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Microscale Synthesis and Characterization of Gold Nanoparticles for the Laboratory Instruction

Shui-Ping Yang*

Department of Chemistry, National Changhua University of Education,
Changhua 50058, Taiwan
yangsp@cc.ncue.edu.tw

Abstract
This experiment developed at a microscale level was in response to green chemistry for undergraduate laboratory instruction. Usually, all equipments used for the synthesis of gold nanoparticles (AuNPs) must be cleaned with aqua regia. These practices are harmful to human health and detrimental to the environment. In our experiment, one-pot reaction was used to directly synthesize colloidal Au in a small clean vial for a short time. The procedure was very easy to proceed and had a high success rate. Characterization of colloidal gold at microscale level was also straightforward, which included three aspects: Tyndall effect, aggregation, and spectrum. A novel characterization regarding the AuNPs aggregation is really valuable, in which the aggregation was tested on a white paper coated with a layer of wax using two liquid balls of colloidal gold. We found that all students could successfully synthesize intense ruby red color of gold nanoparticles in 10 minutes, and managed to characterize the colloidal Au in 10 minutes in this microscale experiment. The amount of $HAuCl_4$ used was only one tenth of those in typical synthesis. The spectrum results in λ_{max} obtained by students were in a range of 520-532 nm. Testing for the AuNPs aggregation and the Tyndall effect were positive. This experiment is consistent with five principles of green chemistry. Working at this experiment has many advantages: reducing the time, cost and waste, and encouraging the students to think about environmental protection. The laboratory instruction revealed that the overwhelming majority of the students had positive responses in the cognitive, affective and psychomotor domains. Moreover, the students felt more valuable that they have an opportunity to permanently preserve their own products of AuNPs by stabilizing with PVP in the original vial.

Keywords: microscale experiment, green chemistry, gold nanoparticle, and laboratory Instruction

Introduction

Gold nanoparticles

Typically, gold nanoparticles (AuNPs) are synthesized in an aqueous solution by reduction of chloroauric acid ($HAuCl_4$, hydrogen tetrachloroaurate). After dissolving $HAuCl_4$ in a deionized water, the solution is rapidly stirred while a reducing agent, such as sodium citrate, is added. This results in Au^{3+} ions to be reduced to neutral gold atoms. As the gold atoms form gradually, they accumulate to form AuNPs, and the solution becomes colloidal. Currently, several synthetic methods for AuNPs, especially in size-and-shape controlled, have been developed [1-3], and its widespread application has been reported [4-6].

Gold nanoparticles and macroscale experiments

With the congress in the emerging discipline, many chemical experiments focused on the synthesis and characterization of AuNPs for the laboratory instruction have been present in chemical education journals [7-9] and on the Internet [10-12]. However, all of these experiments were designed at a macroscle level, rather than at a microscle level. For example, an experimental procedure mentioned: "*Add 20 mL of 1.0 mM $HAuCl_4$ to a 50 mL Erlenmeyer flask… Slowly add 2 mL of 1% $Na_3C_6H5O_7{\cdot}2H_2O$ to the 50 mL flask.*" [12] In typical procedures, all equipments used in the synthesis and characterization of AuNPs must be cleaned with aqua regia [13-15]. For instance, an experimental procedure described: "*Nanoparticles are normally prepared using specially cleaned glassware and avoiding any exposure to organic materials. The Turkevich paper reported cleaning with aqua regia*." [15] Unfortunately, these chemicals used in the experiments are harmful to human health and detrimental to the environment. Furthermore, in reviewing on the synthesis and characterization of AuNPs, we have not found any of the general chemistry laboratory textbooks [16-20] provided undergraduate students with such experiments as teaching materials.

Microscale chemistry

In the 1980s, the microscale chemical experiment (MCE) has begun developing in three agencies (Bowdoin College, Merrimack College, and Brown University) of the United States [21]. It started in organic chemistry experiments originally, and spread to the general chemistry, inorganic chemistry, analytical chemistry, and environmental chemistry experiments [21]. The MCE refers to the use of miniaturize instrument and equipment devices, and the reduction of reagent quantity to a range of 1/10-1/1000 of that in normal experiments. The MCE is a good way to achieve the concept of green chemistry. In the industry, green chemistry is mainly to reduce/eliminate the use and generation of hazardous substances in manufacturing process for preventing harm to the environment. In the education, green chemistry is involved in chemical laboratory instructions. The MCEs and green chemistry experiments can improve the quality for students' interest in learning and teachers' teaching.

The benefits of implementing MCE and green chemistry laboratory include reduced reaction time, improved safety, and major cost savings [21]. Green chemistry and microscale chemistry are complementary pedagogies, allowing the ideas of resource reduction, material substitution, and exposure minimization to be brought effectively into the academic laboratory [21].

Implementation of microscale chemistry

The National Microscale Chemistry Center (NMC2) in the United States was established in January 1993 to promote the use of microscale chemistry as a means of eliminating toxic waste at the source. Its major initial focus is on the offering of workshops, seminars and publications on the operation and advantages of conversion of laboratories to a microscale level [22]. Microscale chemistry is performed by means of drastically reduced amounts of chemicals, safe and easy manipulative techniques, and miniature labware and high quality skills [22]. *Journal of Chemical Education* offers the Microscale Laboratory column. Since 2005, this journal has published about 50 MCEs, which were mostly organic chemistry experiments [23], and fewer experiments in general chemistry [24]. Our experiment focuses on the development of the synthesis and characterization of AuNPs at a microscale level.

Green chemistry

The twelve Principles of Green Chemistry were originally published by current assistant administrator Paul Anastas and John Warner of United States Environmental Protection Agency [25]. The twelve principles are: prevention, atom economy, less hazardous chemical syntheses, designing safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feedstocks, reduce derivatives, catalysis, design for degradation, real-time analysis for pollution prevention, and inherently safer chemistry for accident prevention [26-27]. Our experiment developed at a microscale level attempted to respond to green chemistry for undergraduate laboratory instruction.

Instructional Strategies and Considerations

Chemistry-major freshmen students as individuals, a group of one student, worked this AuNPs experiment at a microscale level for a three-hour laboratory sessions. The students were first introduced to experimental process, content background, especially in the synthesis and characterization of AuNPs, and concepts of microscale chemistry and green chemistry. The students then manipulated experimental procedures and wrote their own reports and learning feedback. By the way, the synthesis of AuNPs (excluding the characterization) at a microscale level had been performed within 40 minutes in an event that a class of high-school students visited the chemistry of department in our university. All of the students were a first experience in the synthesis of AuNPs. Valuably, they can success to synthesize colloidal AuNPs and most of the students had positive responses for the synthesis. Examples of the students' feedback are as follows:

"*I am so happy that I am able to synthesize gold nanoparticles myself, and bring it to home for permanent preservation.*"

"*I like this experiment, gold nanoparticles is very easily synthesized, and the change in color is attractive.*"

The main pedagogical characteristics of this laboratory instruction included two aspects to be expected. In terms of pedagogical characteristics: emphasis on students' reflections in between microscale and macroscale, accent on students' introspection in green chemistry and environmental protection, as well as emphasis on the significance of multi-style design with chemical experiments. In terms of content knowledge and laboratory technique: comprehending the synthesis and characterization of AuNPs, proficiency in the technique of microscale chemistry, expertizing in taking UV-visible absorption spectrum and in testing for the aggregation using liquid balls, as well as understanding in the nanoparticles and green chemistry.

Many teachers/instructors misunderstood that this experiment is very expensive due to the use of gold. Actually, each experiment/student/group only spent in a low cost experiment at a microscale level. The price of hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$) is about USD 100 per 1.0 gram. A 0.041 g of $HAuCl_4 \cdot 4H_2O$ can suffice for 50 experiments, or for 50 students/groups. By calculation, each experiment/student/group merely spent (USD 100 / 1.0 g) × (0.041 g / 50 students) = USD 0.082 / student. That is, it is equivalent to JPY 8.1/student, TWD 2.5/student, and GBP 0.052 / student. Thus, the use of gold for this microscale experiment is cost-effective.

Experimental Section

Chemicals and Equipments

The following chemicals and equipments are needed for each student/group to perform this microscale experiment, in addition to a 100.0-mL volumetric flask, three 100-mL Erlenmeyer flasks equipped with silicone rubber stoppers and two spectrophotometers, which are intended for a whole class.

- Forty drops (2.0 mL) of 1.0 mM chloroauric acid ($HAuCl_4$)
- Ten drops (0.50 mL) of 34.0 mM sodium citrate ($Na_3C_6H_5O_7$)
- Two drops of 0.3% poly(vinylpyrrolidone) (PVP)
- Four disposal Pasteur pipettes (LDPE) (Any pipettes must not be used before.)
- One 3-mL Glass vial with Teflon cap (This vial must not be used before.)
- One hot plate with a magnetic stirrer
- One 100-mL beaker containing half full of tap water
- Quarter sheets of A4-size white paper and a little white wax

- A few granular sodium chloride (NaCl)
- One 1.5-mL disposable plastic cuvette and about 5-mL of distilled water
- One red light laser pointer for detecting the Tyndall effect

Preparation of solutions

The instructor/TA needs to prepare the followings:

- 100.0 mL of 1.0 mM $HAuCl_4$: place 0.041 g of hydrogen tetrachloroaurate(III) tetrahydrate ($HAuCl_4 \cdot 4H_2O$, molar mass 411.85 g/mol) in a 100.0 mL of volumetric flask. Add distilled water to the flask, using a funnel or wash bottle, until the level nears the calibration mark. Then add distilled water using a disposal pipette to reach the calibration mark and mix it thoroughly. This solution is enough for either 50 experiments or one experiment for 50 students/groups. The solid $HAuCl_4 \cdot 4H_2O$ with minimum 99% assay is available from Chowa Chemicals Inc, Japan.
- 100.0 mL of 34.0 mM $Na_3C_6H_5O_7$: place 1.00 g of sodium citrate dehydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, molar mass 294.10 g/mol) in a 100.0 mL of volumetric flask. Add distilled water to the flask, using a funnel or wash bottle, until the level nears the calibration mark. Then add distilled water using a disposal pipette to reach the calibration mark and mix it thoroughly.
- 100 mL of about 0.3% PVP: dissolve about 0.3 g of PVP (average molar mass 40,000 g/mol) in 100 mL of distilled water in a 100 mL of Erlenmeyer flask. Tightly plug the flask with a rubber stopper and mix the solution thoroughly.

Experimental Procedures

Synthesis of gold nanoparticles (AuNPs): With a clean disposal Pasteur pipette, add 40 drops (2.0 mL) of 1.0 mM $HAuCl_4$ and 10 drops (0.50 mL) of 34.0 mM $Na_3C_6H_5O_7$ into a 3-mL vial which is not need to clean but can directly be used. Close the cap tightly. Place the sealed vial to the a half full of boiling water in a small beaker. Heat the solution until it shows a deep red color (about 10 min). Remove the vial from the beaker. Allow it to cool.

Characterization of AuNPs: In taking the Tyndall effect: the remaining solution in original vial was feasible using a laser pointer. In the aggregation and stabilization, placing only 2 × 2 drops of the AuNPs solution on quarter sheets of white paper coated with a layer of wax to form two liquid balls are sufficient in the comparison of color change by adding a few granules of sodium chloride to a ball. In taking the spectrum, pouring only 15 drops of the AuNPs solution into a 1.5-mL disposable plastic cuvette and two-fold dilution was practicable.

Stabilization of AuNPs: To preserve the AuNPs under stable conditions, put the diluted solution in the cuvette into the original vial. Put two drops of 0.3% PVP solution into it. Cover the cap tightly and shake the mixture uniformly. You can permanently preserve in the vial the AuNPs solution you synthesized.

Safety Precautions

Chemical splash goggles, protective clothing and gloves must be worn throughout the entire experiment. The hot water or boiling water baths should be handled with care to avoid burns. Chemicals used as much diluted solutions, 1.0 mM $HAuCl_4$, 38.8 mM $Na_3C_6H_5O_7$ and 0.3% PVP, are not dangerous. However, hydrogen tetrachloroaurate(III) and sodium citrate are slightly hazardous and may cause burns/irritation of skin and eyes. Poly(vinylpyrrolidone) is hygroscopic and may cause eye, skin, and respiratory tract irritation. Hydrogen tetrachloroaurate(III), sodium citrate, and poly(vinylpyrrolidone) spilled on skin or your clothing should be washed off with water immediately and thoroughly. The three chemicals spilled above on eyes must be washed immediately, and inner surface of the eyelid must be rinsed with copious amounts of water for at least 15 minutes. Get medical aid immediately.

Results and Discussion

Microscale Synthesis

In terms of the microscale synthesis, the mixture color was observed to change from colorless to blue to purple to intense ruby red, indicates the regeneration of Au nanoparticles (AuNPs) as shown sequentially in Figures 1a-1d. The change colors are consistent with that in the macroscale synthesis.

(a) Colorless appeared in the beginning stage.

(b) Blue color presented in an intermediate process.

(c) Purple color presented at a later stage.

(d) Ruby red color appeared at the end of the synthesis.

Figure 1. The color changes observed in the progress of the Au nanoparticle synthesis.

Tyndall effect

In terms of the Tyndall effect, students can observe a beam of the red light through the AuNPs solution by irradiating using a laser pointer, whereas no beam is appeared in the

$HAuCl_4$ solution. Figure 2 shows that in left vial the AuNPs solution can be confirmed its colloidal presence and in right vial the $HAuCl_4$ solution can be confirmed its true-solution property.

The particles in colloidal solution are large enough to reflect or scatter light in all directions. The Tyndall effect is due to light scattering when a light beam is irradiated to present through a colloid containing particles within 1-200 nm. For a light scattering, the colloid particles are stable and do not separate, while the suspension particles do separate on standing. In a true solution the dispersed particles are too small to scatter visible light. Based on the scatter light properties, intense ruby red color of AuNPs presented a stable and less separately scattering light means the size of these particles within 1-200 nm.

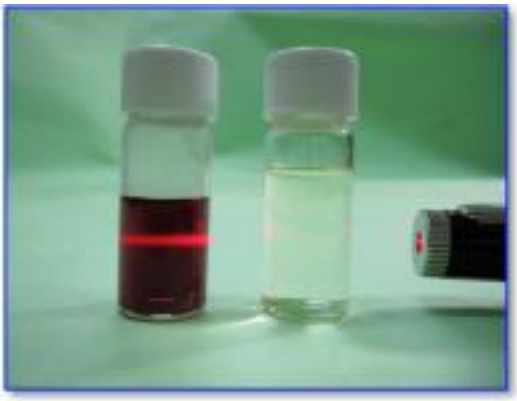

Figure 2. The colloidal AuNPs solution (left) presented the Tyndall effect, while the $HAuCl_4$ solution with the behavior of a true solution (right) does not.

Figure 3. The aggregation of AuNPs by adding granular sodium chloride to change color from ruby red to dark gray, at the right side of a liquid ball.

Particle Aggregation

In terms of the particle aggregation, students can clearly observe the change of color of the AuNPs solution from intense ruby red to dark gray by adding granular sodium chloride, as shown in Figure 3. This is because of increasing the AuNPs size by adding electrolytes yields a blue-green color or dark gray shift from a ruby red color.

Electrolytes, such as sodium chloride, contain two types of ions, one is cation with positive charge and the other is anion with negative charge. Each Au nanoparticle has negative electrical charges; in this case citrate ions are on its surface, which allows the individual AuNPs to repel each other. As sodium chloride is added to the AuNPs solution, the Na^+ ions are attracted to the negative charges of AuNPs so that this reduces the nanoparticles repelling each other. Thus they are able to aggregate, making larger nanoparticles. The size-color effect is consistent with the aggregation.

Absorption Spectrum

In terms of taking the spectrum, the results, in maxmum absorption wavelength (λ_{max}) of AuNPs, obtained by students were in a range of 520-532 nm. The results are close to literature values, 520-528 nm. Figure 4 shows a student's absorption spectrum of AuNPs using a UV-visible spectrophotometer, and the λ_{max} was 529 nm.

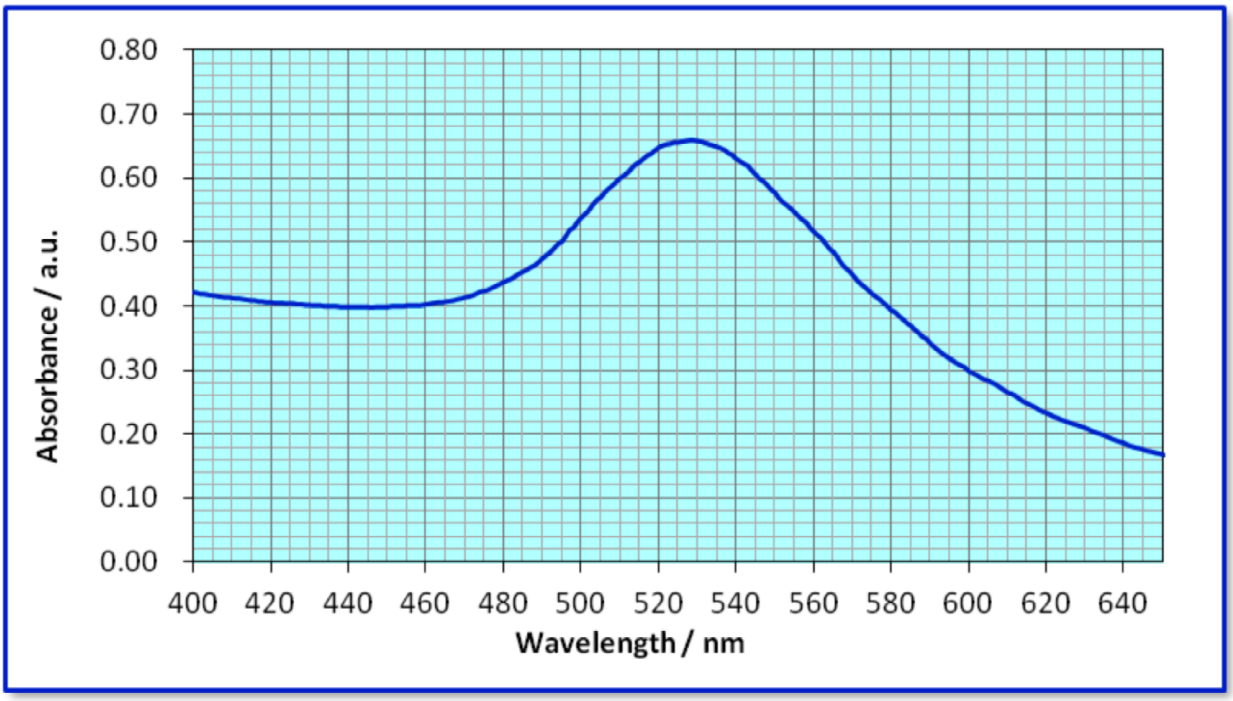

Figure 4. A student's absorption spectrum of gold nonaparticles

Learning Feedback

Students' learning feedback is summarized into three categories: cognitive, affective, and psychomotor domains, and evaluated by the qualitative analysis − positive response, negative response, and combination of positive and negative responses. Representatives of students' learning feedbacks are described below.

– Cognitive domains (positive response)

"*Waxing should be coated evenly on the paper to prevent liquid balls (droplets) from penetrating into the paper.*"

"*Electrolyte was added so that the negative charge of gold nanoparticles on outter layer is offset away. This eliminate the nanoparticles repel each other and produce aggregation.*"

"*This experiment uses a very little amount of chemicals. It is consistent with the idea of green chemistry*"

"*Heating a mixture inside a vial in a hot water bath makes the temperature constant.*"

"*The microscale experiment in the synthesis and characterization is really simpler than the typical experiment. It is very easy to follow and understand in this way.*"

– Affective domain (positive response)

"*This way at a microscale level eliminated the steps of cleaning and rinsing equipments so that I improved operational efficiency and reduced chances of failure.*"

"*The microscale method eliminates troubles of cleaning equipments, and reduces the difficulty of the operation. I believe that high-school students can easily synthesize, identify and understand gold nanoparticles.*"

"*I thought it was very joyful to preserve our own experimental products, the Au nanoparticles we synthesized.*"

– Psychomotor domain (positive response)

"*I followed the experimental procedure and found that gold nanoparticles can be actually synthesized and characterized in a simpler way.*"

– Cognitive domains (combination of positive and negative responses)

"*Coating a thin layer of white wax on a white paper to make liquid balls is a good idea. Perhaps, coating wax inside a petri dish is better because it can be cleaned and reused and to be more environmental friendly.*"

Conclusions

We found that all students can successfully synthesize intense ruby red color of the gold nanoparticles in 10 minutes, and facilitate the characterization of the colloidal gold in 10 minutes in this experiment at a microscale level which the amount of $HAuCl_4$ used was only one tenth of those in a typical synthesis at a macroscale level.

This experiment at a microscale level is consistent with five of twelve principles of green chemistry: prevention, less hazardous chemical syntheses, designing safer chemicals, reduceing derivatives and inherently safer chemistry for accident prevention. In additional, working in this experiment has many advantages: reducing the time, cost and waste, as well as encouraging the students to think about environmental protection.

According to the qualitative analysis of students' learning feedback, the laboratory instruction using in our experiments reveal that the overwhelming majority of the students had positive responses in the cognitive domain, affective domain and psychomotor domain. Moreover, the students felt more valuable that they have an opportunity to permanently preserve their own results of Au nanoparticles by stabilizing with PVP in the original vial.

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References

[1] Nehl, C. L.; Liao, H.; and Hafner, J. H., "Optical Properties of Star-Shaped Gold Nanoparticles" *Nano Lett.*, **2006**, *6* (4), 683–688.

[2] Chen, H.; Kou, X.; Yang, Z.; Ni, W. and Wang, J., "Shape- and Size-Dependent Refractive Index Sensitivity of Gold Nanoparticles", *Langmuir*, **2008**, *24* (10), 5233–5237.

[3] Sau, T. K.; Pal, A.; Jana, N. R.; Wang, Z. L. and Pal, T., "Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles", *Journal of Nanoparticle Research*, **2001**, *3*, 257–261.

[4] Zhang, T.; Dong, Y.; Sun, Y.; Chen, P.; Yang, Y.; Zhou, C.; Xu, L.; Yang, Z. and Liu, D., "DNA Bimodified Gold Nanoparticles", *Langmuir*, **2012**, *28* (4), 1966–1970.

[5] Sironi, L.; Freddi, S.; Caccia, M.; Pozzi, P.; Rossetti, L.; Pallavicini, P.; Donà, A.; Cabrini, E.; Gualtieri, M.; Rivolta, I.; Panariti, A.; D'Alfonso, L.; Collini, M. and Chirico, G., "Gold Branched Nanoparticles for Cellular Treatments", *J. Phys. Chem. C*, **2012**, *116* (34), 18407–18418.

[6] Chen, T.; Yang, M.; Wang, X.; Tan L. H. and Chen, H., "Controlled Assembly of Eccentrically Encapsulated Gold Nanoparticles", *J. Am. Chem. Soc.*, **2008**, *130* (36), 11858–11859.

[7] Sharma, R. K.; Gulati, S. and Mehta, S., "Preparation of Gold Nanoparticles Using Tea: A Green Chemistry Experiment", *J. Chem. Educ.*, **2012**, *89* (10), 1316–1318.

[8] Gerber, R. W. and Oliver-Hoyo, M., "Building a Low-Cost, Six-Electrode Instrument To Measure Electrical Properties of Self-Assembled Monolayers of Gold Nanoparticles", *J. Chem. Educ.*, **2007**, *84* (7), 1177–1179.

[9] Goia, D. V.; Andreescu, D. and Andreescu, S., "Integration of Nanomaterials into the Undergraduate Chemistry Curriculum: Synthesis and Characterization of Gold Nanoparticles", *Chemical Educator*, August, **2007**, *12*(4), 256-259.

[10] "Citrate Synthesis of Gold Nanoparticles", MRSEC Education Group, University of Wisconsin – Madison, http://education.mrsec.wisc.edu/277.htm. Retrieved on 30 August 2013.

[11] "Synthesis and Characterization of Gold Nanoparticles", National Taiwan University, http://www.ch.ntu.edu.tw/~genchem99/doc/T26_gold%20nanoparticle.pdf. Retrieved on 30 August 2013.

[12] "Synthesis of Colloidal Gold", The Sage Colleges, http://www.sage.edu/rsc/academics/nanoscience/asset/Colloidal_Gold.pdf. Retrieved on 30 August 2013.

[13] Kemal, L.; Jiang, X. C.; Wong K. and Yu, A. B., "Experiment and Theoretical Study of Poly(vinyl pyrrolidone)-controlled Gold Nanoparticles", *J. Phys. Chem. C*, **2008**, *112* (40), 15656–15664.

[14] ana, N. R.; Gearheart, J. and Murphy, C. J., "Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles", *Langmuir*, **2001**, 17, 6782–6786.

[15] "Synthesis of Gold Nanoparticles", Oklahoma State University, http://frontpage.okstate.edu/nanotech/Lab/Lab1/gold.%20np.prep.081406.pdf. Retrieved on 30 August 2013.

[16] Greco, T. G.; Rickard, L. H. and Weiss, G. S., "Experiments in General Chemistry: Principles and Modern Application" 9th ed., Prentice Hall, Upper Saddle River, 2006.

[17] Wink, D. J.; Gislason, S. F. and Kuehn, J. E., "Working with Chemistry: A Laboratory Inquiry Program" 2nd ed., W. H. Freeman and Company, New York, 2005.

[18] Hassell, C. A.; Marshall, P. and Hill, J. W., "Chemical Investigations for Changing Times" 10th ed.,Prentice Hall, Upper Saddle River, 2004.

[19] Murov, S. and Stedjee, B., "Experiments in Basic Chemistry" 4th Ed., John Wiley & Sons: New York, 2004.

[20 Szafran, Z.; Pike, R. M. and Foster, J. C., "Microscale general chemistry laboratory: with selected macroscale experiments" 2nd ed., John Wiley & Sons, New York, 2003.

[21] Singh, M. M.; Szafran, Z. and Pike, R. M., "Microscale Chemistry and Green Chemistry: Complementary Pedagogies", *J. Chem. Educ.*, **1999**, *76* (12), 1684–1686.

[22] "The National Microscale Chemistry Center", http://www.microscale.org/. Retrieved on 30 August 2013.

[23] Eggen, P.-O.; Grønneberg, T.; Kvittingen, L., "Small-Scale and Low-Cost Electrodes for "Standard" Reduction Potential Measurements", *J. Chem. Educ.*, **2007**, *84*, 671–673.

[24] Ibanez, J. G.; Mayen-Mondragon, R.; Moran-Moran, M. T.; Alatorre-Ordaz, A.; Mattson, B.; Eskestrand, S., "Laboratory Experiments on the Electrochemical Remediation of the Environment. Part 7: Microscale Production of Ozone", *J. Chem. Educ.*, **2005**, *82*, 1546–1548.

[25] Anastas, P. and Warner, J., "Green Chemistry: Theory and Practice", Oxford University Press, New York, 1998.

[26] "The 12 Principles of Green Chemistry", United States Environmental Protection Agency, http://www.epa.gov/sciencematters/june2011/principles.htm. Retrieved on 30 August 2013.

[27] "The Twelve Principles of Green Chemistry", http://www.acs.org/content/acs/en/greenchemistry/about/principles/12-principles-of-green-chemistry.html. Retrieved on 30 August 2013.