6-4-2007

A Series of Vertically Integrated Nanotechnology Experiments for the Undergraduate Curriculum

Kevin W. Kittredge

Lesley E. Russell

Michael C. Leopold
University of Richmond, mleopold@richmond.edu

This is a pre-publication author manuscript of the final, published article.

Recommended Citation

K.W. Kittredge, L.E. Russell,* and M.C. Leopold, "A Series of Vertically Integrated Nanotechnology Experiments for the Undergraduate Curriculum," *Chemical Educator* 2007, *12*(3), 155-158.

A Series of Vertically Integrated Nanotechnology Experiments for the Undergraduate Curriculum

Kevin W. Kittredge*, Lesley E. Russell,[†] and Michael C. Leopold[†]

* Dept. of Chemistry and Biochemistry, Miami University Middletown, Middletown OH 45042

[†]Department of Chemistry, Gottwald Center for the Sciences, University of Richmond Richmond, Virginia, 23173

Abstract

We have designed three nanotechnology experiments that are vertically integrated for an undergraduate chemistry curriculum. They are an evolving set of experiments for sequential courses in an undergraduate chemistry program. These experiments are designed to match the student's level of understanding for each particular course. The participating student is involved in a "research" project that progresses in both theory and experimental technique. Students benefit from these vertically integrated experiments by being involved in multiple facets of a simulated research project. This mimics a traditional research project under an advisor's supervision without the undesired drawback of an unknown outcome.

Keywords: Laboratory Instruction, Nanotechnology, Organic Chemistry, Analytical Chemistry, Physical Chemistry, Synthesis, Electrochemistry, UV-vis Spectroscopy,

* To whom correspondence should be addressed. Email: kittrekw@muohio.edu.
Phone: 513.727.3398. Fax: 513.727.3450

A Series of Vertically Integrated Nanotechnology Experiments for the Undergraduate Curriculum

Kevin W. Kittredge*, Lesley X. Russell,† and Michael C. Leopold†

*Department of Chemistry and Biochemistry, Miami University Middletown, Middletown OH 45042

†Department of Chemistry, Gottwald Center for the Sciences, University of Richmond Richmond, Virginia, 23173

Introduction

In 1999 the National Science Foundation released the research initiative "Nanotechnology for the Twenty-First Century: Toward a New Industrial Revolution".*(1)* The report describes areas of interest in nanotechnology and recognizes the multi-disciplinary nature of the field. In order to succeed, this national nanotechnology initiative must involve collaboration among its various participants. This collaborative effort is expected to yield a variety of discoveries that may help facilitate a new technological revolution. Herein lies the challenge presented to current university educators. How do we instruct today's students in such a diverse field while also maintaining the integrity of each sub-discipline in the various chemical sciences? Our goal was to enhance student understanding of this rapidly developing and important field of science without sacrificing key subject material.

The Department of Energy has reported the important research directions in nanoscale science, engineering and technology in conjunction with the national research initiative.*(2)* They describe various research opportunities that could be undertaken by cooperative efforts between the national laboratories, universities, and industry. From their findings, it is readily apparent how the variety of research and applications of nanotechnology affects energy, defense, and the environment. What remains to be seen is what other areas will also be affected by nanotechnology, and how strongly our current students will be able to contribute to this emerging field.

Presenting nanotechnology in a university's current course curriculum is a novel challenge. One question that must be asked is in which subject area in a particular discipline does nanotechnology belong? Arguments may be made about which field should teach subject matter pertaining to nanotechnology. For example, chemists may make the nano-materials that in turn are studied by physicists and subsequently developed into devices by electrical engineers. Or, biologists may isolate proteins that are arranged in an ordered fashion by material scientists and used as sensors by chemists in analytical instrumentation. These two examples are only a glimpse into the breadth of the evolving field of nanotechnology. All subject matter in the various physical and biological sciences must incorporate nanotechnology at some level and are interdependent on one another. With this complexity in mind, exposing students to a variety of disciplines in a logical fashion is a formidable task for educators.

As educators we have the responsibility to prepare our science and engineering undergraduate students in emerging technological fields. Today's students will most undoubtedly encounter nanotechnology in their careers. Thus, it becomes imperative that nanoscience/technology be included in their studies. A probable side benefit of including nanotechnology in the curriculum is the attraction of students to the physical or biological sciences. Currently there are very few developed and tested experiments relating to nanotechnology in undergraduate programs. Specialized material like that of the Materials Science program at the University of Wisconsin is not applicable to a more generalized curriculum and is targeted for advanced students already committed to their program of study.*(3)* There are also a few advanced undergraduate experiments that do address nanotechnology, but they are designed exclusively for a single course and are encountered later in a student's studies.*(4,5)* As of this date and to our knowledge there are not any specific course textbooks that address the topic of nanotechnology at the undergraduate level.

Our primary objective was to develop a series of vertically integrated experiments that an undergraduate program with modest resources may adapt. One important objective is that these experiments must be done at minimal cost, both in terms of materials (chemicals and instrumentation) and faculty time. We designed a series of experiments that may be inserted into a current undergraduate curricula without requiring additional specialized courses or elaborate instrumentation/capital facilities (i.e. clean rooms, specialized fabrication, etc.). In addition, vast expertise on the part of the faculty instructor is also not a necessity for implementation of the proposed set of experiments.

Here, we propose a program where students follow a series of experiments with a predetermined outcome throughout a traditional A.B. or B.S. curriculum in chemistry or biochemistry. The inclusion of this material does not diminish course content by exclusion of other subject matter and enhances other course materials by relying on the interdisciplinary nature of research. As the student progresses through their studies, he or she participates in a rigorous series of experiments where fundamental knowledge and skills are learned. Inclusion of these experiments has a positive cooperative learning effect and strengthens an undergraduate curriculum.

We developed nanotechnology/science experiments with the philosophy that students will increase their understanding in specialized areas as they proceed through their academic curricula. This series of experiments maintains a sense of continuity by being developed through several courses, thereby mimicking a research project. This research project follows the student's program of study as they progress from lower division organic chemistry through analytical chemistry to upper division physical chemistry, a sequence normally completed by students in three academic years. As students learn new sub-disciplines in chemistry, they incorporate material and experiences from their prior courses. Each new experiment is written as a lab report that includes the prior experiment(s). Thus, students are required to revise and augment an existing lab report at each stage. This process of writing and rewriting not only improves a student's writing skills, but also helps him or her retain previously learned material and to focus on the interdisciplinary nature of chemical research. This final report turned into the instructor is similar both in content and format to a manuscript that may be found in a professional journal. Seeing first hand the connections and overlapping interests between the various sub-disciplines in chemistry, a student becomes more vested in the learning process and enthusiastic about science. This translates into producing better chemists and increasing enrollment in scientific programs.

In the rapidly evolving field of nanotechnology, interest in the organized assembly of nano-scale structures into functional materials has intensified greatly.*(6-10)* Metallic nanoparticles continue to garner much attention in this area and are the focus of our experiments. First introduced by Brust and coworkers,*(11)* one of the more interesting nanoparticles being investigated are metallic gold cores, several nanometers in diameter, passivated with a peripheral layer of alkanethiols. Due to their inherent stability, versatility, and ease of handling, these particular nanoparticles have attracted much attention and have been termed Monolayer-Protected Clusters (MPCs).*(12,13)* Functionalized MPCs are created via simple place-exchange reactions,*(14-16)* where thiol ligands with terminal functional groups are incorporated into the peripheral skin of the MPCs.

Crown ethers (CE) are well-known ionophores for metal ions and have often been targeted for connection to molecular scaffolds for the purpose of metal ion sensing materials.*(17)* Crown ethers are popular in this respect since they feature inherent sensor selectivity, their ring structures are able to coordinate only specifically sized ions. For example, the 15-crown-5 moiety is known to reversibly coordinate to ions like Na^+, K^+, and Ag^+.*(18)* Chen reported the modification of large, colloidal nanoparticles with crown ether (15-crown-5) ligands to selectively bind or "sandwich" solution metal ions (K^+ and Na^+), stimulating both aggregation and a colorimetric indicator response.*(19)* Again, coordination of a specific metal ion in a sandwich between neighboring nanoparticles causes the red solution to suddenly change to blue, an indication of the metal driven aggregation within the system. More recently, Chen also reported the use of MPCs possessing both crown ethers and carboxylic acid functional groups.*(20)* These bifunctionalized MPCs were successfully used to coordinate and detect K^+ ions four orders of magnitude faster than MPCs with only CE functional groups. Chen used these systems to detect the presence of K^+ and Na^+ in human urine, a common use for metal ion sensors.

We have designed a set of nanotechnology based experiments where a student will synthesize a thiol modified crown ether and proceed to study its metal chelation properties by performing redox probe voltammetry at a self-assembled monolayer of crown ether alkanthiolates. Finally, the students prepare crown ether-capped monolayer protected clusters and examine their coordination kinetics with different metal ions using spectrophotometry.

Experimental

The details of each experiment may be found in the Supplementary Material. These include the hazards and safety precautions for each individual experiment.

SPECIFIC EXPERIMENTS:

Organic Chemistry

Traditionally organic chemistry is taken in the student's sophomore year. This experiment is designed to be conducted in the second semester where the student has already been exposed to the necessary prerequisite spectroscopic techniques and synthetic skills. The overall reaction involves a two-step synthesis of a macrocylic crown ether with a pendant alkyl thiol, 2-(10-mercaptodecyloxymethyl)-15-crown-5 ether, starting from the precursor alcohol. The crown ether is reacted with an alkyldibromide via a Williamson Ether Synthesis followed by preparation of the thiol in a nucleophilic substitution reaction. For each reaction, the student purifies his or her compound by chromatography using SiO_2 with hexane/ethyl acetate as the eluent. The compounds are characterized by infrared spectroscopy, ^{1}H NMR, and/or ^{13}C NMR spectroscopy depending on the available instrumentation. The laboratory report should describe the synthetic procedures, spectroscopic data, and discussion of the mechanism for formation of the ether subsequent thiol.

Analytical Chemistry

Students generally enroll in analytical chemistry in the fall of their third year following organic chemistry. In this course, students will compare the selectivity of 15-crown-5 for K^+ ion over Na^+ ion in a solution of the positively charged redox couple ruthenium hexamine, $Ru(NH_3)_6^{2+/3+}$ (RuHex) functioning as the reporter ion.*(21)* The first part of the experiment involves using well-established procedures *(22)* to synthesize a planar two-dimensional self-assembled monolayer (SAM) of 15-crown-5 terminated alkanethiolates. The surface coverage of the SAM can be assessed by observing the solution voltammetry of the RuHex. Students compare the RuHex voltammetry of a bare gold electrode to a gold surface is covered with the densely packed crown ether SAM (CE-SAM). They observe that electron transfer between the surface and any electroactive species in an electrolytic solution is suppressed when the surface is covered, with the voltammetry showing peak splitting that is less reversible than at a bare substrate (Figure 2).*(22)* Next, they compare the electrochemistry of the freely diffusing probe RuHex at the CE-SAM in the presence and the absence of Na^+. The positively charged RuHex molecules exhibit characteristic diffusing behavior at the CE-SAMs in the absence of Na^+, indicating the molecule can access the electrode surface through defects in the monolayer. However, once Na^+ ions are coordinated into the crown ether moieties the CE-SAM retains a layer of positive charge on its periphery and is more effective at blocking the approach of the RuHex to the electrode surface, subsequently eliminating or reducing the diffusion based electrochemistry. This behavior is also seen for K^+, albeit attenuated when compared to Na^+.(see Supplementary Material)

Physical Chemistry

Students generally take one year of physical chemistry starting in the spring of their junior year or fall of their senior year. This experiment includes the preparation of 2-(10-mercaptodecyloxymethyl)-15-crown-5 ether capped 3-dimensional monolayer protected clusters (CE-MPC) and studying the changes in the plasmon band for the free and the bound Na^+ and K^+ metal ions.*(19)* Students initially prepare a monolayer protected cluster capped with an alkanethiol using the Brust protocol*(11)* followed by a ligand exchange with the crown ether.*(14-16)*. They then complex the 15-crown-5 nanoparticle with Na^+ ion and observe a slight shift in the UV-visible spectra absorption maximum around 528 nm compared to the uncomplexed species. Then while adding increasing amounts of K^+ ion and monitoring the changes in the absorbance maximum they observe an even greater shift. As the concentration of K^+ ion increases, the colloidal plasmon band at 528 nm decreases and an irreversible red shift in the surface plasmon band is observed. Addition of excess Na^+ ion demonstrates the selectivity of the 15-crown-5 modified nanoparticles to preferentially bind K^+ ions in a unique "sandwich" chelation (i.e. two crown ether moieties coordinate one K^+ ion)*(23)*. Students observe that changes in the absorption spectra are quite sensitive to minute quantities of metal cations. Lastly, they again prepare Na^+ coordinated CE-MPCs and add K^+ ion and monitor the kinetics of coordination. Students calculate the reaction orders for the two metal ions as well as the second-order rate constant. They also learn about the sensitivity of these systems towards metal ions and their potential usefulness as specific ion sensors.*(23)*

Conclusion

We have designed three nanotechnology experiments that are vertically integrated for an undergraduate chemistry curriculum. They are an evolving set of experiments for sequential courses in an undergraduate chemistry program. These experiments are designed to match the student's level of understanding for each particular course. The participating student is involved in a "research" project that progresses in both theory and experimental technique. Students benefit from these vertically integrated experiments by being involved in multiple facets of a simulated research project. This mimics a traditional research project under the supervision of an advisor without the undesired drawback of an unknown outcome. Initially, the student synthesizes a target molecule, 2-(10-mercaptodecyloxymethyl)-15-crown-5 ether, via two successive substitutions, the first a Williamson Ether Synthesis followed by a S_N2 reaction in their organic chemistry course. They learn molecular characterization techniques such as NMR and IR as well as isolation and purification methods, namely chromatography. In their next course, commonly analytical chemistry, the student prepares a 2-dimensional self-assembled monolayer and studies the electrochemistry of a freely diffusing probe molecule, ruthenium hexamine, in the presence and absence of sodium (Na^+) and potassium (K^+) ions for the CE-SAM modified surface. Lastly, in their physical chemistry course, the student prepares an 2-(10-mercaptodecyloxymethyl)-15-crown-5 ether capped 3-dimensional monolayer protected clusters and explores the selective ion-binding of metal cations (Na^+ and K^+) by titration and UV-vis spectroscopy. Complexation of crown ethers with two different metal cations results in a dramatic visible color change. Lastly, the student examines the origins of the strong plasmon emissions that appear in the UV-vis spectra for these alkyl crown ether capped nanoparticles. In each course the student is required to write reports that are inclusive of all material from each previous class. A vertically integrated curriculum that incorporates nanotechnology prepares our students to answer the challenges of society and the scientific community.

Acknowledgements

KWK wishes to acknowledge the National Science Foundation (CHE-0303830) and MCL Virginia's Commonwealth Health Research Board for generously supporting this research.

References

(1) "Nanotechnology for the Twenty-First Century: Toward a New Industrial Revolution," Interagency Working Group on Nano Science, Engineering and Technology (IWGN), National Science Foundation, 1999.
(2) "Nanoscale Science, Engineering, and Technology Research Directions," Office of Basic Energy Science (BES) Nanoscience/Nanotechnology (N/N) Group, Department of Energy, 2000.
(3) Web site of the Material Research Center, University of Wisconsin.
(4) Craig, V. S. J.; Jones, A. C.; Senden, T. J. *J. Chem. Educ.* **2001**, *78*, 345-346.
(5) Laughlin, J. B.; Sarquis, J. L.; Jones, V. M.; Cox, J. A. *J. Chem. Educ.* **2000**, *77*, 77-79.
(6) Walt, D. R. *Nature Materials* **2002**, *1*, 17-18.
(7) Wu, C. *Prism* **2004**, *14*, 1-5.
(8) Cobbe, S.; Connolly, S.; Ryan, D.; Nagle, L.; Eritja, R.; Fitzmaurice, D. *J. Phys. Chem. B* **2003**, *107*, 470-477.
(9) Nagle, L.; Ryan, D.; Cobbe, S.; Fitzmaurice, D. *Nano Letters* **2003**, *3*, 51-53.
(10) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607-609.
(11) Brust, M.; Walker, M.; Bethell, D.; Schriffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801-802.
(12) Feldheim, D. L.; Foss, C. A., Jr.; Editors *Metal Nanoparticles: Synthesis, Characterization, and Applications*, 2002.
(13) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27-36.
(14) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782-3789.
(15) Templeton, A. C.; Hostetler, M. J.; Warmoth, E. K.; Chen, S.; Hartshorn, C. M.; Krishnamurthy, V., M; Forbes, M. D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 4845-4849.
(16) Ingram, R. S.; Hostetler, M. J.; Murray, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 9175.
(17) Gokel, G. W.; Leevy, W. M.; Weber Michelle, E. *Chem. Rev.* **2004**, *104*, 2723-2750.
(18) Samant, R. A.; Ijeri, V. S.; Srivastava, A. K. *J. Chem. Eng. Data* **2003**, *48*, 203-207.
(19) Lin, S.-Y.; Liu, S.-W.; Lin, C.-M.; Chen, C.-h. *Anal. Chem.* **2002**, *74*, 330-335.
(20) Lin, S.-Y.; Chen, C.-h.; Lin, M.-C.; Hsu, H.-F. *Anal. Chem.* **2005**, *77*, 4821-4828.
(21) Flink, S.; Boukamp, B. A.; Berg, A. v. d.; Veggel, F. C. J. M. v.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 4652-4657.
(22) Hu, J.; Zhang, J.; Liu, F.; Kittredge, K. W.; Whitesell, J., K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 1464-1470.
(23) Pompano, R. R.; Wortley, P. G.; Moatz, L. M.; Tognarelli, D. J.; Kittredge, K. W.; Leopold, M. C. *Thin Solid Films* **2006**, *510*, 311-319.