

# Controllable Synthesis of Silver Nanoparticles Using Citrate as Complexing Agent: Characterization of Nanoparticles and Effect of pH on Size and Crystallinity

**Kamali, Mahdi\***<sup>+</sup>

*Chemical Processes Research Department, Engineering Research Center, University of Isfahan,  
P.O. Box 81746-73441 Isfahan, I.R. IRAN*

**Ghorashi, Sayed Ali Akbar\***

*Department of Physics, Faculty of Science, University of Isfahan, P.O. Box 82746-73441 Isfahan, I.R. IRAN*

**Asadollahi, Mohammad Ali**

*Department of Biotechnology, Faculty of Advanced Sciences and Technologies, University of Isfahan,  
P.O. Box 81746-73441 Isfahan, I.R. IRAN*

**ABSTRACT:** A method for the controllable synthesis of silver nanoparticles based on a complexing agent method was developed. Citric acid was used as a complexing agent. The effect of pH (1.6 to 5.17) on the size and net height (as obtained from XRD analyses) of silver nanoparticles was investigated. The nanoparticles (10 to 40 nm) were characterized using XRD, TEM, SEM, EDX, UV-Vis spectroscopy and TG/DTG instrument. It was found that pH has a significant influence on both size and crystallinity of the nanoparticles. This is due to the effect of pH on the distribution of citrate ion species which in turn affects the size and crystallinity of the nanoparticles. Increasing the pH value enhances the percentage of [citrate<sup>3-</sup>] ion species which allows lower size and higher crystallinity of the nanoparticles. Thus, we were able to develop a method for the controllable synthesis of nanoparticles based on the pH.

**KEY WORDS:** Silver nanoparticles, Ion species, Controllable synthesis, Crystallinity, Complexing agent.

## INTRODUCTION

Recently, silver nanoparticles have attracted worldwide research interest due to their unique physical and chemical properties which lead to numerous potential applications. For instance, they can be used as catalysts [1-3], sensors

and biosensors [4-6], antimicrobial agents [7], and have applications in optical [8-10], electrical [11, 12] and biological [13, 14] industries.

Several methods including chemical reduction [15, 16],

---

\* To whom correspondence should be addressed.

+ E-mail: m.kamali@eng.ui.ac.ir , m.kamali@chem.ui.ac.ir

• Other address: Department of Physics, University of Houston, Houston, TX 77204-550, USA  
1021-9986/12/4/21 8/\$/2.80

hydro and solvothermal [17, 18], radiational [19, 20], laser ablation [21], and microemulsion [22] methods have been used to synthesize silver nanoparticles. Since the size of nanoparticles can affect their properties, the ability to control the size of nanoparticles during synthesis is of crucial importance. Although a variety of methods have been reported for the controlled synthesis of silver nanoparticles [23-25], introducing an efficient and simple method for the controllable synthesis of silver nanoparticles is still a challenge. In this work, we have developed a method for the controlled synthesis of silver nanopowders which is based on citrate as a complexing agent. The role of Citrate Ion Species (CIS) on the control of size and crystallinity of silver nanoparticles was also investigated.

## EXPERIMENTAL SECTION

### Chemicals

Silver nitrate ( $\text{AgNO}_3$ ) was provided by Irana Company (Isfahan, Iran) with 99.99 % purity and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) were purchased from Merck (Germany).

### Synthesis of silver nanoparticles

Silver nitrate (1.7 g) and citric acid (4.2 g), as complexing agent, were dissolved in 9.2 mL distilled water in separate well-cleaned dry beakers. They were mixed together at pH 1.6- 5.17 that it was adjusted by using appropriate amounts of  $\text{NH}_4\text{OH}$  solution. This solution was then heated on a stirring hot plate at 250 °C for 45 min.

Heating the mixture led to the evaporation of water and dehydration followed by decomposition of the complexed silver ions, foaming and formation of fluffy ultra fine powder of silver.

### Influence of pH

Variation of pH affects CIS ratio. Therefore, to study the impact of the CIS ratio on the synthesis of nanoparticles samples were prepared with different pH values by adjusting the concentration of ammonium hydroxide. Five samples were characterized with X-Ray Diffraction (XRD) after adjusting their pH at 1.6 (without  $\text{NH}_4\text{OH}$ ), 3.07, 4.24, 5, and 5.17.

### Characterization

XRD patterns of samples were measured using  $\text{Cu K}\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ) on a D8Advance (Bruker, Germany)

instrument. Transmission Electron Microscopy (TEM, Philips CM10), Scanning Electron Microscopy (SEM, Seron Technology AIS 2500) and Energy Dispersive X-ray (EDX) analysis were performed to analyze the size, morphology and purity of silver nanoparticles. Formation of silver nanoparticles was also confirmed by UV-visible spectroscopy (JASCO V-670 Spectrophotometer). The thermal properties of synthesized silver nanoparticles were determined using TG/DTA instrument (Setaram Instrumentation, Labsys TG-DSC1600).

## RESULTS AND DISCUSSION

### X-Ray diffraction characterization

The XRD patterns of the synthesized silver nanoparticles are shown in Fig.1a. The four diffraction peaks, obtained at 39.980°, 44.280°, 64.460°, and 77.320° angles, respectively, could be completely attributed to the face-centered cubic (fcc) crystalline nature of the sample. We chose a main peak for the comparative study and size and net height of the main peaks were compared for all samples at various pH values (Fig. 1b). The mean sizes of obtained silver nanoparticles at different pH values were estimated from Scherrer equation. The mean sizes were found to be 27.2, 25.7, 25.4, 25.2, 19.2 for pH values of 1.6, 3.07, 4.24, 5, 5.17, respectively.

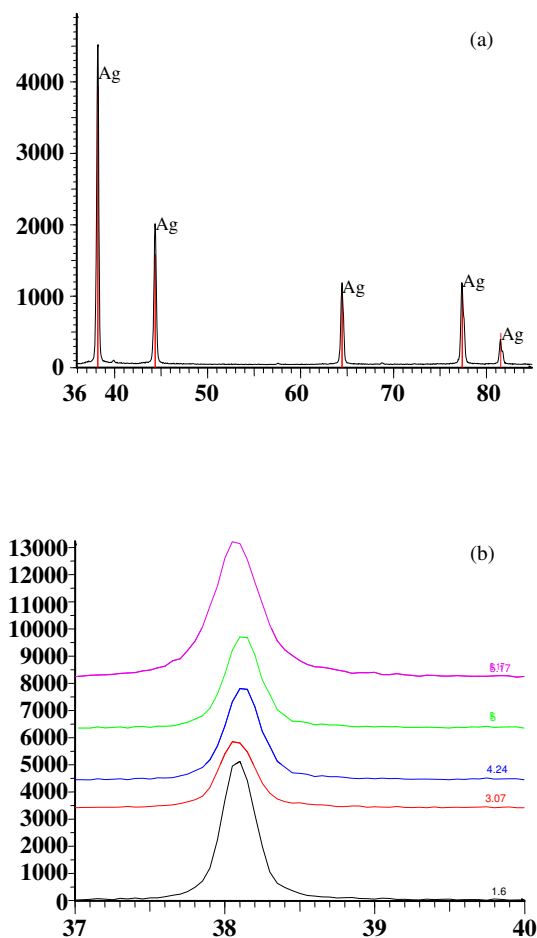
### Electron microscopy characterization

Fig. 2 depicts TEM photograph for one of the synthesized samples that proves formation of nanoparticles for this sample. As seen in the figure, silver nanoparticles have semispherical morphology and the size of nanoparticles varies from 10 to 40 nm. SEM photograph of silver nanoparticles (Fig. 3a) also confirms the spherical morphology of nanoparticles. The purity of the prepared sample was determined by EDX spectrum of the silver nanoparticles (Fig. 3b). Appearance of the other peaks such as oxygen and carbon is probably due to the thermal process used in the synthesis of nanoparticles.

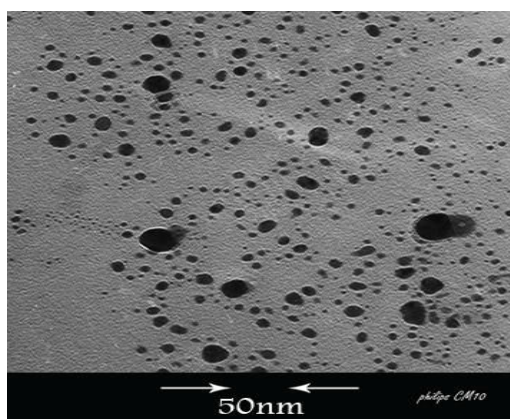
As seen in fig. 3b the purity of silver nanoparticles is about 90%. Also from Fig. 2 and Fig. 3a it can be concluded that the synthesized silver nanoparticles have spherical morphology.

### UV-Vis spectroscopy

Formation of silver nanoparticles was confirmed by UV-Vis spectroscopy as well (Fig. 4). Sample for this test



**Fig 1:** XRD pattern of Ag nanoparticles (a) A full pattern (b) A main peak for comparison (sample without any ammonium hydroxide addition; 1.6, used for full pattern and main peaks are in all of pH from 1.6 to 5.17).



**Fig 2.** TEM image of Ag nanoparticles of an arbitrary sample (10 to 40 nm).

was prepared by dispersing silver nanoparticles in water in an ultrasonic bath. Silver nanoparticles show a surface Plasmon absorption band about 425 nm. Optical properties of metal nanoparticles are more sensitive to shape than size [26]. Since all samples in this work had semispherical geometry, a random sample was taken for this test.

#### **Thermal properties**

The TG/DTG graph for a random sample of silver nanoparticles is illustrated in Fig. 5. As it can be seen, there is only a distinguished peak at 57.4 °C which continues to 110 °C. This peak indicates the loss of water in the sample. There is not any more phase change or weight loss from 110 °C to 800 °C which suggests crystallinity stability of nanoparticles at high temperatures.

#### **pH effect**

Fig. 6 shows the effect of pH on the size and net height of different samples. Increasing pH led to the reduced size of the synthesized silver nanoparticles using citric acid as complexing agent (Fig. 6). A similar pattern has been shown by others when citrate was used as complexing agent [27]. However, it should be noted that obtaining a small average size of silver nanoparticles using complexing agents such as citrate is a challenge. The reported average size of nanoparticles in similar works varies from 50 to 100 nm and it can even be as high as 200 nm [28]. In this work, however, we were able to reduce the average size of nanoparticles to less than 30 nm even at low pH values (Fig. 1b and Fig. 2).

Increasing pH also led to greater net height of nanoparticles. Since net height is a measure of crystallinity, it can be concluded that higher crystallinity is obtained at higher pH values.

The CIS percentages were calculated through known pH values (Table 1) [29].

Then, the profile of obtained sizes and net heights were plotted with respect to percentages of different ion species ( $[\text{citrate}]$ ,  $[\text{citrate}^-]$ ,  $[\text{citrate}^{2-}]$ ,  $[\text{citrate}^{3-}]$ ) (Fig. 7). The Power of Complexing Species (PCS) and Forces between Complexing Species (FCS) were used as two parameters to better discuss the effect of CIS percentage on the size and net height of the particles, respectively.

The profile of size and net height versus  $[\text{citrate}]$  percentage are shown in Fig. 7-a. Since  $[\text{citrate}]$  has

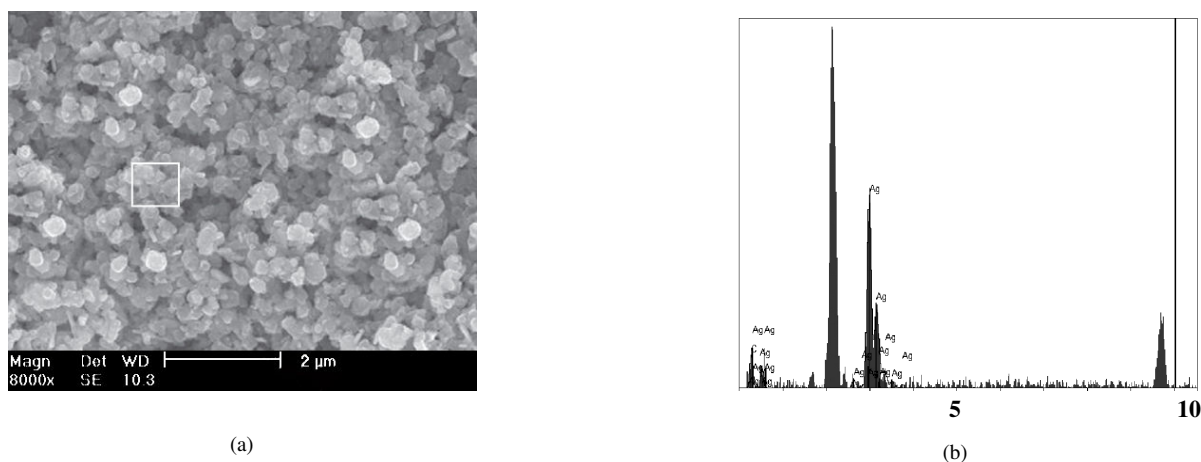


Fig. 3: SEM Image (a) and EDX (b) of silver nanoparticles both for arbitrary sample that used in TEM. Inset: Representative EDX analysis of the spherical silver particles marked with box.

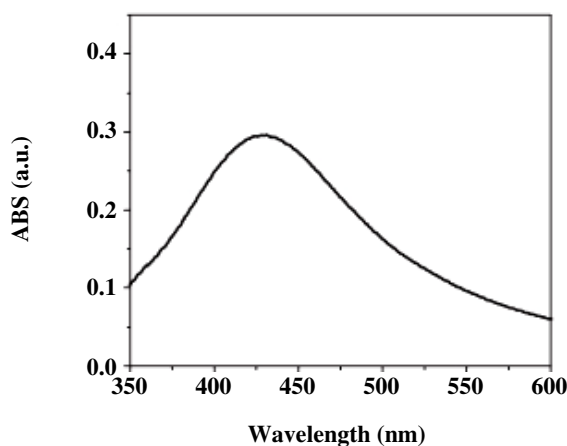


Fig. 4: UV-Vis absorption spectra of silver nanoparticles.

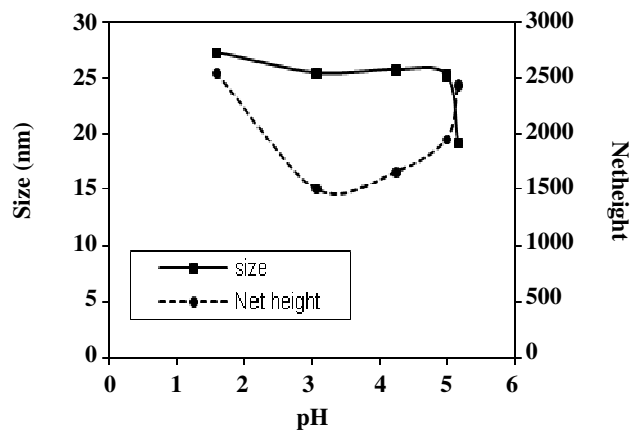


Fig. 6: Graph of size and net height with respect to pH.

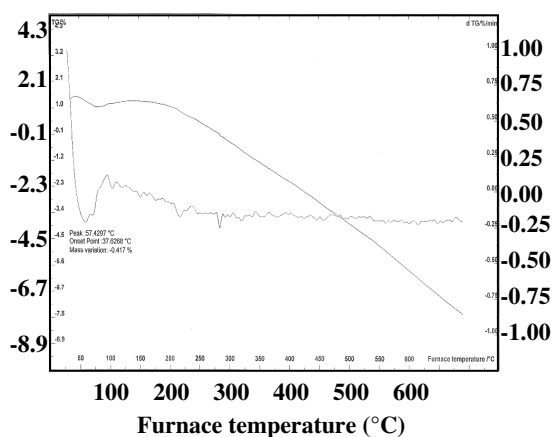


Fig. 5: TG/DTG graph of silver nanoparticles in 0-900 °C thermal range.

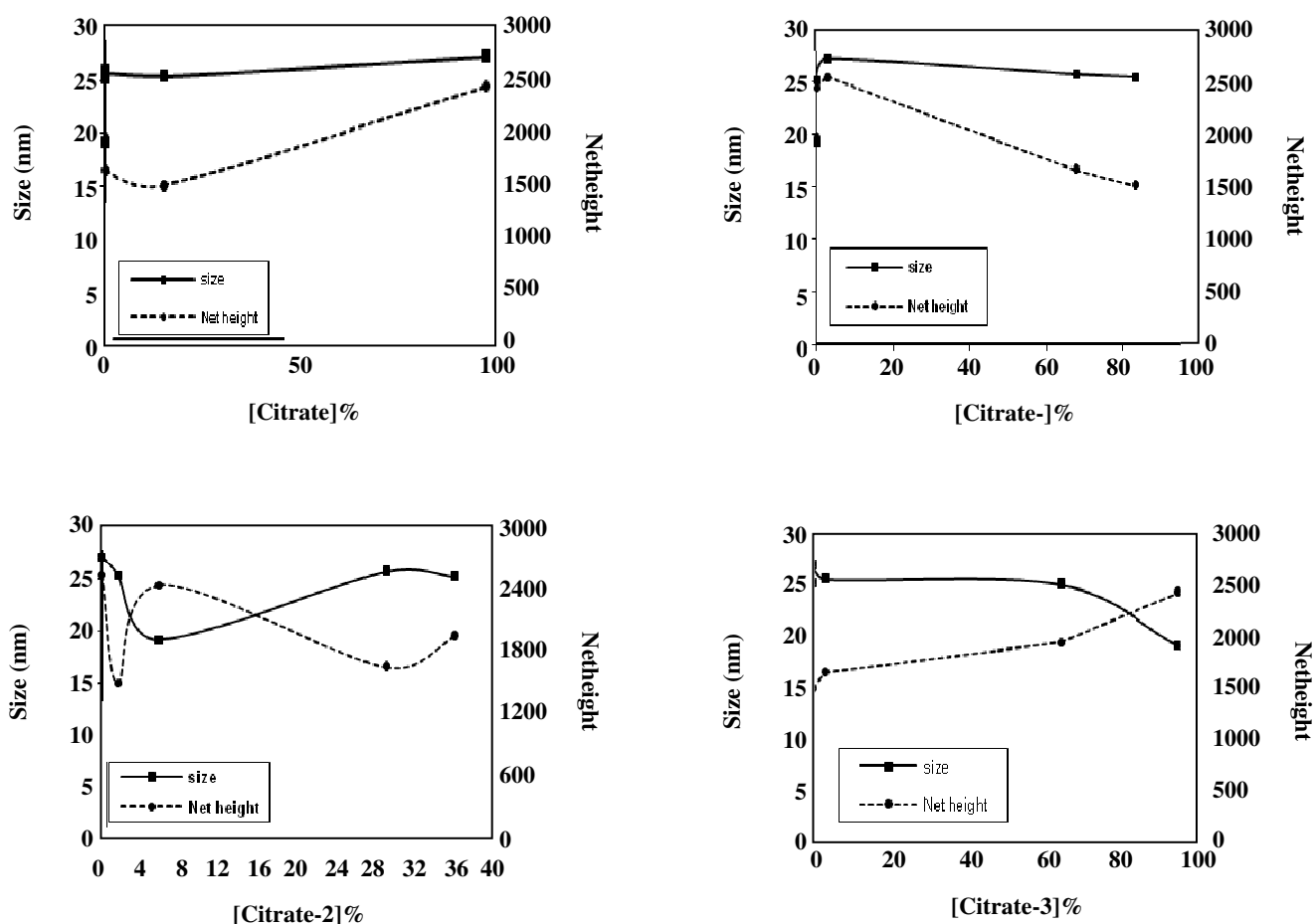
the weakest PCS, higher sizes are obtained when the percentage of [citrate] increases. However, due to hydrogen bonds, [citrate] has high FCS and this causes higher crystallinity and consequently larger net heights for the particles.

[citrate<sup>-</sup>] has higher PCS and lower FCS (due to the formation of internal hydrogen bonds) as compared to [citrate]. Therefore as expected increasing [citrate<sup>-</sup>] is concomitant with increased size and reduced net height for the particles (Fig. 7-b).

PCS and FCS are not completely independent parameters and at some point there might be a significant interaction between these two parameters. This can be observed in [citrate<sup>2-</sup>] for which there is not a predictable trend for the size and net height of particles when the [citrate<sup>2-</sup>] percentage increases (Fig. 7-c). However, it should be

Table 1: Percentages of species in different pH values.

pH	Species	[citrate]	[citrate <sup>-</sup> ]	[citrate <sup>-2</sup> ]	[citrate <sup>-3</sup> ]
	1.6		97.2 %	2.8 %	0 %
3.07		14.9 %	83.4 %	1.67 %	0 %
4.24		0 %	67.8 %	29 %	3.2 %
5		0 %	0 %	36 %	64 %
5.17		0 %	0 %	6 %	94 %

Fig. 7: Graph of size and net height with respect to [citrate] (a) [citrate<sup>-</sup>] (b) [citrate<sup>-2</sup>] (c) [citrate<sup>-3</sup>] (d) percentages.

mentioned that we did not perform the experiments at [citrate<sup>-2</sup>] percentage higher than 36%. Therefore it is likely that we can observe a better trend for the size and net height as the [citrate<sup>-2</sup>] percentage goes beyond 36%.

The most interesting results were obtained for [citrate<sup>-3</sup>] where increasing [citrate<sup>-3</sup>] percentage resulted in lower

size and higher net height for the particles (Fig. 7-d). The [citrate<sup>-3</sup>] has the highest PCS and FCS because of dissociated internal hydrogen bonds and homogeneity of intermolecular forces. The high PCS and FCS resulted in smaller size and higher net height (crystallinity) for the particles, respectively. This is consistent with the results

in Fig. 6 where increasing pH (i.e. higher [citrate<sup>3-</sup>] percentage) led to the best reaction conditions (smallest size and highest net height) for synthesizing the silver nanoparticles. The results are also in agreement with the observations in our lab when we used oxalic acid, ascorbic acid, and tartaric acid as complexing agents (unpublished data).

Obtaining spherical morphology for the nanoparticles at low pH values is very important as the spherical morphology is desired in many applications due to the symmetry of the nanoparticles [30]. Although CIS concentration changed the size and crystallinity of the nanoparticles it did not have any effect on the geometry of nanoparticles. Thus, the spherical morphology was obtained for all samples regardless of CIS concentration.

In most of the reported synthetic methods [15-24], nanoparticles are synthesized in the presence of a stabilizer such as surfactants or ionic polymers. However, these stabilizers cannot be easily removed from the silver colloids and this would consequently influence the physical and chemical properties of the synthesized nanoparticles [25].

Yin et al. [25] used citrate as stabilizer and formaldehydes as reducing agent simultaneously but citrate was used in this work to play role as stabilizer, reducing as well as complexing agent. The multiple role of citrate has already been reported [28, 31]. We synthesized the nanoparticles as powders and compared to other methods for preparing powdered nanoparticles [32], this method offers suitable size and crystallinity for mass production of powdered nanoparticles.

It should be noted that the contribution of citrate in the synthesis of nanoparticles is not completely understood but our analysis of the role of citrate is in good agreement with the experimental results.

## CONCLUSIONS

A method was demonstrated for the controllable synthesis of silver nanoparticles using citric acid as complexing agent. It was shown that pH plays a critical role in the synthesis of silver nanoparticles since it affects the CIS percentage. The CIS percentage will in turn influence the PCS and FCS of different ion species. The best conditions for the synthesis of silver nanoparticles were obtained at high pH values where the [citrate<sup>3-</sup>] has the highest percentage. It was possible to reduce the average size of nanoparticles to less than 30 nm even

at low pH values without affecting the spherical geometry of nanoparticles. The method we used did not require any stabilizer or ionic polymer which is an advantage compared to other synthetic methods. The nanoparticles were obtained as powder with suitable size and crystallinity for mass production.

## Acknowledgements

The authors would like to thank Mr. M. Askari and Mr. Gh. Nematollahi for the scientific discussions, Mr. Sobhani from Islamic Azad University-Shahreza Branch, for TG/DTG analysis and Mrs. Karbasi from Isfahan University of Technology, for SEM analysis.

Received : Apr. 21, 2010 ; Accepted : March 6, 2012

## REFERENCES

- [1] Kundu S., Mandal M., Kumar Ghosh S., Pal T., Photochemical Deposition of SERS Active Silver Nanoparticles on Silica Gel and Their Application as Catalysts for the Reduction of Aromatic Nitro Compounds, *J. Colloid Interf. Sci.*, **272**, p. 134 (2004).
- [2] Jia X., Ma X., Wei D., Dong J., Qian W., Direct Formation of Silver Nanoparticles in Cuttlebone-Derived Organic Matrix for Catalytic Applications, *Coll. Surf. A Phys. Cochem. Aspects*, **330**, p. 234 (2008).
- [3] Balamurugan A., Ho K-C., Chen S-M., One-pot Synthesis of Highly Stable Silver Nanoparticles-Conducting Polymer Nanocomposite and Its Catalytic Application, *Syn. Metals*, **159**, p. 2544 (2009).
- [4] Hamer M., Carballo R., Rezzano IN., Polyallylamine-Chlorophyllide Derivatized Gold and Silver Nanoparticles as Optical Probes for Sensor Applications, *Sen. Act. B: Chemical*, **145**, p. 250 (2010).
- [5] Lin J., He C., Zhao Y., Zhang S., One-Step Synthesis of Silver Nanoparticles/Carbon Nanotubes/Chitosan Film and its Application in Glucose Biosensor, *Sen. Act. B: Chemical*, **137**, p. 768 (2009).
- [6] Li M-G., Shang Y-J., Gao Y-C., Wang G-F., Fang B., Preparation of Novel Mercury-Doped Silver Nanoparticles Film Glassy Carbon Electrode and its Application for Electrochemical Biosensor, *Anal. Biochem.*, **34**, p. 52 (2005).

- [7] Naik R.R., Stringer S.J., Agarwal G., Jones S.E., Stone M.O., Biomimetic Synthesis and Patterning of Silver Nanoparticles, *Nature Mater.*, **1**, p. 169 (2002).
- [8] Roldán M.V., Scaffardi L.B., de Sanctis O., Pellegrini N., Optical Properties and Extinction Spectroscopy to Characterize the Synthesis of Amine Capped Silver Nanoparticles, *Mater. Chem. Phys.*, **112**, p. 984 (2008).
- [9] Majles Ara M.H., Dehghani Z., Sahraei R., Nabiyouni G., Non-Linear Optical Properties of Silver Nanoparticles Prepared by Hydrogen Reduction Method, *Opt. Commun.*, **283**, p. 1650 (2010).
- [10] Pinchuk A.O., Schatz G.C., Nanoparticle Optical Properties: Far- and Near-Field Electrodynamic Coupling in a Chain of Silver Spherical Nanoparticles, *Mat. Sci. Eng.:B*, **149**, p. 251 (2008).
- [11] Rejikumar P.R., Jyothy P.V., Mathew S., Thomas V., Unnikrishnan N.V., Effect of Silver Nanoparticles on the Dielectric Properties of Holmium Doped silica Glass, *Physica B: Condensed Matter*, **405**, p. 1513 (2010).
- [12] Liu J., Li X., Zeng X.X., Silver Nanoparticles Prepared by Chemical Reduction-Protection Method, and Their Application in Electrically Conductive Silver Nanopaste, *J. Alloy Compd.*, **494**, p. 84 (2010).
- [13] Madaeni S.S., Akbarzadeh Arbatan T., Preparation and Characterization of Microfiltration Membrane Embedded with Silver Nano-Particles, *Iran. J. Chem. Chem. Eng.*, **29**(4), p. 105 (2010)
- [14] Vimala K., Murali Mohan Y., Samba Sivudu K., Varaprasad K., Ravindra S., Narayana Reddy N., Padma Y., Sreedhar B., MohanaRaju K., Fabrication of Porous Chitosan Films Impregnated with Silver Nanoparticles: A Facile Approach for Superior Antibacterial Application, *Coll. Surf. B: Biointerfaces*, **76**, p. 248 (2010).
- [15] Wang H., Qiao X., Chen J., Ding S., Preparation of Silver Nanoparticles by Chemical Reduction Method, *Coll. Surf. A: Physicochem. Eng. Aspects*, **56**, p. 111 (2005).
- [16] Spadaro D., Barletta E., Barreca F., Curro G., Neri F., Synthesis of PMA Stabilized Silver Nanoparticles by Chemical Reduction Process Under a Two-Step UV Irradiation, *Appl. Surf. Sci.*, **256**, p. 3812 (2010).
- [17] Rosemary M.J., Pradeep T., Solvothermal Synthesis of Silver Nanoparticles from Thiolates, *J. Colloid Interf. Sci.*, **268**, p. 81 (2003).
- [18] Zou J., Xu Y., Hou B., Wu D., Sun Y., Controlled Growth of Silver Nanoparticles in a Hydrothermal Process, *China Partic.*, **5**, p. 206 (2007).
- [19] Liu Y., Chen S., Zhong L., Wu G., Preparation of High-Stable Silver Nanoparticle Dispersion by Using Sodium Alginate as a Stabilizer Under Gamma Radiation, *Radiat. Phys. Chem.*, **78**, p. 251 (2009).
- [20] Shin J., Kim Y., Lee K., Lim Y.M., Nho Y.C., Significant Effects of Sodium Acetate, an Impurity Present in Poly(Vinyl Alcohol) Solution on the Radiolytic Formation of Silver Nanoparticle, *Radiat. Phys. Chem.*, **77**, p. 871 (2008).
- [21] Tsuji T., Iryo K., Watanabe N., Tsuji M., Preparation of Silver Nanoparticles by Laser Ablation in Solution: Influence of Laser Wavelength on Particle Size, *Appl. Surf. Sci.*, **202**, p. 80 (2002).
- [22] Zhang W., Qiao X., Chen J., Synthesis of Silver Nanoparticles: Effects of Concerned Parameters in Water/Oil Microemulsion, *Mat. Sci. Eng.:B*, **142**, p. 1 (2007).
- [23] Dadosh T., Synthesis of Uniform Silver Nanoparticles with a Controllable Size, *Mater. Lett.*, **63**, p. 2236 (2009).
- [24] Villegas M.A., Garcı́a M.A., Paje S.E., Lopis J.L., Parameters Controlling Silver Nanoparticle Growth in Sol-Gel Silica Coating, *Mater. Res. Bull.*, **40**, p. 1210 (2005).
- [25] Yin H., Yamamoto T., Wada Y., Yanagida S., Large-Scale and Size-Controlled Synthesis of Silver Nanoparticles Under Microwave Irradiation, *Mater. Chem. Phys.*, **83**, p. 66 (2004).
- [26] Zhang J.Z., "Optical Properties and Spectroscopy of Nanomaterials", World Scientific, New York, (2009), p 205.
- [27] Dong X., Ji X., Wu H., Zhao L., Li J., Yang W., Shape Control of Silver Nanoparticles by Stepwise Citrate Reduction, *J. Phys. Chem. C*, **113**, p. 6573 (2009).
- [28] Pillai Z.S., Kamat P.V., What Factors Control the Size and Shape of Silver Nanoparticles in the Citrate Ion Reduction Method, *J. Phys. Chem. B*, **108**, p. 945 (2004).

- [29] Skoog D.A., West D.M., Holler F.J., Crouch S.R., "Fundamentals of Analytical Chemistry", 8th edition, Brooks Cole, (2004), P 399.
- [30] Reyes Y., Paulis M., Leiza J.R., Modeling the Equilibrium Morphology of Nanodroplets in the Presence of Nanofillers, *J. Colloid Interf. Sci.*, **352**, p. 359 (2010).
- [31] Jiang X.C., Chen C.Y., Chen W.M., Yu A.B., Role of Citric Acid in the Formation of Silver Nanoplates through a Synergistic Reduction Approach, *Langmuir*, **26**, p. 4400 (2010).
- [32] Lee S.H., Oh S.M., Park D.W., Preparation of Silver Nanopowder by Thermal Plasma, *Mat. Sci. Eng. C*, **27**, p. 1286 (2007).