



Chiang Mai J. Sci. 2011; 38(1) : 31-38

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Contributed Paper

## Monodispersity and Stability of Gold Nanoparticles Stabilized by Using Polyvinyl Alcohol

Pichitchai Pimpang, and Supab Choopun\*

Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, and ThEP center, CHE, Bangkok 10400, Thailand.

\*Author for correspondence; e-mail: [supab99@gmail.com](mailto:supab99@gmail.com)

Received : 12 April 2010

Accepted: 5 July 2010

### ABSTRACT

Gold nanoparticles (Au NPs) have been prepared by reduction of hydrogen tetrachloroaurate aqueous solution ( $\text{HAuCl}_4$ ) with trisodium citrate and stabilized with polyvinyl alcohol (PVA). The optimization of Au NPs was obtained by varying the volume of trisodium citrate from 0.4 - 0.8 mL, and characterized by UV-vis spectroscopy and transmission electron microscopy (TEM). It was found that the absorbance spectra exhibited its absorption peak at around 520 nm for all cases, with a minimum value at 0.7 mL of trisodium citrate. This suggested that the size of Au NPs to be smallest at condition 0.7 mL trisodium citrate, thereby indicating the optimum conditions. Stability of Au NPs was achieved by monitoring absorbance of Au NPs over regular time periods. It was found that wavelength at maximum absorbance changed with time after synthesis except for the 0.7 mL condition which was stable. This suggested that, at condition 0.7 mL, the Au NPs were quite stable up to 700 hours; this could be explored for further applications. Moreover, TEM results showed Au NPs obtained at optimum condition exhibited near spherical shapes with a mean diameter and standard deviation of 4.5 and 1.4 nm, respectively. Also moreover, FT-IR result suggested that Au NPs were coated with a PVA layer.

**Keywords:** gold nanoparticles, nanomaterials, optical materials and properties, electron microscopy, characterization methods.

### 1. INTRODUCTION

Recently, metallic nanoparticles have caught attention due to their novel properties, including high surface area and exceptional surface activity providing excellent catalytic, optical and electrical properties. In particular, nanoparticles obtained from the noble metals, such as those of silver or gold are of increased interest [1]. Gold nanoparticles (Au NPs)

generally exhibit plasmon absorption bands, depending on their size and shape [1-3], they have a wide variety of potential applications. For example, effective drug delivery to a cancerous tumor, biomedical, a wide range of cosmetic and beauty applications, biosensors and catalysts [1]. Numerous physical and chemical methods have been employed in the

preparation of Au NPs such as arc discharge, laser ablation, grinding, radiolytic techniques, chemical reduction, photochemistry, and sonochemistry [1, 4-8].

Au NPs with narrow size distribution are generally fabricated by a chemical reduction method, typically performed by reducing a  $\text{HAuCl}_4$  aqueous solution using a reducing agent such as sodium citrate, sodium borohydride, or other organic compounds. The use of stabilizers such as polyvinyl alcohol (PVA), polyethylene glycol (PEG), Polyvinylpyrrolidone (PVP), Hyperbranched polyethylenimines, Phosphine, thiol, polythiophene, Poly(3-thiophene acetic acid) (PTAA) and poly(acrylic acid) (PAA), or organic solvent to protect Au NPs against agglomeration is necessary [1, 9-18]. Thus, stability can be seen as one of the important issues for preparation of Au NPs. The stability issue that we are interested is the stability of particle size over a period of time by monitoring particle size as a function of time. There is a report on monitoring absorbance value of Au NPs as a function of time [19]. For our work, we have monitored wavelength at maximum absorbance as a function of time in order to study stability. It has been reported that the red-shift of wavelength at maximum absorbance is caused by the aggregation of Au NPs [20].

Thus, in this work stability over a period of time and optimization of Au NPs stabilized by using PVA are investigated. PVA was chosen because it is reported to be the best stabilizer of metal powders in water suspensions [21] being expected to be constant for Au NP colloids.

## 2. EXPERIMENTALS

### 2.1 Preparation of Aqueous Gold Nanoparticles

Au NPs were prepared by a chemical reduction method from gold sheets (96.5%).

Firstly, a  $\text{HAuCl}_4$  aqueous solution was prepared by adding 1.07 g of gold sheets in the presence of 260 mL of 5% aqua regia [22, 23] ( $\text{HCl}:\text{HNO}_3$ , 3:1) in a 500 mL pyrex flask, boiling and stirring for 10 hours while adding distilled water every 2 hours. After filtering the solution, distilled water was added to keep the solution at a constant volume of 260 mL. A  $\text{HAuCl}_4$  aqueous solution with a concentration of 20.0 mM was obtained from this final 260 mL solution. Then, 1.0 mM of this  $\text{HAuCl}_4$  aqueous solution of 30 mL was magnetically stirred and boiled before a reducing agent of 40 wt% trisodium citrate (99%, Fisher Scientific) was added at various volumes ranging from 0.4 - 0.8 mL. As the reducing agent was added, the color of solution changed from an initial yellow to red. Finally, 1 mL of 5 wt% PVA (99.5%, Fluka; MW 67000) was rapidly added to the red solution, the final solution being cooled by water to room temperature. The resulting red solution was composed of Au NPs.

### 2.2 Characterization of Gold Nanoparticles

Au NPs were characterized by UV-vis spectroscopy, transmission electron microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FT-IR Spectroscopy). The UV-vis absorption spectra of Au NPs were recorded in the range of 400-900 nm using a 1 cm cuvette. A typical sample for TEM was prepared by drying naturally a drop of solution containing Au NPs at room temperature on a carbon-coated copper grid, this crystallization being obtained by a selected area electron diffraction pattern (SADP). The concentration of Au NPs was determined using a calibration technique with standard solutions of 10 ppm Au NPs [Purest Colloids, Inc.]. In addition, the stability of Au NPs was observed by monitoring their absorbance at fixed periods of time.

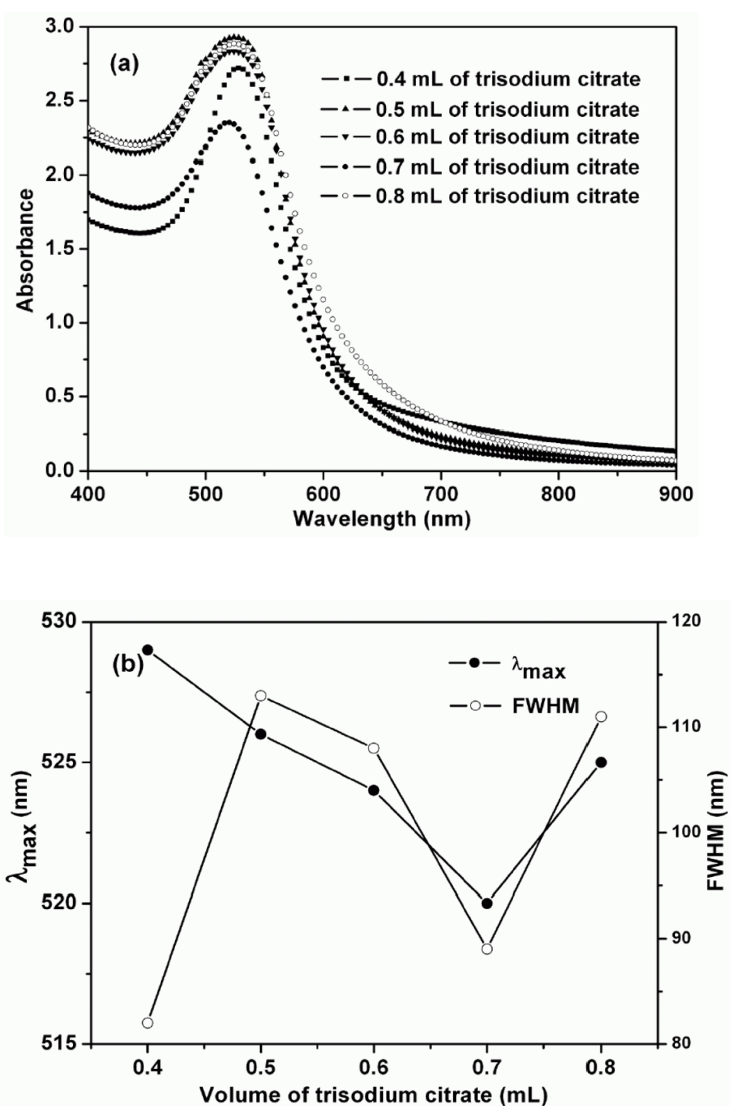
### 3. RESULTS AND DISCUSSION

#### 3.1 Optimization of Gold Nanoparticles

The optimization of Au NPs was performed by varying a volume of trisodium citrate from 0.4 - 0.8 mL in the presence of PVA (see Figure 1a). This showed absorbance spectra of Au NPs synthesized by employing trisodium citrate after synthesis for 700 hours. For all cases, the absorbance spectra exhibited its absorption peak at around 520 nm.

A  $\lambda_{\max}$ , defined as wavelength at maximum absorbance and obtained from the absorbance spectra of Figure 1a, was plotted in Fig. 1b as a function of trisodium citrate volume accompanying a full width at half maximum (FWHM) value.

It can be seen that the  $\lambda_{\max}$  decreased with the increasing volume of trisodium citrate until it reached a minimum value at 0.7 mL. Normally,  $\lambda_{\max}$  can be related to particle size



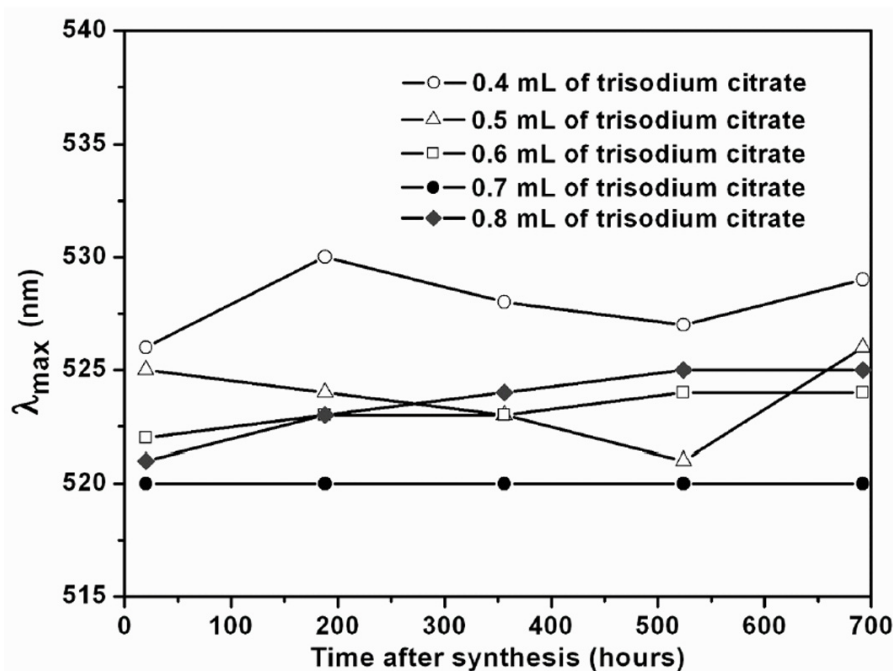
**Figure 1.** (a) Absorbance spectra of Au NPs, (b)  $\lambda_{\max}$ , and full width at half maximum (FWHM) of Au NPs in various volume of trisodium citrate at 700 hours after synthesis.

of nanoparticles [24]. This suggested that the minimum size of Au NPs occurred at condition 0.7 mL trisodium citrate. Moreover, FWHM related to a size distribution [24], for condition of 0.4 mL, it had a minimum value, indicating the narrowest size distribution. However, there were precipitated particles in solutions indicating agglomeration of Au NPs which was confirmed by the presence of a maximum value of  $\lambda_{\max}$ . Thus, at 0.7 mL condition, FWHM had its minimum value without precipitated particles.

Since the Au NPs obtained exhibited smallest size and narrowest size distribution at condition of 0.7 mL, the optimization condition for synthesis of Au NPs in this experiment was determined to be at 0.7 mL of trisodium citrate volume in the presence of PVA.

### 3.2 Stability of Gold Nanoparticles

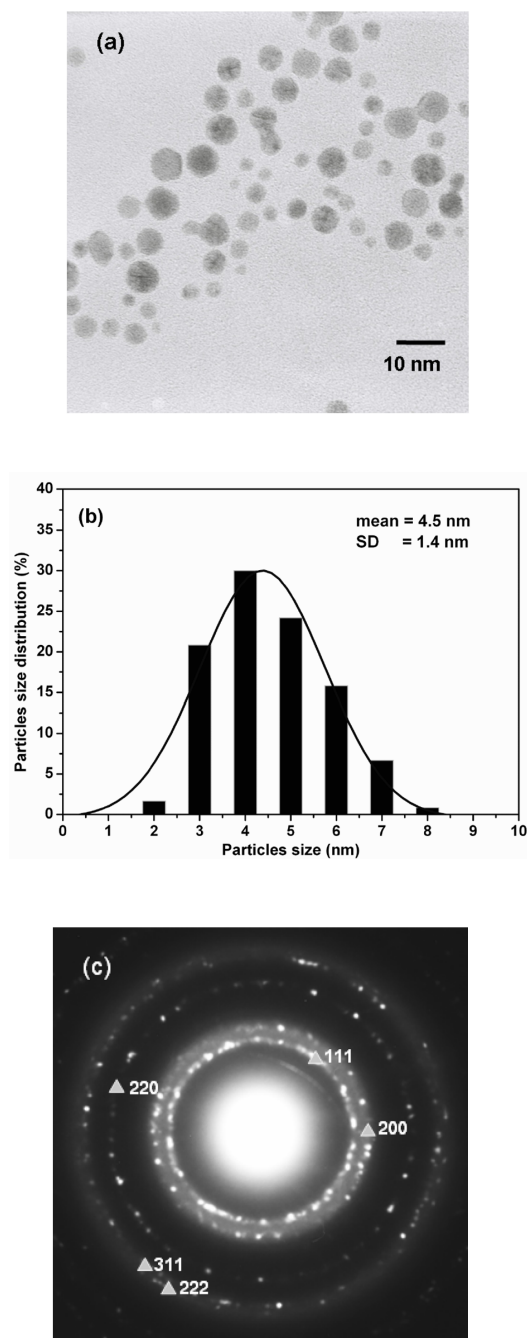
Stability of Au NPs was performed by monitoring absorbance of Au NPs at a period of times. Figure 2 showed  $\lambda_{\max}$  of Au NPs in various volumes of trisodium citrate, and at regular periods of time (observed at 10 -700 hours after synthesis). It can be seen that  $\lambda_{\max}$  changed with time after synthesis except for the 0.7 mL condition when  $\lambda_{\max}$  was stable with time. This suggested that at condition of 0.7 mL, the Au NPs were quite stable up to 700 hours, and confirmed the optimization condition at 0.7 mL of trisodium citrate volume as discussed above. Noteworthy is that the Au NPs solutions were maintained at normal room temperature during the stability experiment.



**Figure 2.**  $\lambda_{\max}$  of Au NPs in various volumes of trisodium citrate, and after various periods of time.

### 3.3 Characterization of Gold Nanoparticles

Figure 3a shows a TEM image, 3b a size distribution histogram with Gaussian curve fitted to the data, and 3c the selected area diffraction pattern (SADP) of an Au NP. This was synthesized at the optimization condition of 0.7 mL trisodium citrate after synthesis for 700 hours. The TEM image shows Au NPs to exhibit an approximately spherical shape with an aspect ratio of 1.08. The aspect ratio is defined as the ratio between length and diameter of Au NP. The size distribution histogram of particles, fitted with a Gaussian curve, obtained a mean diameter and standard deviation of 4.5 and 1.4 nm, respectively. The low standard deviation value of 1.4 nm confirmed the narrow size distribution as seen in low FWHM of absorbance peak (Figure 1b). Monodispersity of colloids or nanoparticles includes the particles uniform in size and shape [25, 26]. It can be directly observed from TEM result that showed Au NPs were uniform nanospheres in size of 3-6 nm indicating monodispersity. Moreover, the indirect observation can be done by observing a peak in absorbance spectra. The single peak suggested that Au NPs colloids contain a spherical in shape. SADP in Figure 3c showed a ring pattern with some spots indicating the polycrystalline property of Au NP. The SADP rings can be assigned to the (111), (200), (220), (311) and (222) planes according to the standard diffraction pattern of JCPDS No. 04-0784. This indicated Au NPs to be in the face-centered cubic (fcc) structure, having additionally a lattice parameter  $a = 4.10 \text{ \AA}$  (a measure from Figure 3c). Au NPs, synthesized at optimization condition of 0.7 mL trisodium citrate after synthesis for 700 hours, were calibrated with a standard concentration of 10 ppm of Au NPs in the diameter range 2 - 4 nm and a concentration of 60 ppm.



**Figure 3.** (a) TEM image, (b) size distribution histogram of Au NPs by using the 0.7 mL of trisodium citrate of Figure 3(a) with Gaussian curve fitted to the data and (c) Selected area diffraction pattern (SADP) is depicted in Figure 3(a).

### 3.4 Effect of PVA Molecule

Figure 4 showed FT-IR spectra of PVA and PVA stabilized Au NPs. It was found that FT-IR spectra showed a different frequency and bandwidth between pure PVA and Au NPs with PVA, especially at O-H stretching region at around  $3,390\text{ cm}^{-1}$ . The O-H symmetric stretching vibration frequency at  $3,390\text{ cm}^{-1}$  was clearly observed for pure PVA

while the broad absorption bands at  $3,418\text{ cm}^{-1}$  for gold nanoparticles with PVA was observed. The presence of the hydroxyl vibrational bands in the gold nanoparticles suggested the presence of PVA and confirmed the PVA coating on Au NPs. It should be noted that the blue-shift of hydroxyl peak due to Au NPs was observed and it was in agreement with other reports [11, 27].

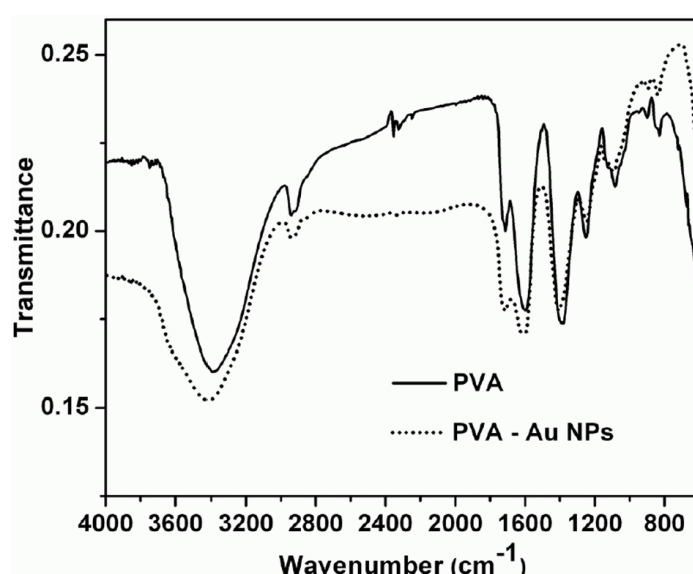


Figure 4. FT-IR spectra of PVA (solid line) and PVA stabilized Au NPs (dot line).

## 4. CONCLUSION

Gold nanoparticles were successfully prepared by reduction of hydrogen tetrachloroaurate aqueous solution with trisodium citrate and stabilized with PVA. The optimization of Au NPs was determined from an absorbance spectra of 0.7 mL of trisodium citrate which gave the smallest size and narrowest size distribution of Au NPs. Stability of Au NPs at condition 0.7 mL was up to 700 hours at normal room temperature; this could be explored for further applications. TEM results confirmed that the Au NPs derived at optimum condition exhibited a near spherical shape, having a mean diameter

and standard deviation of 4.5 and 1.4 nm, respectively. TEM results suggested that the obtained Au NPs were monodispersity. Moreover, FT-IR result suggested that Au NPs were coated with a PVA layer.

## ACKNOWLEDGEMENTS

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



## REFERENCES

- [1] Pimpang P., Sutham W., Mangkorntong N., Mangkorntong P. and Choopun S., Effect of Stabilizer on Preparation of Silver and Gold Nanoparticle Using Grinding Method, *Chiang Mai J. Sci.*, 2008; **35**: 250-257.
- [2] Kelly K.L., Coronado E., Zhao L.L. and Schatz G.C., The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, *J. Phys. Chem. B*, 2003; **107**: 668-677.
- [3] Hornyak G.L., Patrissi C.J. and Martin C.R., Fabrication, Characterization, and Optical Properties of Gold Nanoparticle/Porous Alumina Composites: The Nonscattering Maxwell-Garnett Limit, *J. Phys. Chem. B*, 1997; **101**: 1548-1555.
- [4] Lung J.K., Huang J.C., Tien D.C., Liao C.Y., Tseng K.H., Tsung T.T., Koa W.S., Tsai T.H., Jwo C.S., Lin H.M. and Stobinski L., Preparation of Gold Nanoparticles by Arc Discharge in Water, *J. Alloy. Compd.*, 2007; **434-435**: 655-658.
- [5] Pyatenco A., Shimokawa K., Yamaguchi M., Nishimura O. and Suzuki M., Synthesis of Silver Nanoparticles by Laser Ablation in Pure Water, *Appl. Phys. A*, 2004; **79**: 803-806.
- [6] Henglein A. and Meisel D., Radiolytic Control of The Size of Colloidal Gold Nanoparticles, *Langmuir*, 1998; **14**: 7392-7396.
- [7] Wang W., Chen Q., Jiang C., Yang D., Liu X. and Xu S., One-Step Synthesis of Biocompatible Gold Nanoparticles Using Gallic Acid in The Presence of Poly-(N-Vinyl-2-Pyrrolidone), *Colloid. Surface. A*, 2007; **301**: 73-79.
- [8] Salkar R.A., Jeevanahdam P., Aruna S., Koltypin Y. and Gedanken A., The Sonochemical Preparation of Amorphous Silver Nanoparticles, *J. Mater. Chem.*, 1999; **9**: 1333-1335.
- [9] Wang W., Chen Q., Jiang C., Yang D., Liu X. and Xu S., One-Step Synthesis of Biocompatible Gold Nanoparticles Using Gallic Acid in The Presence of Poly-(N-Vinyl-2-Pyrrolidone), *Colloid. Surface. A*, 2007; **301**: 73-79.
- [10] Tang X.L., Jiang P., Ge G.L., Tsuji M., Xie S.S. and Guo Y.J., Poly(N-vinyl-2-pyrrolidone) (PVP)-Capped Dendritic Gold Nanoparticles by a One-Step Hydrothermal Route and Their High SERS Effect, *Langmuir* 2008, **24**, 1763-1768.
- [11] Jiang G., Wang L., Chen T., Yu H. and Chen C., Preparation of Gold Nanoparticles in The Presence of Poly (Benzyl Ether) Alcohol Dendrons, *Mater. Chem. and Phys.*, 2006; **98**: 76-82.
- [12] Tang Q., Cheng F., Lou X.L., Liu H.J. and Chen Y., Comparative Study of Thiol-Free Amphiphilic Hyperbranched and Linear Polymers for The Stabilization of Large Gold Nanoparticles in Organic Solvent, *J. Colloid Interf. Sci.*, 2009; **337**: 485-491.
- [13] Cho W.S., Cho M., Jeong J., Choi M., Han B.S., Shin H.S., Hong J., Chung B.H., Jeong J. and Cho M.H., Size-Dependent Tissue Kinetics of PEG-Coated Gold Nanoparticles, *Toxicol. Appl. Pharm.*, 2010; **245**: 116-123.
- [14] Brust M., Walker M., Bethell D., Schiffrin D.J. and Whyman R., Synthesis of Thiolderivatized Gold Nanoparticles in a 2-Phase Liquid-Liquid System, *J. Chem. Soc., Chem. Commun.*, 1994: 801-802.
- [15] Zhang Z., Wang F., Chen F. and Shi G., Preparation of Polythiophene Coated Gold Nanoparticles, *Mater. Lett.*, 2006; **60**: 1039-1042.
- [16] Templeton A.C., Wuelfing M.P. and Murray R.W., Monolayer Protected Cluster Molecules, *Acc. Chem. Res.*, 2000; **33**: 27-36.

- [17] Grabar K.C., Freeman R.G., Hommer M.B. and Natan M.J., Preparation and Characterization of Au Colloid Monolayers, *Anal. Chem.*, 1995; **67**: 735-743.
- [18] Jiang Y., Shen Y. and Wu P., Self-Assembly of Multilayer Films Containing Gold Nanoparticles Via Hydrogen Bonding, *J. Colloid Interf. Sci.*, Articles in press.
- [19] Tang Q., Cheng F., Lou X.L., Liu H.J. and Chen Y., Comparative Study of Thiol-free Amphiphilic Hyperbranched and Linear Polymers for the Stabilization of Large Gold Nanoparticles in Organic Solvent, *J. Colloid Interf. Sci.*, 2009; **337**: 485-491.
- [20] Nasir S.M. and Nur H., Gold Nanoparticles Embedded on the Surface of Polyvinyl Alcohol Layer, *J. Fund. Sci.*, 2008; **4**: 245-252.
- [21] Antsiferov V.N. and Khramtsov V.D., Stabilization of Water Suspensions of Metal Powders, *J. Eng. Phys. Them.*, 1993; **64**: 475-478.
- [22] Ah C.S., Yun W.S., Yun Y.J. and Ha D.H., Gold Nanoparticles and Method of Synthesizing The Same, US Patent pending (2006).
- [23] Bonaccorso F., Calogero G., Di Marco G., Marago O.M., Gucciardi P.G., Giorgianni U., Channon K. and Sabatino G., Fabrication of Gold Tips by Chemical Etching in Aqua Regia, *Rev. Sci. Instrum.*, 2007; **78**: 103702-1-103702-4.
- [24] Bohren C.F. and Huffman D.R., *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, Canada, 1983.
- [25] Pietrowski M. and Wojciechowska M., Microwave-assisted Synthesis of Spherical Monodispersed Magnesium Fluoride, *Journal of Fluorine Chemistry*, 2007; **128**: 219-223.
- [26] Yakutik I.M., Shevchenko G.P. and Rakhmanov S.K., The Formation of Monodisperse Spherical Silver Particles, *Colloid. Surface. A*, 2004; **242**: 175-179.
- [27] Nasir S.M. and Nur H., Gold Nanoparticles Embedded on the Surface of Polyvinyl Alcohol Layer, *J. Fund. Sci.*, 2008; **4**: 245-252.