting SAMs
    - Scanning probe lithograpy
      - Nanoshaving
      - Nanografting
      - Dip-pen
  - Self-assembly versus covalent grafting
- **Chapter 14: Soft-Lithography**
  - Microcontact printing
  - Micromolding and related techniques
    - Overview
    - Replica molding
    - Microtransfer molding
    - Micromolding in capillaries
    - Solvent-assisted micromolding
  - Nanoimprinting lithography
- **Chapter 15: Molecular Nanopatterns on Surfaces**
  - Ordering with non-covalent interactions
  - Templating
  - Reactivity
  - Spectroscopy
  - Beyond molecular nanopatterns: the case of DNA (DNA origami)
- **Chapter 16: Block Copolymers (thin films)**
  - Amphiphiles (copolymers):
    - In solution
    - In bulk (thin films)
      - Spatial confinement

- Epitaxial self-assembly
- Nanocomposites

D. Microporous and mesoporous materials

- **Chapter 17: Microporous and Mesoporous Materials**
  - Control over pore size and functionality
    - Modular self-assembly of MOFs
    - Mesoscale soft building blocks
    - Block copolymers
  - Micro- and mesoporosity in 2D
    - Metal-ligand interactions
    - H-bonding
    - VdW interactions

E. Nanoparticles (preparation and properties)

- **Chapter 18: Nanocrystals**
  - Size-dependent properties (intro)
  - Metal nanoparticles
    - Size-dependent properties
      - Surface plasmon resonance
      - Current-voltage characteristics
    - Synthesis
      - Nucleation theory
      - Water-based synthesis
      - Organic solution-based synthesis
    - Ligand chemistry
      - Place exchange
      - Functionalization
    - NP encapsulation
      - Polymer-stabilized nanoclusters
      - Dendron-stabilized nanoparticles
    - Application: *Catalysis*
      - Homogeneous catalysis:
        - In water
        - In organic solvents
        - In fluorous/organic biphasic solvents
    - Surfactants as templates
    - Reactivity towards oxidation
    - Surface-enhanced Raman spectroscopy (SERS)
    - Metal-clusters as emissive centers
      - Fluorescence from small silver clusters
      - Zeolites as host material for silver clusters
      - Thermally created luminescent material
      - Energy conversion for solar panels
  - Semiconductor nanoparticles
    - Size-dependent properties
      - Bulk semiconductors
      - Nanocrystalline semiconductors (optical properties)
    - Synthesis
      - Arrested precipitation in solution
      - Synthesis in structure medium
      - Molecular precursor method (monodisperse NCs)
      - Example: CdSe

- Growth kinetics
    - Core/shell structures
- Optical and electronic properties of NC assemblies
- Soft lithography of capped nanoclusters
- Organizing NCs by evaporation

o Applications
- Bioscience
    - Coupling inorganic NPs and biomolecules
    - DNA-manipulated self-assembly and aggregation
    - Biosensing and biolabeling
- Materials science
    - Heterogeneous catalysis

➢ **Chapter 19: Nanotubes, Nanorods, Nanowires**

o Metallic nanorods
- Preparation and characteristics of barcoded Au composite nanorods
- Self-assembly of nanorods
    - DNA end-functionalization
    - Magnetic materials
    - Hierarchical ordering
    - Nanoelectronics

o Semiconductor nanowires
- Anisotropic crystal growth (methods)
    - Capping agents
    - Template-directed synthesis, against
        - Features on solid substrate
        - SA molecular structures
        - Channels in porous materials
- Vapor-liquid-solid synthesis (VLS) of single-crystal nanowires
    - Example: Ge wire from Au catalyst
    - Example: Si wire from Fe-Si nanocluster
    - Longitudinal superlattices
    - Axial nanowire heterostructures
    - Branching
    - Single-source precursors

o Properties and applications
- Reduction in melting point
- Mechanical properties
- Electron transport properties (w/ QSE's)
- Optical properties (w/ QSE's)

o Inorganic nanotubes
- Growth methods
- Examples:
    - Mo_2S nanotubes
    - WS_2 nanotubes
    - CdSe nanotubes
    - VO_x nanotubes
    - TiO_2 nanotubes
        - Porous template-confined growth
        - Polymer fibers as templates
    - SiO_2 nanotubes
- Template coating
- Useful properties

o Organic nanotubes
- Fullerenes
- Carbon nanotubes

- TubeFETS
- CNTs as sensors
- Aligning CNTs

F. 2D materials

- **Chapter 20: 2D Materials**