Chiang Mai J. Sci. 2008; 35(2) : 250-257
www.science.cmu.ac.th/journal-science/josci.html
Contributed Paper

Effect of Stabilizer on Preparation of Silver and Gold Nanoparticle Using Grinding Method

Pichitchai Pimpang, Withun Sutham, Nikorn Mangkorntong, Pongsri Mangkorntong and Supab Choopun*

Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

*Author for correspondence; e-mail: supab@science.cmu.ac.th

Received: 5 March 2008
Accepted: 29 May 2008.

ABSTRACT

Silver and gold nanoparticles were prepared by grinding method using stabilizers such as de-ionized water, ethylene glycol (EG) and 5 wt% polyvinyl alcohol (PVA). From the observation, it was found that the solution's color of silver particle changed from clear color to light yellow or brown and that of gold particle changed from yellow to light blue. This indicated that the size of silver and gold particle was reduced. In addition, the optical properties of silver and gold nanoparticles were studied by UV-vis spectroscopy. It was found that the absorbance and transmission spectra of silver and gold nanoparticles depended on the type of stabilizing agent and grinding time. In addition, the observed color of nanoparticles could be explained using Maxwell triangle and in agreement with the color observed by naked eyes.

Keywords: silver and gold colloid, silver and gold nanoparticle, stabilizer.

1. INTRODUCTION

Recently, metallic nanoparticles have gained interest due to the unique properties including high surface area and exceptional surface activity providing excellent catalytic, optical and electrical properties [1]. In particular, nanoparticles made from the noble metals, such as those of silver or gold, with their associated strong plasmon resonance, have increased interest [2]. Silver and gold nanoparticles generally exhibit plasmon absorption bands that depend on their size and shape [3–5]. Gold nanoparticles have a wide variety of potential applications, for instance, an effective drug delivery in a cancerous tumour [6], biomedicals [7], in a wide range of cosmetic and beauty applications [8], biosensors [2, 7, 9] and catalysts [10 – 13]. Silver nanoparticles have a potential to eliminate bacteria and fungi [14, 15] for cosmetic and beauty applications [8] and have self-cleaning properties [16]. Current techniques used to produce gold nanoparticles are typically divided into chemical and physical techniques. Chemical techniques usually use toxic chemicals which can be dangerous for our environment. Physical techniques include ball milling, UV and IR radiation, aerosol technology and lithography [17–20]. Typically, these techniques require the use of some stabilizers to protect gold nanoparticles against agglomeration. Gold nanoparticles prepared by using ethylene glycol (EG) and polyvinyle alcohol (PVA) as the dispersion stabilizer have been reported [21-23].

In the present study, silver and gold nanoparticles were prepared by a simple hand grinding method. The effect of stabilizer on the preparation of silver and gold nanoparticles via optical properties will be investigated.

2. MATERIAL AND METHODS

Silver nanoparticles were prepared by hand grinding method in an agate mortar using de-ionized water, EG (99%, POCH S.A.) and 5 wt% PVA (99.5%, Fluka) for stabilizers and grinding time for 6, 12 and 18 hours. Gold nanoparticles were prepared by hand grinding method using 5 wt% PVA for stabilizer and grinding time for 4, 6 and 8 hours. The starting grinding materials were 1.0 grams of silver powder 2-3.5 micron (99.9%, Aldrich), and 0.1 grams of gold foil 3.5 x 3.5 cm (96.5%). The absorption and transmission characteristics of silver and gold nanoparticles were studied by ultraviolet – visible (UV– Vis) spectroscopy in the range of 300 – 900 nm. A maximum wavelength (λ_{max}) is defined as wavelength that has maximum absorbance. The results of UV–Vis spectra of silver and gold nano-particles were compared with Mie theory and previous reports.

3. RESULTS AND DISCUSSION

Silver nanoparticles: The solution colors of grinded silver particles using EG and 5 wt% PVA for stabilizer changed from clear color to light yellow or brown indicating a reduction of particle size[1]. Normally, particle size can relate on the color of solution according to Mie theory [24] and the properties of surface plasmon resonance. But the silver particles using de-ionized water for stabilizer seemed to agglomerate and had a bigger size. Figure 1-3 showed the UV–vis absorbance and transmission of silver nanoparticles using EG, 5 wt% PVA and de-ionized water. The blue region of UV–vis was absorbed by silver nanoparticles more than green and red regions. In transmission mode, the red region of UV–vis was transmitted by silver nanoparticles more than green and blue regions.

The absorbance spectra exhibited a maximum wavelength (λ_{max}) at 407 – 415 nm for EG stabilizer and 417 – 420 nm for PVA stabilizer. According to Mie theory [24-25], λ_{max} of absorbance spectra can relate to particle diameter. Thus, our results indicated that the obtained silver nanoparticles using EG and PVA as a stabilizer had diameter of 120 and 140 nm, respectively. Silver nanoparticles with light yellow color have been reported a particles size of 120 nm [26].

It can be seen that using longer grinding time resulted in higher absorbance value. The characteristic curve of silver nanoparticles using PVA is better than EG indicating that PVA is a more suitable stabilizer for preparing silver nanoparticles than EG. Moreover, PVA is a more suitable stabilizer because the color of silver started to change at shorter grinding time (6 hr for PVA and 12 hr for EG). For our elementary experiment, we have assumed that silver and gold nanoparticles have the same characteristics because both are noble metal and are in the same group in periodic table. Thus, PVA was used as a stabilizer for preparing gold nanoparticles. However, our future experiment will be on using EG or other stabilizer for preparing gold nanoparticles.

The explanation for why difference stabilizer gives different characteristics of absorbance/transmission curves of silver nanoparticles was the following. The stabilizer acted as the protection from agglomeration of nanoparticles. The stabilizer attached to the

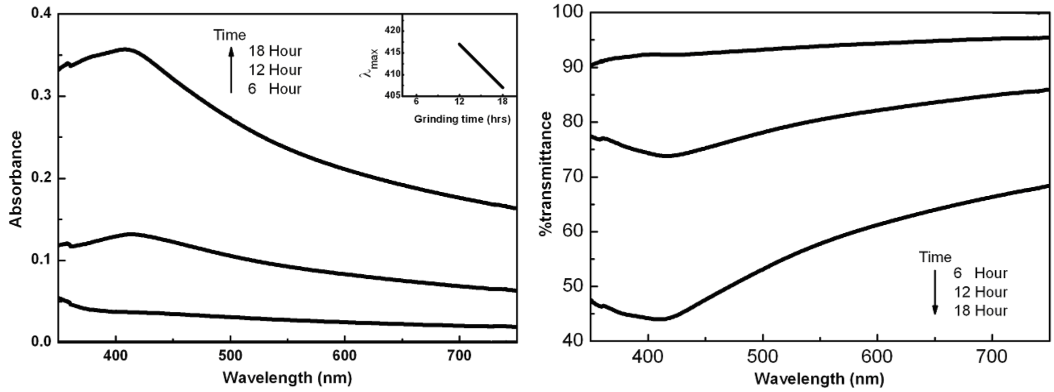

Figure 1. Ultraviolet–visible absorbance and transmission spectra of silver nanoparticles using EG as a stabilizer.

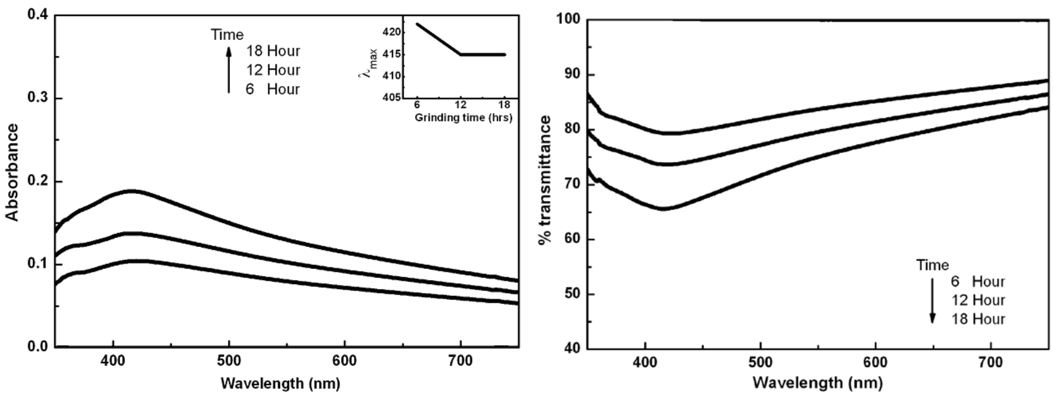

Figure 2. Ultraviolet–visible absorbance and transmission spectra of silver nanoparticles using PVA as a stabilizer.

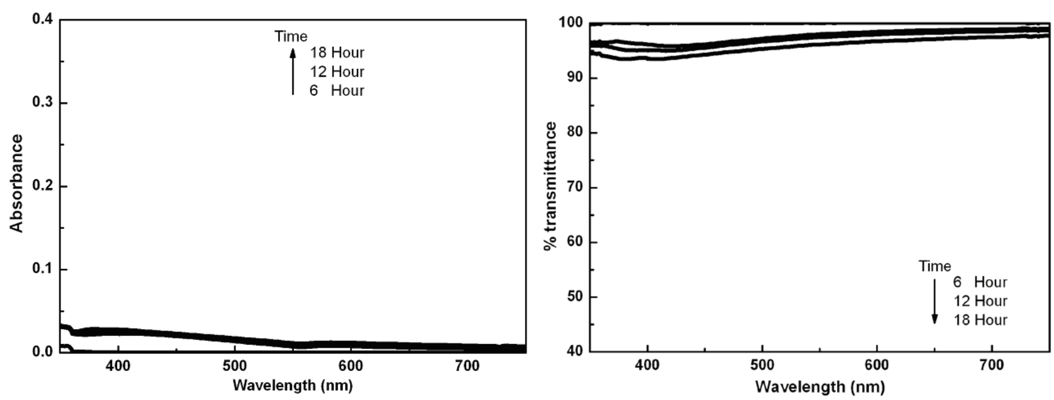

Figure 3. Ultraviolet–visible absorbance and transmission spectra of silver nanoparticles using de-ionized water as a stabilizer.

particle by chemical bonding and prevented nanoparticle to agglomerate to form bigger particles. The different stabilizers have different ability to attach to nanoparticles. Thus, the different stabilizers gave the different characteristics of absorbance/transmission curves.

Gold nanoparticles: The solution color of gold nanoparticles using PVA for stabilizer changed from yellow to light blue indicating a reduction of particle size [3]. It is worth to note that the grinding time for gold nanoparticles was different than for that of silver nanoparticles. The reason for choosing different grinding time for silver and gold was the effect of grinding time on color change. For silver, the color started to change after grinding for 6 hr and slowly changed with grinding time. But for gold, the color started to change at shorter grinding time (4 hr) and quickly changed with grinding time. Thus, we used shorter grinding time for gold and longer grinding time for silver.

Figure 4 showed the UV–vis absorbance and transmission of gold nanoparticles. The red region of UV–vis was absorbed by gold nanoparticles more than green and blue regions. In transmission mode, the blue region of UV–vis was transmitted by gold nanoparticles more than green and red regions. The absorbance spectra exhibited a maximum wavelength (λ_{max}) at 650 – 700 nm indicating particle diameter of 150 nm from Mie theory. Gold nanoparticles with light blue color have been reported a particles size of 150 nm [27].

Similarly to silver nanoparticles, the longer the grinding time was used the higher the absorbance value became suggesting the higher concentration of nanoparticles. Thus, the effect of grinding time was increasing the number of nanoparticles. The longer the grinding time, the higher the number of nanoparticles can be obtained.

In addition, the observed color of nano-particles could be explained by using Maxwell triangle. The color position (x, y, z) was estimated from transmission spectra using in eq.(1 - 4) below:

$$x = \frac{\bar{X}}{\bar{X}+\bar{Y}+\bar{Z}} \qquad \text{.........} (1)$$

$$y = \frac{\bar{X}}{\bar{X}+\bar{Y}+\bar{Z}} \qquad \text{.........} (2)$$

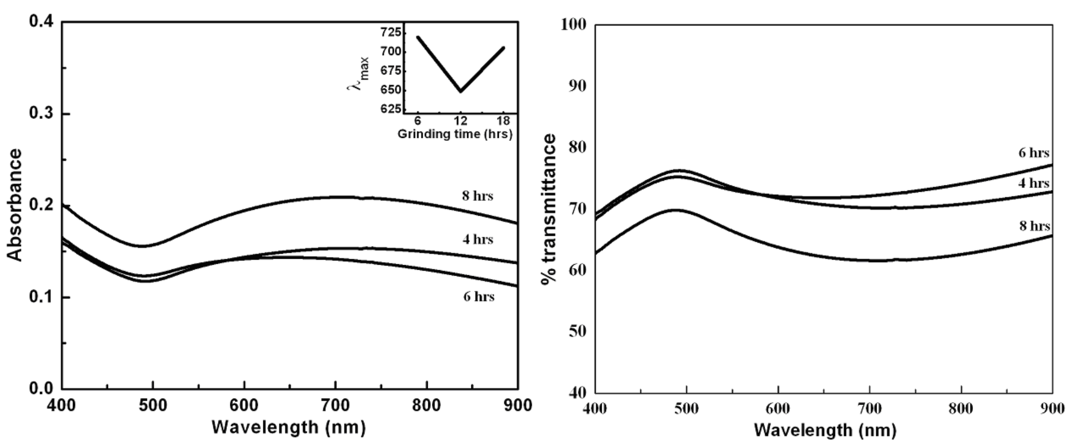

Figure 4. Ultraviolet–visible absorbance and transmission spectra of gold nanoparticles using PVA as a stabilizer.

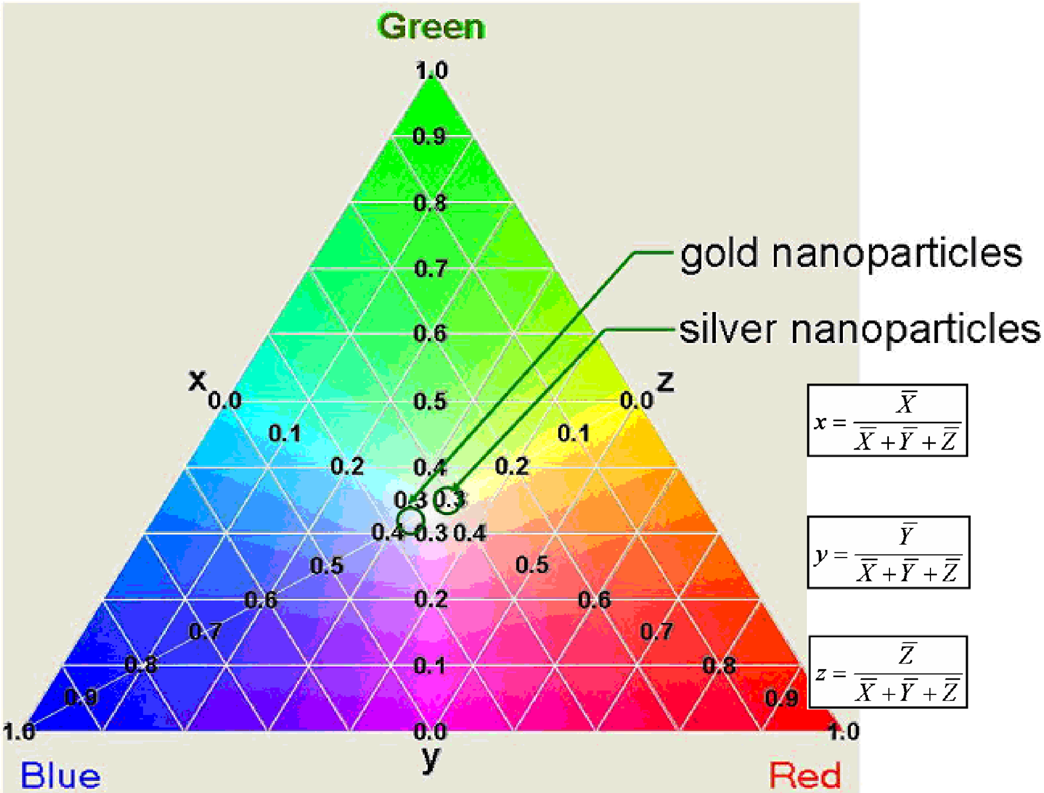

Figure 5. The estimated color position of silver and gold nanoparticles in Maxwell Triangle.

$$z = \frac{\bar{Z}}{\bar{X}+\bar{Y}+\bar{Z}} \qquad \text{.......... (3)}$$

$$x + y + z = 1 \qquad \text{.......... (4)}$$

When $\bar{X}$ is an average of percent transmission on red region (wavelength 625 - 740 nm). $\bar{Y}$ is an average of percent transmission on green region (wavelength 500–565nm). $\bar{Z}$ is an average of percent transmission on blue region (wavelength 450 - 485 nm) .The Maxwell triangle is shown in Figure 5. The estimated color position of silver and gold nanoparticles in Maxwell Triangle was summarized in Table 1. Also, the estimated color position (x, y, z) was shown in Figure 5. It can be seen that the obtained color from Maxwell triangle was in agreement with the color observed by naked eyes.

As seen in Maxwell Triangle, the meaning of absorbance and transmittance to the application are the color of solution. One example of application in bio-sensor is using the color change of gold solution as a pregnancy test [28].

4. CONCLUSIONS

Silver and gold nanoparticles were prepared by hand grinding method using stabilizers of de-ionized water, EG and 5 wt% PVA. The silver nanoparticles agglomerated when de-ionized water was used as a stabilizer. Solution's color of silver particles changed from clear color to light yellow or brown in EG and 5 wt% PVA. Solution's color of gold particles with 5 wt% PVA changed from yellow to light blue. The change of color indicated the reduction of particle size. The absorbance and transmission spectra of silver and gold nanoparticles depended on

Table 1. The summary of estimated color position of silver and gold nanoparticles in Maxwell triangle.

sample	Stabilizer	Grinding time (Hr.)	color	x	y	z
Silver nanoparticles	EG	6	Clear	0.33	0.33	0.33
		12	Light yellow	0.35	0.33	0.32
		18	Light yellow	0.36	0.33	0.31
	PVA	6	Light yellow	0.34	0.34	0.32
		12	Light yellow	0.34	0.34	0.32
		18	Light yellow	0.35	0.33	0.32
	de-ionized water	6	Clear	0.33	0.33	0.33
		12	Clear	0.33	0.33	0.33
		18	Clear	0.33	0.33	0.33
Gold nanoparticles	PVA	4	Light blue	0.32	0.34	0.34
		6	Light blue	0.32	0.34	0.34
		8	Light blue	0.33	0.33	0.34

the type of stabilizing agent and grinding time. According to Mie theory, the obtained silver and gold nanoparticles using PVA as a stabilizer had diameter of 140 and 150 nm, respectively. It was found that PVA is a more suitable stabilizer for preparing silver nanoparticles than EG because of better characteristic spectra and shorter grinding time. This maybe due to PVA has better ability to prevent nanoparticle to agglomerate. Also, it was found that the longer the grinding time, the higher the number of nanoparticles can be obtained. In addition, the observed color of nanoparticles could be explained using Maxwell triangle and in agreement with the color observed by naked eyes.

Acknowledgements

This work was partially supported by the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network. Pichitchai Pimpang would like to acknowledge the Graduate School, Chiang Mai University for financial support.

References

[1] Popa M., Pradell T., Crespo D., Jose M. and Moreno C., Stable silver colloidal dispersions using short chain polyethylene glycol, *Colloid. Surface A.*, 2007; 303: 184 - 190.

[2] Aslan K., Lakowicz J.R. and Geddes C.D., Tunable plasmonic glucose sensing based on the dissociation of Con A-aggregated dextran-coated gold colloids, *Anal. Chem. Acta*, 2004; 517: 139 - 144.

[3] Hornyyak G.L., Patrissi C.J. and Martin C.R., Fabrication, Characterization, and Optical Properties of Gold Nano-particles/Porous Alumina Composite: The Nanoscaterring Maxwell-Garnett Limit, *J. Phys. Chem. B.*, 1997; 101: 1548-1555.

[4] Henglein A., Physicochemical properties of small metal particles in solution: "microelectrode" reactions, chemisorp-

tion, composite metal particles, and the atom-to-metal transition, *J. Phys. Chem. A.*, 1993; 97: 5447 - 5450.

[5] Zhu J., Wang Y.C., Yan S.N. and Lu Y.M., Electrochemical Synthesis and Absorption Properties of Gold Nanorods, *J. Wuhan Univ. Technol.*, 2003; 18: 6-9.

[6] Han G., Ghosh P. De M. and Rotello V. M., Drug and Gene Delivery using Gold Nanoparticles, *J. Nanobiotech.*, 2007; 3:40 - 45.

[7] Castaneda M.T., Merkoc A., Pumera M. and Alegret S., Electrochemical genosensors for Biomedical applications based on gold nanoparticles, *Biosens. Bioelectron.*, 2007; 22: 1961–1967

[8] Yacaman M.J., *Silver Nanoparticles for Antibacterial and Antiviral Applications,* 2006, [Online]. Availiable: http://www.otc.utexas.edu/ATdisplay.jsp?id=110&m=Nano

[9] Carney J.,Braven H., Seal J. and Whitworth E., *Present and future applications of gold in rapid assays,* 2006, [Online]. Available: http://www.devicelink.com/ivdt/archive/06/03/012.html [2007, August 5].

[10] Remediakis I.N., Lopez N. and Norskov J.K., CO oxidation on gold nanoparticles: Theoretical studies. *Appl. Catal. A.. Gen.*, 2005; 291: 13 – 20.

[11] Haruta M., Nanoparticulate Gold Catalysts for Low-Temperature CO Oxidation, *J. New. Mat. Electrochem. Systems*, 2004; 7: 163 - 172.

[12] Tai Y., Murakamia J., Tajiri K., Ohashi F., Date M. and Tsubota S., Oxidation of carbon monoxide on Au nanoparticles in titania and titania-coated silica aerogels, *Appl. Catal. A. Gen.*, 2004; 268: 183 - 187.

[13] Mallick K. and Scurrell M.S., CO oxidation over gold nanoparticles supported on TiO_2 and TiO_2-ZnO: catalytic activity effects due to surface modification of TiO2 with ZnO. *Appl. Catal. A. Gen.*, 2003; 253: 527–536.

[14] Lok C., Ho C., Chen R., He Q., Yu W., Sun H., Tam P.K., Chiu J. and Che C., Silver-nanoparticles: partial oxidation and antibacterial activities, *J. Biol. Inorg. Chem.*, 2007; 12: 527 - 534.

[15] Raffi M., Hussain F., Bhatti T.M., Akhter J.I., Hameed A. and Hasan M.M., Antibacterial Characterization of Silver Nanoparticles against, *J. Mater. Sci. Technol.*, 2008; 24: 192 - 196.

[16] Zabicky J., *Textiles Stain Repellency and Self Cleaning,* 2006, [Online]. Available: http://portal.jce.ac.il/courses/nano/NanomaterialsProjects/Self-cleaning.pdf [2007, August 7].

[17] Zhou Y., Wang C.Y., Zhu Y.R. and Chen Z.Y., Formation of Silver Nanowires by a Novel Solid-Liquid Phase Arc Discharge Method, *Chem. Mater.*, 1999; 11: 545 - 546.

[18] Magnusson M.H., Deppert K., Malm J.O., Bovin J.O. and Samuelson L., Characterization of III-V Semiconductor Nanoparticles Using TEM Techniques, *Eur. Phys. J.*, 1999; 9: 547 - 550.

[19] Tolles W.M., Nanoscience and nanotechnology in Europe, *Nanotechnology*, 1996; 7: 59.

[20] Lung J., Huanga J., Tien D., Liao C, Tseng K, Tsung T, Kao W., Tsai T, Jwo C., Lin H. and Stobinski L., Preparation of gold nanoparticles by arc discharge in water, *J. Alloy. Compd.*, 2007; 434 - 435: 655 - 658.

[21] Ah C.S., Yun W.S., Yun Y.J. and Ha D.H., Gold nanoparticles and method of synthesizing the same. U. S. Patent, in press.

[22] Khanna, P.K., Gokhale R., Subbarao V.V.V.S., Vishwanath A.K., Das B.K. and Satyanarayana C.V., PVA stabilized gold nanoparticles by use of unexplored albeit

Conventional Reducing Agent. *Mater, Chem. Phy.*, 2005; 92: 229 - 233.

[23] Tao J., *Effect of Molecular Weight and Solution Concentration on Electrospinning of PVA,* 2003, [Online]. Available: http://en.wikipedia.org/wiki/Polyvinyl_alcohol [2007, July 21].

[24] Bohren C.F. and Huffman D.R., *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, Canada, 1940: 57-103.

[25] Laven P., *A computer program for scattering of light from a sphere using Mie theory & the Debye series,* 2006, [Online]. Available: http://www.philiplaven.com/index1.html [2007, August 24].

[26] Kathleen A., *Size Matters,* 2005, [Online]. Available: http://www.discovernano.northwestern.edu/whatis/index_html/sizematters_html [2007, July 20].

[27] Ralph A., *Making and conjugating colloidal metals* [Online]. Available: http://www.anisci.wisc.edu/facstaff/Faculty/pages/albrecht_web/Programs/microscopy/colloid.html [2007, July 20].

[28] Pregnancy Tests Using DNA Tags and Other Tricks [Online]. Available: http://nanopedia.case.edu/NWPage.php?page=dna.diagnostics. [2008, April 28].