Digest Journal of Nanomaterials and Biostructures Vol. 7, No. 4, October-December 2012, p. 1527-1534

SILVER NANOPARTICLES SYNTHESIS WITH DIFFERENT CONCENTRATIONS OF POLYVINYLPYRROLIDONE

DAGMARA MALINA*, AGNIESZKA SOBCZAK-KUPIEC,
ZBIGNIEW WZOREK, ZYGMUNT KOWALSKI
Institute of Inorganic Chemistry and Technology, Cracow University of Technology, 24 Warszawska St, 31-155 Cracow, Poland

The effect of poly(N-vinylpyrrolidone) (PVP) concentration on the synthesis and properties of silver nanoparticles (AgNPs) was investigated. Nanoparticles have been prepared by a chemical reduction method from the aqueous solution of silver nitrate and PVP as a stabilizing agent in the presence of sodium borohydride as a reducing agent. The nanosized silver colloids have been characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), UV-Vis spectroscopy and transformed infrared spectroscopy (FT-IR). Dynamic Light Scattering (DLS) measurements using Zetasizer Nano ZS were applied to size estimation of AgNPs. The results confirmed that silver nanoparticles were formed in each sample independently of PVP content, however the stabilizer concentration in range of 1.0 % to 10.0 % leads to the synthesis of AgNPs with a size in the narrow range of nano-scale and small amounts of larger clusters. The PVP content had a significant influence on silver nanoparticles morphology and optical properties.

(Received July 27, 2012; Accepted October 2, 2012)

Keywords: Silver nanoparticles, Silver colloid, poly(N-vinylpyrrolidone), Stabilizer, Chemical reduction

1. Introduction

The synthesis methods, stability and characteristics of silver nanoparticles have become the subject of many studies in recent years. Currently nanomaterials based on AgNPs are applied in electronic, optic, chemical, textile industries, as well as in pharmacy, cosmetology, medicine, food production and packing where they play a significant role as substrates for synthesis, catalytic materials, sensors, conductors, detergents or antimicrobial coatings [1-4]. There are many methods of silver nanoparticles synthesis but the most widespread and most common ones are chemical reduction processes involving the reduction of silver salt by a reducing agent in the presence of suitable stabilizer. Usually stabilizers are required to obtain stable, monodispersed nanoparticles. They are used to protect the particles from the aggregation and in their presence the probability of nanoparticles collision and coalescence decreases due to the reaction between functional groups of the stabilizer and nanoparticle. Therefore, silver-silver nanoparticle bonds do not form and agglomeration is enhanced by formation of the stabilizing agent layer on the surface of nanoparticles [1,4-7].

A number of chemicals can be used as protecting agents in the synthesis of AgNPs. Henglein and Giersig [8] synthesized stable nanoparticles using the capping effects of citrate. Also in the method of Patakfalvi and Dékány, citrate present in the solution played an important role in stabilization [9]. If no sodium citrate was added to the solution, the silver particles formed aggregates and precipitated. Another stabilizing agent is gallic acid, which acts as both a reducer and stabilizer. In this case, the oxidation reaction of phenol groups in gallic acid was responsible for the reduction of silver ions. The produced quinoid compound with a ketoenol-system could be

---

*Corresponding author: dagmaramalina@chemia.pk.edu.pl adsorbed on the surface of silver nanoparticles [10]. Other stabilizers used are e.g. SDS (sodium dodecyl sulfate) [11] and CTAB (cetyl trimethyl ammonium bromide) [12]. However, the most commonly applied stabilizers and protective agents in nanoparticles synthesis are polymers: gelatin, D-sorbitol [5], PVP [1,5,7,13,14], PVA (polyvinyl alcohol) [15,16] and PMVE (poly(methylvinylether)) [15]. Among all polymer stabilizers of silver nanoparticles, poly(N-vinylpyrrolidone) is considered an excellent dispersant as it exhibits favourable protecting properties owing to its unique structure [1,17,18]. PVP is a homopolymer with a polyvinyl backbone and its repeating units contain a highly polar amide group that confers hydrophilic and polar-attracting properties, and also non-polar methylene groups both in the backbone and in the ring that confer hydrophobic properties [19]. The N and O in the polar groups have a strong affinity for silver ions and silver nanoparticles3. PVP by its structural features is used in a wide variety of applications in medicine (e.g. as a drug carrier, a component of plasma substitute or wound dressing) and technological domains (e.g. in aerosol hair sprays, pigment dispersions, cosmetics) [19-23]. The PVP protective mechanism of silver nanoparticles formation has been currently described by many researchers. In general, the PVP protective mechanism is divided into three stages. The first stage involves the formation of coordinative bonding between the stabilizer and silver ions - PVP donates a lone pair of electrons of oxygen and nitrogen to sp orbitals of silver ions. Secondly, the formed complex promotes silver nucleation which leads to the aggregation of silver atoms. Shin et al. [6] define these aggregates as primary nanoparticles. Finally, the primary AgNPs coalesce with each other or interact with PVP and form larger aggregates also known as secondary nanoparticles [5-7]. Summarizing, PVP on one hand promotes the nucleation of AgNPs and on the other hand it also effectively stabilizes the dispersed silver nanoparticles [1,18,24].

In this paper, we demonstrated the effect of the PVP concentration on the preparation of nanosized stable silver colloids. Based on experimental data we focused on the PVP concentration in the AgNPs preparation method and its effect on the resultant silver nanoparticle morphology and optical properties.

2. Experimental part

2.1. Methods

Characterization of nanosized silver colloids was achieved by different techniques. The SEM (Scannig Electron Microscopy) images were obtained on a JEOL JSM 7500F with BSE detector (Back Scaterred Electrons) and EDS detector (Energy Dispersive X-ray Spectroscopy). The samples were prepared by dispersing a drop of the silver colloid on a copper holder coated with a chromium film. The particles size distribution was analyzed by DLS measurement technique (Dynamic Light Scattering) using Zetasizer Nano ZS (Malvern Instruments UK). The UV-Vis absorption spectra were carried out on Specord 205 spectrophotometer over the wavelength range of 330 to 700 nm with a 2 nm resolution. FT-IR spectra were measured on a Scimitar Series FTS 2000 Digilab spectrophotometer using KBr pellets. Measurements were made in the range of middle infrared of 4000-400 cm^{-1} at a resolution of 4 cm^{-1} with the use of 16 scans.

2.2. Materials

The chemical materials of silver nitrate (>99.9% $AgNO_3$) and sodium borohydride (98% $NaBH_4$) were purchased from POCh Chemical Company. PVP (M.W. 8000) was from Acros Organics. All of the chemicals were used without further purification. Redistilled water was used to prepare all of the solutions.

2.3. Samples preparation

The solutions of PVP in different concentrations (0.1 %, 0.2 %, 0.5 %, 0.7 %, 1.0 %, 1.5 %, 3.0 %, 5.0 %, 10.0 %, 15.0 %) were prepared by dissolving appropriate amounts of PVP in redistilled water. To 95 ml of each of these solutions, 0.039 g of solid $AgNO_3$ (250 ppm of Ag) was added and allowed to dissolve stirring constantly on a magnetic stirrer plate (solution A). The $NaBH_4$ solution was prepared by dissolving the required amount (molar ratio $NaBH_4/AgNO_3$ = 0.39) in 5 ml of the appropriate PVP solution (solution B). The concentration of PVP in solution A and solution B had to be the same. After the complete dissolution of silver salt, solution B was added dropwise (about 1 drop/sec.) to solution A. The reaction mixture was mixed vigorously at room temperature for 15 min. After the synthesis of all the silver colloids, they were centrifuged at 13 000 rpm for 20 min. After decanting the supernatant, the residue was suspended in redistilled water and cooled down to 4 °C in the dark.

3. Results and discussion

3.1. Formation of silver nanoparticles

The nanosized silver colloids were prepared by a chemical reduction process in aqueous solution in the presence of PVP as a stabilizing agent. After the synthesis each sample was clear and transparent. Usually with the increase of PVP content the colloid was getting darker. The UV-Vis spectra illustrates strong peaks in all samples, which proves AgNPs formation. The samples with PVP concentration less than 1.0 % and greater than 5.0 % have very broad peaks compared to other samples (Fig. 1). Colloids with PVP concentration ranging from 1.0 % to 5.0 % show a very strong plasmon resonance band centred between 402 and 440 nm depending on a sample. According to the literature, the absorption maximum for silver nanoparticles with sizes ranging from 2 to 100 nm is within 405 and 503 nm, but our data indicate that in the samples with PVP concentration above 5.0 %, the position of the maximum absorption is highly shifted to a larger wavelength and the obtained nanoparticles show a plasmon resonance band located in the range of 540 to 618 nm causing a colour change of the colloids. At PVP content below 1.0 %, the maximum absorption wavelength gives rise to a slight blue shift. Based on the UV- Vis spectra it can be concluded that in all samples silver nanoparticles are formed independently of the PVP concentration. However, with the increase of stabilizer amount, the position of maximum absorption wavelength is highly shifted to a larger wavelength. It is observed that the band position depends on the particle size and protective agents concentration, therefore, it is expected that silver nanoparticles with the PVP concentration between 1.0 % and 5.0 % with very strong plasmon resonance and narrowest peaks have tight size distribution. Other samples with the PVP concentration less than 1.0 % and greater than 5.0 % have very broad peaks and large size distribution.

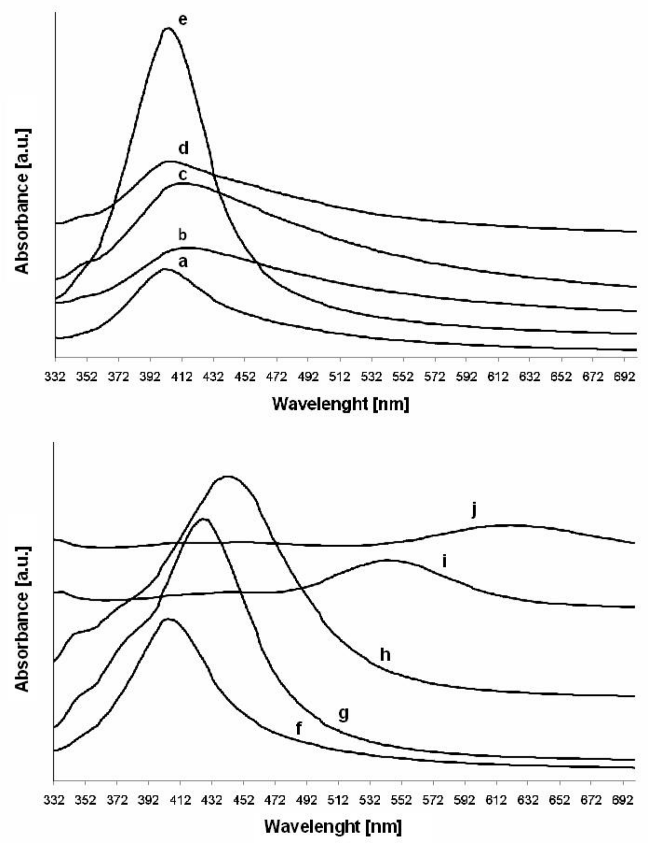

Fig. 1. UV-Vis absorption spectra of silver nanoparticles obtained at different PVP concentration [%]: (a) 0.1; (b) 0.2; (c) 0.5; (d) 0.7; (e) 1.0; (f) 1.5; (g) 3.0; (h) 5.0; (i) 10.0; (j) 15.0

.

3.2. Silver nanoparticles morphology

The BSE-SEM images, elemental analysis with EDS and DLS measurements confirmed the presence of silver nanoparticles in all tested solutions (Figs. 2, 3). Therefore, they exhibit differences in size, size distribution and capacity for aggregation depending on the sample. It was observed that the stabilizer concentration below 1.0 % caused the formation of particles with broad size distribution from nanosized to micrometer sized particles and Z-Average diameter reached over 80 nm (Fig. 3 a). The PVP concentration less than 1.0 % is insufficient to prevent the agglomeration of all of the manufactured nanoparticles. In such a small amount of stabilizer, of all the silver atoms cannot form coordination bonds with the stabilizer, thus they coalesce with each other and form large agglomerates. A 1.0 % concentration of the stabilizer leads to the formation of small nanoparticles with narrower size distribution (Fig. 2 a). They are evenly arranged, do not form large clusters and the Z-Average diameter is 36.59 ± 0.68 nm. The silver colloids with PVP concentration in the range of 1.5 % to 10.0 % are shown in Figs. 3 b and 3 c.

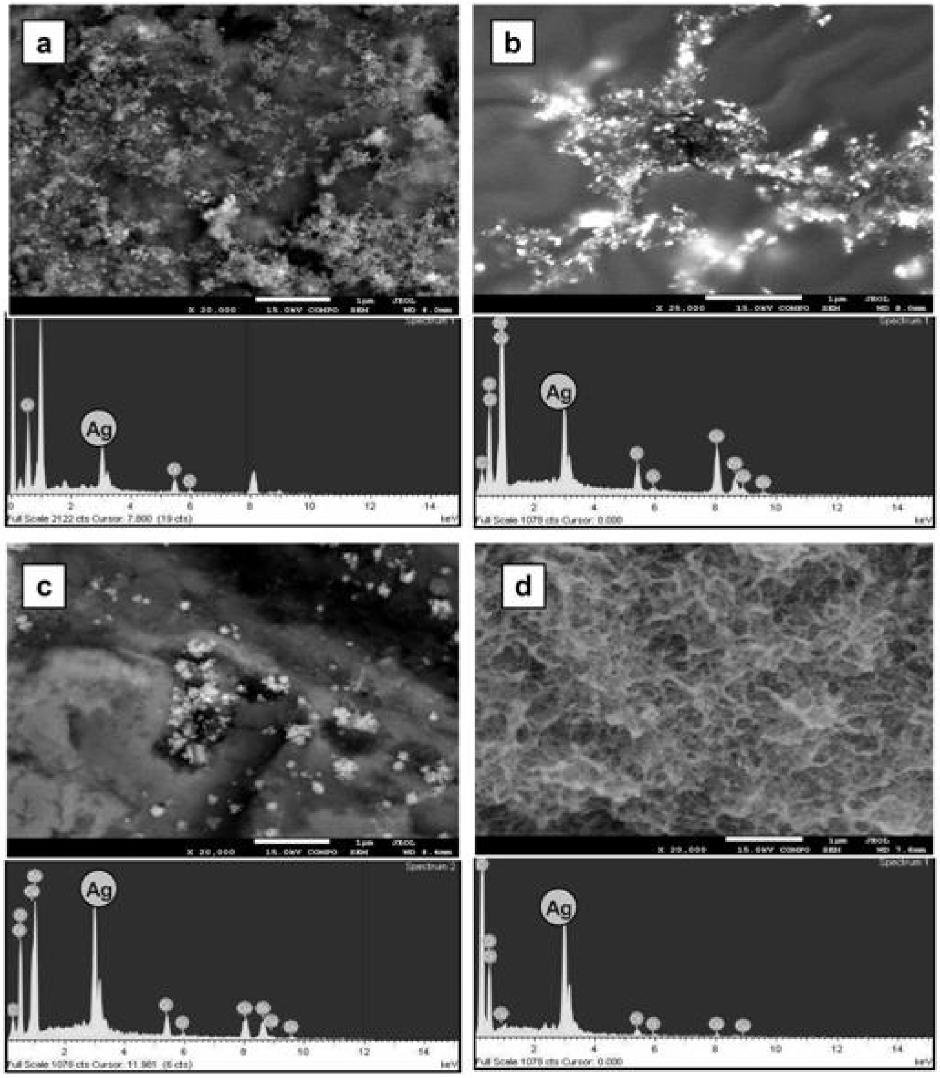

Fig. 2. SEM images of silver suspensions obtained at different PVP concentrations [%]: (a) 1.0; (b) 3.0; (c) 10.0; (d) 15.0

In this area the resulting AgNPs are easy to coalesce into larger agglomerates and do not evenly cover the entire surface of the holder. With the increasing stabilizer content larger nanoparticle clusters are formed. However, the size distribution by volume of AgNPs with the PVP concentration in the range of 1.5 % to 10.0 % is similar, with the Z-Average diameter between around 20 to 30 ± 0.21-0.43 nm (Figs. 3 c-3 e). As seen from Figs. 2 d and 3 f, the 15.0 % concentration of PVP leads to the formation of a dense polymer network evenly coated with silver nanoparticles whose Z-Average diameter is 47.34 ± 0.40 nm. In this case the average size of AgNPs is higher and the size distribution is broader in comparison with the silver nanocolloids with smaller amounts of stabilizer. AgNPs are distributed over the entire surface of the sample, although observation of morphology is impossible due to the amount of stabilizer. The PVP protective mechanism is observed in all of the samples containing 1.0 % stabilizer or more. The stabilizer concentration less than 1.0 % is insufficient to the formation of uniform nanosized particles. However, with the increasing PVP concentration more clusters are formed, but it has no significant effect on particles size distribution. A 15.0 % concentration of stabilizer leads to the formation of a dense polymeric network, which precludes the observation of nanostructures. Moreover, such a large amount of the stabilizer can prevent nanoparticles reactions with other compounds due to entanglement in the dense network of the stabilizer. Summarizing, based on the BSE-SEM images, elemental analysis with EDS and DLS measurements it can be concluded that

PVP concentration in the range of 1.0 % to 10.0 % leads to the synthesis of AgNPs with a size in the narrow range of nano-scale and small amounts of larger clusters.

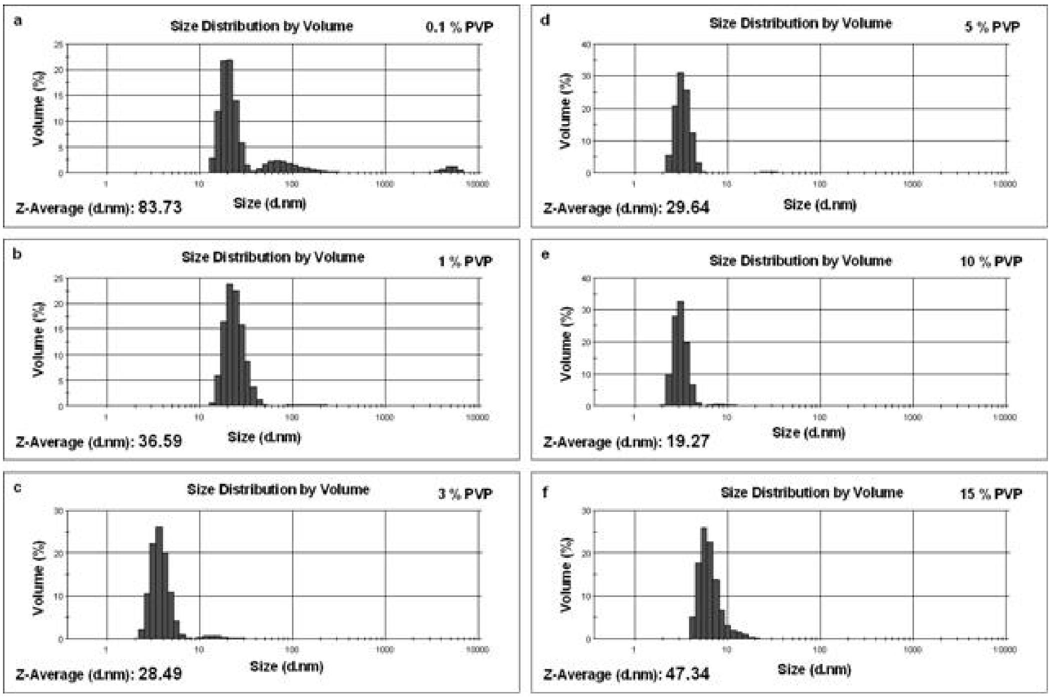

Fig. 3. DLS-images of diameter distribution by volume of nanosized silver colloids with different PVP concentration [%]:(a) 0.1; (b) 1.0; (c) 3.0; (d) 5.0; (e) 10.0; (f) 15.0

3.3. PVP protective effect on silver nanoparticles

Fig. 4 shows the infrared spectra of pure PVP and AgNPs prepared with a different concentration of PVP. It has been found that all spectra of the silver nanocolloids are nearly identical to that of pure PVP. The common feature of all of the spectra is a strong band at 1676 cm^{-1} which can be attributed to an amide carbonyl from PVP. According to the literature [5,18,25], the amide carbonyl stretch absorption is positioned between 1695 cm^{-1} and 1615 cm^{-1}. In all of the spectra the broad absorption band also appeared at 1462 cm^{-1} and 1423 cm^{-1} which resulted from the vibration of the tertiary nitrogen. Other observed bands at 2953 cm^{-1} and 2874 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of C-H bond, and at 3447 cm^{-1} assigned to -OH group of H_2O. In general, chemical groups described above are not involved in the stabilization process of the AgNPs by PVP. However, the slightly visible differentiating shifts in the spectra of pure PVP and silver colloids suggest coordination between silver nanoparticles and stabilizer. Comparing with the spectrum of PVP, the peaks of C-N at 1011 cm^{-1} are shifted to higher frequency (red shift) at 1028 cm^{-1}. This shift indicates that pyrrolidyl nitrogen electrons are involved in the formation of silver nanoparticles by donation of electrons from N to Ag or coordination between these atoms. Another blue shift of the absorption band appearing at 1529 cm^{-1} to 1524 cm^{-1} was observed. This band displacement corresponds to the coordination of amide carbonyl oxygen with silver particles. According to Wang et al. [1] the particles with a diameter shorter than 50 nm were protected by a coordination bond between N in PVP and Ag, and for the bigger particles both N and O in PVP coordinated with silver.

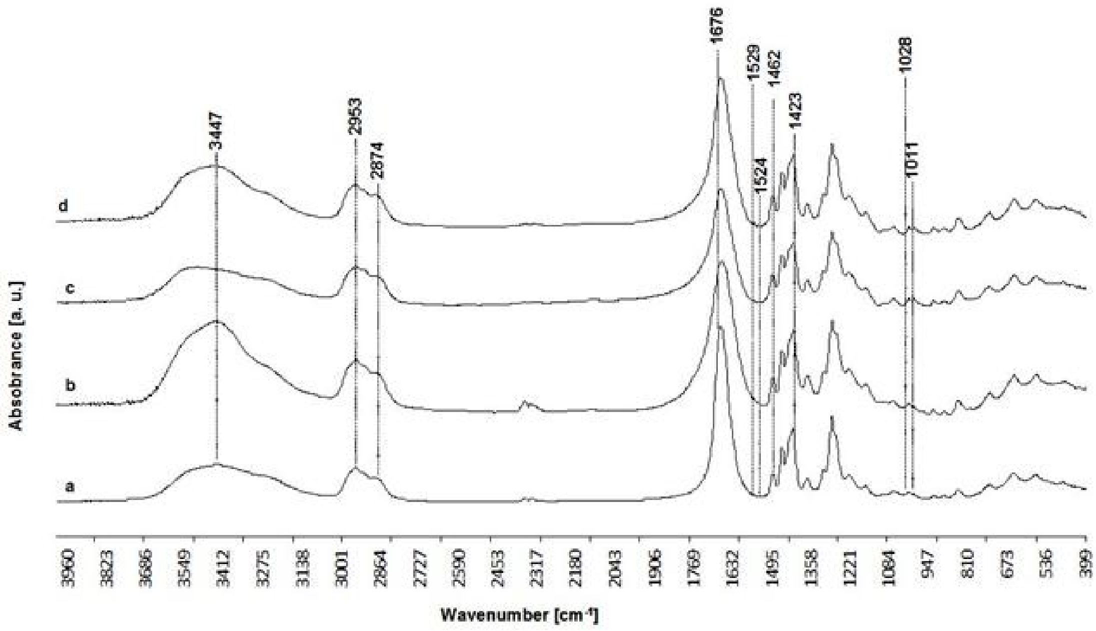

Fig. 4. FT-IR spectra of PVP and nanosized silver colloids with different PVP concentration [%]: (a) pure PVP; (b) 3.0; (c) 10.0; (d) 15.0

4. Conclusion

In the experiments connected with the present work, we successfully prepared colloidal silver nanoparticles stabilized with PVP in a simple oxidation-reduction reaction in sodium borohydride and silver nitrate in aqueous solution. The nanoparticles synthesized were found to be stable for several months, so they can be used for a long time after preparation. Based on the results presented above can be concluded that all of the silver colloids exhibit absorbance in the visible region, and the wavelength at the maximum absorption highly shifts towards a longer one with the increase of PVP concentration. The BSE-SEM images, elemental analysis with EDS and DLS measurements confirmed differences in size, size distribution and capacity for aggregation depending on the PVP concentration. The stabilizer concentration in range of 1.0 % to 10.0 % leads to the synthesis of AgNPs with a size in the narrow range of nano-scale and small amounts of larger clusters. The FT-IR data illustrated chemical reaction between the silver nanoparticles and polymeric stabilizer, by coordination of the silver particles with pyrrolidyl nitrogen and the oxygen atom in PVP.

Acknowledgment

The research was supported by The National Centre for Science in Poland.

References

[1] H. Wang, X. Qiao, J. Chen, X. Wang, S. Ding, Mater. Chem. Phys. **94**, 449 (2005).
[2] J. Xu, X. Han, H. Liu, Y. Hu, Colloid. Surface A **237**, 179 (2006).
[3] D. Chen, X. Qiao, X. Qiu, J. Chen, J. Mater. Sci. **44**, 1076 (2009).
[4] A. Zielińska, E. Skwarek, A. Zalewska, M. Gazda, J. Hupka, Procedia Chemistry **1**, 560 (2009).
[5] Z. Zhang, B. Zhao, L. Hu, J. Solid State Chem. **121**, 105 (1996).
[6] H. S. Shin, H. J. Yang, S. B. Kim, M. S. Lee, J. Colloid Interface Sci. **274**, 89 (2004).

[7] W.-J. Jin, H. K. Lee, E. H. Jeong, W. H. Park, J. H. Youk, Macromol. Rapid Commun. **26**, 1903 (2005).
[8] A. Henglein, M. Giersig, J. Phys. Chem. B **103**, 9533 (1999).
[9] R. J. Patakfalvi, I. Dékány, J. Therm. Anal. Calorim. **79**, 587 (2005).
[10] G. A. Martínez-Castañón, N. Niño-Martínez, F. Martínez-Gutierrez, J. R. Martínez-Mendoza, F. J. Ruiz, Nanopart. Res. **10**, 1343 (2008).
[11] K. C. Song, S. M. Lee, T. S. Park, B. S. Lee, Korean J. Chem. Eng. **26**, 153 (2009).
[12] J. K. Liu, X. H. Yang, X. G. Tian, Powder Technol. **184**, 21 (2009).
[13] S. Kittler, C. Greulich, M. Köller, M. Epple, Materialwiss. Werkstofftech. **40**, 258 (2009).
[14] C. Kan, C. Wang, J. Zhu, H. Li, J. Solid State Chem. **183**, 858 (2010).
[15] G. Carotenuto, Appl. Organomet. Chem. **15**, 344 (2001).
[16] T. Bera, P. Ramachandrarao, J. Mater. Sci. **44**, 2264 (2009).
[17] H. Ma, S. Huang, X. Feng, X. Zhang, F. Tian, F. Yong, W. Pan, Y. Wang, S. Chen, ChemPhysChem **7**, 333 (2006).
[18] D. Debnath, C. Kim, H. Kim, K. E. Geckeler, Macromol. Rapid Commun. **31**, 549 (2010).
[19] X. Xu, Q. Wang, H. C. Choi, Y. H. Kim, J. Membr. Sci. **348**, 231 (2010).
[20] J. M. D'Souza, R. L. Schowen, E. M. Topp , J. Control. Release **94**, 91 (2004).
[21] T. Kaneda, Y. Tsutsumi, Y. Yoshioka, H. Kamada, Y. Yamamoto, H. Kodaira, S. Tsunoda, T. Okamoto, Y. Mukai, H. Shibata, S. Nakagawa, T. Mayumi, Biomaterials **25**, 3259 (2004).
[22] F. Hassouna, S. Therias, G. Mailhot, J.- L. Gardett, Polym. Degrad. Stab. **94**, 2257 (2009).
[23] B. Tyliszczak, K. Pielichowski, Technical Transactions: Chemistry **1**, 159 (2007).
[24] S. Tang, X. Meng, H. Lu, S. Zhu, Mater. Chem. Phys. **116**, 464 (2009).
[25] A. Slistan-Grijalva, R. Herrera-Urbina, J. F. Rivas-Silvac, M. Ávalos-Borja, F. F. Castillón-Barraza, A. Posada-Amarillas, Mater. Res. Bull. **43**, 90 (2008).