Infusion of Nanotechnology Vertical Threads into the Chemistry Curriculum

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What’s Going On!

• Infuse nanotechnology concepts into the undergraduate curriculum (NSF-NUE grant) via “vertical threads”

• Add new and modify current laboratory experiments so that they have a “nano” focus while teaching the same concepts

• Expose students to rapidly growing area of nanotechnology—undergraduate research projects
Research/Advanced Analytical Chemistry
- As Core for photo-reactive species- pollutant degradation

Biochemistry
- Modified particles
- DNA extraction / PCR

Analytical Chemistry
- Modified Particles, Extraction
- Analysis by Wet or Instrumental Methods

General Chemistry
- Synthesis, Yield

Research/Advanced Analytical Chemistry
- Photochemical degradation of pollutants

Physical Chemistry
- Particle in a box
- Kinetics

Inorganic Chemistry
- Metal Ion Doping
- Spectroscopy- Band-Gap/Particle Size

General Chemistry/
Quantitative Analysis
- Homogeneous Precipitation
- Kinetics
Magnetite ($\text{Fe}_3\text{O}_4$) Vertical Thread (General Chemistry CHEM 1211)

- Ordered magnetite particles of approximately 20 nm
- Prepare in general chemistry
  - $\text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O}$
- Write and balance equations
- Stoichiometry
- Nanoparticle background
- Magnetic properties
- Surfactant used to keep particles from aggregating
- Percent yield - centrifuge or separate magnetically and weigh product
- Adapted from http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA2/MAIN/FEFLUID/CD2R1.HTM
Magnetite Vertical Thread (Instrumental Analysis, CHEM 3300)

- Prepare magnetite
- Disperse into THF solution of PVC
- Magnetically recover the coated particles
- Mix particles with a simulated oil or hydrocarbon spill, allow remediation to occur
- Remove particles
- Analyze
  - DRIFTS
  - GC-TCD
  - TGA
Magnetite Vertical Thread (Instrumental Analysis, CHEM 3300)

DRIFTS
- Magnetite (black)
  - Fe$_3$O$_4$ 583 cm$^{-1}$
- PVC Coated (pink)
  - C-Cl 1538 cm$^{-1}$
  - CH stretch, 2900 cm$^{-1}$
  - C-C stretch, 1030 cm$^{-1}$
- Octane/PVC (blue)
  - CH stretch, 2900 cm$^{-1}$
  - C-C stretch 950, 1030, 1150 cm$^{-1}$

GC-TCD
- Pink: PVC Coated remediation
- Blue, after, 75% reduction

TGA: not shown
- 45% weight loss of PVC at 250 °C
Magnetite Vertical Thread (Biochemistry, CHEM 3801)

- Ordered magnetite particles of approximately 20 nm
- Coat with aminopropyltriethoxysilane
- Used to extract calf thymus DNA or *E.coli* 60S rDNA

*E.coli* Extraction followed by PCR and restriction digest

- Blue –
  - Calf Thymus DNA in solution
- Green –
  - After extraction with magnetite
Chalcogen Vertical Thread - MoS$_2$ and MoSe$_2$ “Slick 50”

- Dry lubricant
- Used in oil refining as a catalyst to hydrodesulfurization
- Prepare 4 - 5 nm particles from Mo(CO)$_6$
  - Analyze/Follow Kinetics by FT-IR
- Research project using MoS$_2$ nanoparticles as catalysts for destroying carbonate (salt content)
Chalcogen Vertical Thread - MoS$_2$ and MoSe$_2$ (Physical Chemistry CHEM 3401)

Mo(CO)$_6$ IR Spectra

CO stretch at 1982 cm$^{-1}$

disappears < 1 hour

Boil 120 °C, Toluene
Chalcogen Vertical Thread - MoS$_2$ and MoSe$_2$ (Physical Chemistry CHEM 3401)

Pseudo First order Kinetics

UV-Vis for particle size

Luminescence at 390 nm

Results similar for MoSe$_2$
•Reaction of zinc(II) or cadmium(II) with thioacetamide (TAA) under acidic conditions
•13-30 nm particles

•General Chemistry:
  •1 temperature, 70 ºC
  •Vary the TAA concentration
  •Find rate dependence on TAA only
    •Rate=k[H₃O⁺][TAA]
  •Evaluate the rate constant

Reaction Monitored by UV-VIS
•CdS better—bulk absorbance/scatter beyond the absorbance of TAA and allows glass/plastic cuvettes
•ZnS—quartz cell required. Interference from TAA absorbance
Chalcogen Vertical Thread: ZnS/CdS (Physical Chemistry, CHEM 3401)

Temperature Dependent Kinetics

- Vary TAA, Metal ion and pH
- Comprehensive rate law
- Vary Temperature, calculate Energy of Activation

Square - 75 °C
Diamond - 70 °C
Triangle - 65 °C

y = 0.00249x
y = 0.00153x
y = 0.00093x

Concentration of CdS (M)

Time (min)
Chalcogen Vertical Thread -ZnS / CdS Vertical Thread (Physical and Inorganic Chemistry, CHEM 3200 and CHEM 3402)

\[ E_{np} = E_g + \frac{h^2}{8r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi \varepsilon \varepsilon_0 r} \]

- Synthesize using Na$_2$S and sodium polyphosphate
- Particle size using the Brus equation

ZnS bulk band gap: 337 nm
  - Effective Band-Gap: 310 nm
  - Particle size is: 3.7 nm

CdS bulk band gap: 517 nm
  - Effective Band Gap: 326 nm
  - Particle size: 13.1 nm
ZnS doped with 1% Copper, Manganese and Silver
UV-Vis
  Particle size is constant
Tune the emission
  Undoped ZnS (black)
  Cu$^{2+}$ doped (thick gray)
  Mn$^{2+}$ (red)
  Ag$^{+}$ (blue)

These metals produce lower band gap energies compounds with sulfide.

Lower energy transitions from the CB and CB defects to the excited energy level state of the dopant.
Chalcogen Vertical Thread -ZnS / CdS –(Inorganic Chemistry, CHEM 3200)

Surface Effects

- Particles prepared with H₂S in presence of sodium phosphate
- Titrate with HgCl₂
- Forms HgS on the surface of the CdS particles
- 490 nm CdS Luminescence Quenched
- 575 nm emission enhanced
- Then shifts red to 600 nm with increasing Hg²⁺
- Particle size increases
ZnS / CdS Doping Vertical Thread - (Adv. Analytical/ Undergraduate Research, CHEM 4300 and CHEM 3900)

• ZnS, CdS and MoS₂ particles
  • Stabilized with surfactants or TBAB or polyphosphate
• Used to photo degrade chlorinated compounds-
  • EPA priority pollutants
    • HCB, PCP and others
• Monitor by GC/MS, SPME-GC/MS or HPLC

\[
\begin{align*}
  \text{CdS} & \xrightarrow{\text{hv}} \text{CdS(e + h)} \\
  \text{ZnS} & \xrightarrow{\text{hv}} \text{ZnS(e + h)}
\end{align*}
\]

[Chemical reactions and structures are shown here, including the transformation of a chlorinated compound to TEA and DEA through the addition of electrons, chloride ions, and hydrogen.]

Photocatalysis

HCB on CdS in DMF

PCP on ZnS in DMF

Currently examining ZnS and CdS in Methanol and in water. SnO₂, MoS₂ and TiO₂ also will be investigated.

Size, wavelength, surfactant and ion effects
Additional Projects

- **Nano LED’s and Nano Detectors (Solar Cells)**
  - Chemistry/Physics-Electroluminescence Polymers and CdS nanoparticles on ITO and TiO$_2$ on ITO

- **Magnetite**
  - Use magnetic nanoparticles as core for photooxidants such as TiO$_2$, MoS$_2$, ZnS etc.
  - Make removal easier. Real world application

- **Biochemistry lab to mimic cellular uptake**
  - PEG/biomolecule/fluorescent dye labeled magnetite nanoparticles
  - view with epifluorescence microscope

- **PRISM and Project SEED**
Acknowledgements

- National Science Foundation Division of Undergraduate Education: Nanotechnology in Undergraduate Education Grant DUE/NUE 0303994
- ACS Project SEED and Coastal Georgia Local Section of the ACS (Toland Michael; Monica Richardson)
- International Paper Foundation (Project SEED)
- AASU College of Arts and Sciences
  - Dean Wheeler, for Project SEED Mentors (Dr. Nivens and Dr. Lynch)
  - University System of Georgia Technology Matching Grant
- AASU Research and Scholarship Grant/Gignilliat Scholar
- Upper Division Students: Juan Aragon, Elizabeth Baker, Julie Banks, Mar’quita Bullock, Joyce Chow, Nin Dingra, Kevin Edwards, Jennifer Fiser, Sofie Hakansson, Bryan Jacobs, Pat Liloia, Jeremy Olson, Taryn Root, Patrick Sisco and Jowanda Taft