Journal of
NANOSTRUCTURES
JNS
NANOSTRUCTURES
JNS.kashanu.ac.ir

A Simple and High Yield Solvothermal Synthesis of Uniform Silver Nanowires with Controllable Diameters

M. Khademalrasool*, M. Farbod

Physics Department, Shahid Chamran University, Ahvaz, I.R. Iran

Article history:
Received 08/10/2015
Accepted 22/11/2015
Published online 01/12/2015

Keywords:
Silver nanowires
Solvothermal
PVP
NaCl
Tree-like structure

**Corresponding author:*
E-mail address:
mkhademalrasool@yahoo.com
Phone: +98 9163447476
Fax: +98 61 42424067

Abstract

Silver nanowires were synthesized by solvothermal method through reducing silver nitrate ($AgNO_3$) with ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP). In order to prevent the agglomeration of Ag^+ in the initial Ag seeds formation, sodium chloride (NaCl) was added into the solution to form AgCl colloids. By dissolving AgCl in the late stages, Ag^+ ions were released into the solution. So the diameters of silver nanowires could be controlled by modifying the PVP concentration. The effect of reaction time, reaction temperature, and for first time purity of EG over the shape of resulted silver nanowires were investigated. The wire, sphere and tree-like nanostructures were formed with changing these parameters. The structural and optical properties of the silver nanostructures were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), and UV–visible absorption spectrophotometer. In order to synthesis silver nanowires with smaller diameters and longer lengths, the optimum molar ratio of PVP/$AgNO_3$, reaction time, reaction temperature, and EG purity were found to be 1.5, 2.5 h, 160 °C, and 99.5%, respectively.

1. Introduction

One-dimensional metallic nanostructures have been attracted much interest owing to their unique electrical, optical, magnetic, and thermal properties [1]. Of the metals, silver nanostructures exhibit the highest electrical and thermal conductivities and have been extensively studied in many fields, such as catalysis [2], photonics-plasmonics[3,4], molecular sensing using surface-enhanced Raman scattering [5-7], microelectronics devices [8],

sensors [9], and etc. Therefore, the synthesis and characterization of silver nanowires particularly the size controlling have been continued to be an area of active research. Up to now, many approaches have been successfully developed for synthesis of silver nanowires with controllable sizes, such as sonoelectrochemical [10], template [7, 11-13], hydrothermal [1], wet chemical [14-15], and polyol [16] processes. Among these methods, the common chemical reduction method based on polyol process, which is a low cost and versatile process, is usually adopted for silver nanowires synthesis [17]. The polyol synthesis was developed by Fievet et al for the first time as an excellent method for synthesis of metallic nanoparticles [18]. Siekkinen et al. extended this method to fabricate silver nanocubes and nanowires by slow addition of $AgNO_3$ as precursor and PVP as stabilizer to a solution of EG which was used as solvent and reductant [19]. They also used different salts such as NaCl, $FeCl_3$, and $CuCl_2$ as etchant. The experiments were usually carried out in air-open reaction systems. The anion can reduce the concentration of free silver ions in the initial step, and the cation can remove the adsorbed atomic oxygen from the surface of seeds [19-20]. However, in comparison with air-open reaction systems, a sealed reaction system made by autoclave, has been recently reported for the synthesis of silver nanowires. The sealed systems prepare a relatively high-pressure reaction atmosphere comparing with an air-open system by which the growth rate improves [21]. In this work, we have used a simple solvothermal route to synthesis silver nanowires in high yield by using $AgNO_3$ and reducing Ag^+ with EG in presence of PVP and sodium chloride as well. AgCl is formed by adding sodium chloride (NaCl) into the solution in the initial stage. These colloids reduce the concentration of free Ag^+ ions in the initial Ag seeds formation and subsequently Ag^+ ions can be released to the solution slowly. Otherwise, there is no oxidative etching because the absence of oxygen in a sealed autoclave. In order to determine the optimum conditions for the preparation of uniform silver nanowires, the experiments were carried out at various molar ratio of PVP/$AgNO_3$. The effect of reaction temperature, reaction time and purity of EG used in experiments on the formation of silver nanowires was also investigated. Based on our knowledge the effect of EG purity has not been studied previously. The results showed that the purity of EG has a crucial role in the formation of silver nanowires.

2. Materials and methods

2.1. Materials

In our solvothermal synthesis of silver nanowires, starting materials such as EG 99.5%, $AgNO_3$, PVP (MW~55000) and NaCl were used without further purification. EG 99% was also employed to investigate the effect of purity of EG over the shape of silver nanowires.

2.2. Silver nanowire synthesis

In order to synthesis silver nanowires, 0.1 mM NaCl was added to 11.1 ml EG solution of 0.15 M PVP. Next, the mixture was vigorously stirred by ultrasonication. The mixture then was injected drop wised into a vial containing 11.1 ml EG solution of 0.1 M $AgNO_3$ using a syringe pump at a rate of 45 ml/h. The resulting solution was mixed for 5 minutes and subsequently transferred into a 50 ml Teflon-lined autoclave. The autoclave was sealed and heated at 160 °C in a furnace for 2.5 h, then allowed to cool naturally to room temperature. The synthesized nanowires were separated by centrifugation at 3500 rpm for 15 min and

thoroughly washed with acetone. Morphology of the samples was determined by field emission scanning electron microscope (FESEM, Mira Tescan) and scanning electron microscope (SEM,LEO 1455VP). The UV-Visible absorption spectra of the products were also taken by a UV-Vis Spectrophotometer (PG Instruments Ltd model T80). All the measurements were carried out at room temperature. Powder X-ray diffraction (XRD) measurements were also performed using a Philips diffractometer (PW1840 model, Philips, Germany) to determine the crystal structures and phase composition of the silver nanowires. The Fourier transform infrared spectrum (FT-IR) was used to obtain more information about the interaction between the PVP and the Ag on the surface of the nanowires. This analysis has been carried out by Bomem MB-series 102 FT-IR spectrometer. The samples for XRD and SEM measurements were prepared by dropping the solutions onto glass substrates and dried at room temperature. In order to investigate the effect of PVP concentration over the nanowires diameters, a series of experiments with the molar ratios of PVP/$AgNO_3$ 1:1, 1.3:1, 1.5:1, 1.8:1, and 2:1 were performed. In these experiments the $AgNO_3$ concentration was fixed and PVP concentration was changed. The effect of reaction temperature, reaction time and purity of EG on the shape control of nanowires were also investigated.

3. Results and discussion

Fig. 1 shows the XRD pattern of silver nanowires synthesized using 0.15 M PVP (PVP/$AgNO_3$=1.5:1). Five diffraction peaks were observed at 2θ= 38.12°, 44.79°, 64.04°, 78.23°, and 81.53°, which were indexed to the (111), (200), (220), (311), and (222) reflections of pure fcc structure of silver, respectively (JCPDS Card File No. 04-0783) and no impurities was also detected. The lattice constant calculated from this pattern was 4.0859 Å, which was in agreement with the reported value of 4.086 Å [22]. This indicates that pure silver nanowires were obtained under the present synthesis conditions. The intensity ratios of (111)/ (200) and (111)/ (220) peaks were 3.01 and 19.2 respectively, which were relatively higher than the conventional 2.5 and 4 values [22]. Therefore, this would indicate that the {111} planes of silver tend to be preferentially oriented in the solvothermal method. Indeed, it has been demonstrated that PVP molecules could be tightly adsorbed on the {100} planes of pentagonal twinned seeds through Ag-O coordination leaving the {111} planes uncovered. Thereupon, new silver atoms are deposited on {111} surfaces that are in the ends of the silver nanowires, leading to the rapid anisotropic growth along the <110> direction of silver nanowires with a pentagonal cross section [23]. It can be deduced that PVP is necessary for the nanowires synthesis. Fig.1 also illustrates the role of PVP in the preparation of silver nanowires schematically.

The silver nanowires exhibit interesting optical properties directly related to the surface plasmon resonances (SPRs). The SPRs are strongly dependent on the nanowires diameters. The UV-Vis absorption spectra of the silver nanowires usually show two absorption peaks which the stronger one corresponds to the transverse plasmon resonance or the out-plane dipole plasmon resonance of the silver nanowires, and the weaker one is attributed to the out-plane quadruple resonance excitation or the longitudinal mode of long silver nanowires similar to that of the bulk silver [17, 24-25].

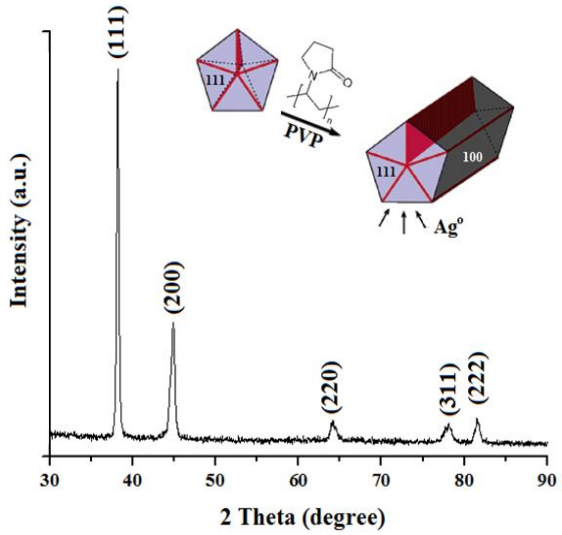

Fig. 1. XRD pattern of silver nanowires synthesized with 0.15 M PVP and schematic illustration of the PVP role in the preparation of silver nanowires.

Fig. 2 shows the UV-Vis absorption spectra taken from the silver nanowires synthesized with different molar ratios of PVP/$AgNO_3$. From Fig. 2 it is clear that there are two peaks at 409-422 nm and at 350 nm which are corresponded to the transverse and longitudinal plasmon resonance, respectively. One can be observed, by increasing the molar ratio from 1:1 to 1.5:1 a blue shift for the strong absorption peak occurs. This phenomenon indicates that the mean diameter size of silver nanowires has decreased. So by changing the PVP concentration one can control the silver nanowires diameter.

Fig. 3a-e show the SEM images of silver nanowires synthesized using NaCl (0.1 mM), $AgNO_3$ (0.1 M) with different molar ratios of PVP/$AgNO_3$ which were chosen as: 1, 1.3, 1.5, 1.8 and 2. The lengths of all samples were ranging from 3 to 40 μm with average size of 10 μm.

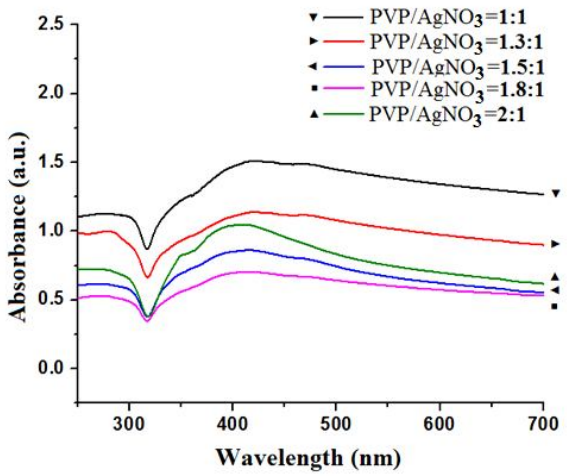

Fig. 2. The UV–Vis absorption spectra of the silver nanowires synthesized using different concentrations of PVP.

The changes in nanowires diameter as a function of the molar ratios have been shown in Fig. 4. As can be observed, by increasing the molar ratio of PVP from 1 up to 1.5, the mean diameter size of the silver nanowires decreased from 445 to 155 nm afterwards increased to 233 nm by further increase of the molar ratio up to 2. It seems at low PVP concentrations the nanowires can grow along both (100) and (110) facets leading to nanorods and nanowires with higher mean diameters. This phenomenon can be attributed to the increase in the solution viscosity. It seems that when the PVP concentration is high, it covers all seeds surfaces which block the anisotropic growth of silver nanowires. Our data indicated that the PVP/$AgNO_3$ molar ratio of 1.5 was an optimum value for the synthesis of nanowires.

Fourier transform infrared spectroscopy was used to investigate the surface chemical state of the final silver nanowires and possible interactions between silver and PVP. Figure 5 represents the FT-IR spectra of silver nanowires synthesized with the molar ratio of PVP/$AgNO_3$ of 1.5 and the pure PVP. The FT-IR spectrum of the pure PVP shows

that the –C=O and –C–H stretching vibration peaks are located around 1660 and 2954 cm^{-1}, respectively. The absorption peak around 1290 cm^{-1} is due to the stretching vibration of –C–N–. Moreover, the peak at around 3438 cm^{-1} represents the O–H stretching vibration. These observations suggest that a bonding between PVP and silver crystal exists. Compared to the pure PVP, the carbonyl absorption peak of Ag-PVP indicates a red-shift from 1660 cm^{-1} to 1652 cm^{-1} which can be due to interaction of silver with PVP. These results are in agreement with other groups' findings [17].

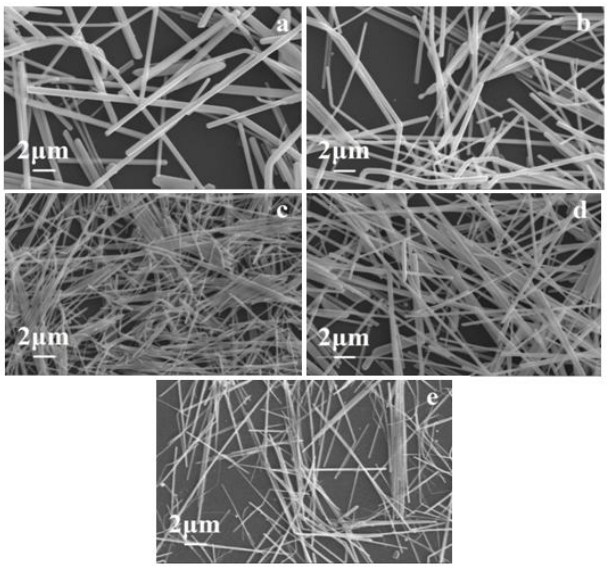

Fig. 3. SEM images of silver nanowires prepared with different molar ratios of PVP/$AgNO_3$ at a fixed temperature of 160 °C: (a) 1; (b) 1.3; (c) 1.5; (d) 1.8; (e) 2.

The synthesis temperature was another key factor to control the shape and size of nanowires. The synthesis temperature was adjusted and tested from 140 to 160, and 180 °C in this work, while the other parameters were kept constant (i.e., 0.1M $AgNO_3$, 0.15 M PVP, and 0.1mM NaCl).

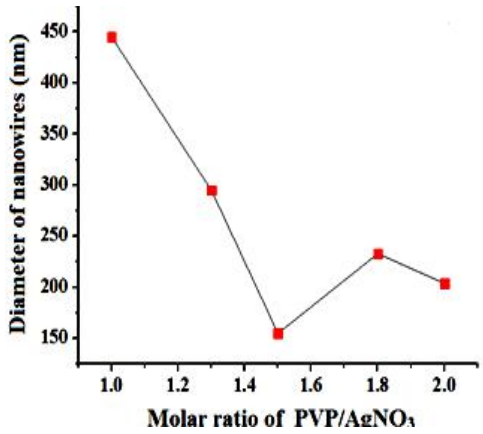

Fig. 4. The changes in silver nanowires diameter as a function of the molar ratios.

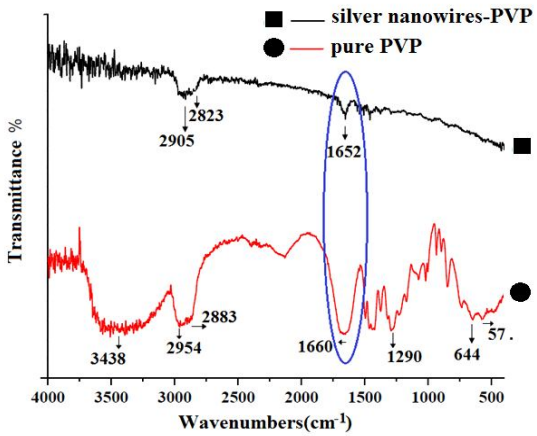

Fig. 5. FT-IR spectra of the silver nanowires-PVP (■) and the pure PVP (●).

By increasing the sintering temperature to 160 °C, silver nanowires with a mean diameter of 155 nm were obtained (Fig. 6b). At 180 ºC, silver nanowires with a mean diameter of 200 nm were formed but their mean length was decreased with respect to the nanowires prepared at 160 ºC (Fig. 6c).

This phenomenon can be attributed to the pressure build up in the solvothermal reactions by which the kinetic energy of the molecules increase and growth rate of nanowires increase subsequently. In order to estimate the pressure inside the reaction vessel, the Peng– Robinson

equation of state is being used [26]. The Peng–Robinson equation is in the below form:

$$P = \left[\frac{RT}{V_m - b}\right] - \left[\frac{a}{V_m^2 + 2bV_m - b^2}\right]$$

Where T and P refer to the reaction temperature and the pressure generated into the autoclave, respectively; V_m is the molar volume of the liquid in the solvothermal reaction vessel. In this equation, parameters of a and b are some constants which depend on the solution.

Based on this equation, when the reaction temperature is raised, vapor pressure of solution in the autoclave increases and the kinetic energy of molecules increase. So their mobility and their bouncing around increase. By increasing their mobility, they are more likely to have a collision and combined which cause an increase in the growth rate.

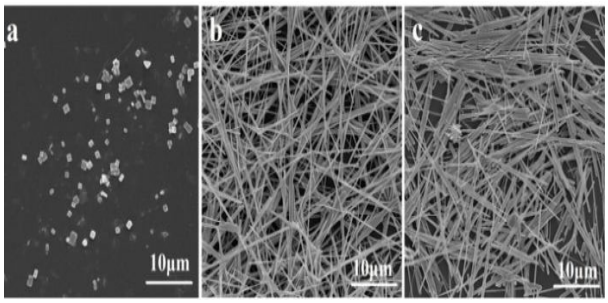

Fig. 6. FESEM images of silver nanowires synthesized at different reaction temperatures at a fixed time of 2.5 h (a) 140 °C; (b) 160 °C; (c) 180 °C.

Fig. 7 shows FESEM images of samples taken from different reaction times at a fixed sintering temperature of 160 ºC. The molar ratio of PVP/$AgNO_3$ was kept constant (1.5). When the reaction time was 1h, a tree-like structure of silver crystals was obtained (Fig. 7a). By increasing the reaction time to 1.5 h, silver nanoparticles with different shapes and sizes were synthesized (Fig. 7b). It has been found that the silver nanowires with uniform sizes can be obtained by increasing the reaction time from 1.5 to 2.5 h. These results indicate that reaction time has important role in the synthesis of silver nanowires. Indeed, by increasing the reaction time, the concentration of molecules in gas phase enhances, therefore the pressure and the reaction rate increase subsequently.

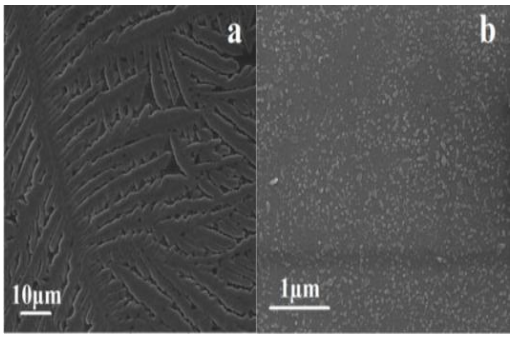

Fig. 7. FESEM images of silver nanowires synthesized at different reaction times at a fixed temperature of 160 °C: (a) 1 h; (b) 1.5 h. The molar ratio of PVP/$AgNO_3$ is the same (1.5).

The purity of EG was found to be a crucial factor over the shape of silver nanowires. Fig.8 shows the SEM of silver nanostructures obtained using EG with different purities. When purity of EG was 99%, the main products were silver nanoparticles (Fig. 8a). But if the experiment was repeated in the same condition by using EG with 99.5% purity, silver nanowires with uniform sizes would obtained (Fig. 8b). The reason can be attributed to the presence of the impurities in the 99% EG that make it more difficult for the solvent molecules to escape from the solution. Therefore the vapor pressure of the solution and the growth rate of nanowires reduce.

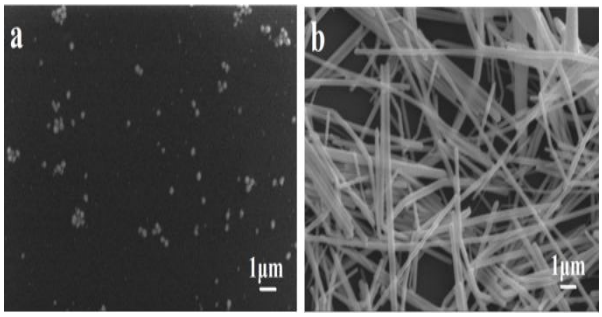

Fig. 8.SEM images of silver nanowires synthesized with different purity percent of EG: (a) 99%; (b) 99.5%.

4. Conclusion

A facile but effective solvothermal method was employed to produce high yield and reproducible sliver nanowires with uniform diameters. The method requires only simple reagents and equipment to control the silver nanowires diameter under appropriate conditions. It was found that the molar ratio of PVP/$AgNO_3$ plays an important role in the formation of silver nanowires with different diameters. By increasing the molar ratio of PVP/$AgNO_3$ from 1 up to 1.5, the mean diameter of silver nanowires decreased from 445 to 155 nm afterwards increased to 233 nm by further increase of the molar ratio of PVP/$AgNO_3$up to 2. So, the molar ratio of 1.5 (PVP/$AgNO_3$) was an optimum value for the synthesis of nanowires. In addition, the investigations showed that the morphologies of silver nanostructures synthesized through the solvothermal method depended strongly on the reaction time, reaction temperature, and purity of EG.

Acknowledgment

The authors acknowledge Shahid Chamran university of Ahvaz for financial support of this work.

References

[1] Z. Wang, J. Liu, X. Chen, J. Wan, Y. Qian, Chem. Eur. J. 11 (2005) 160-163.

[2] M.A. Kostowskyj, R.J. Gilliam, D.W. Kirk, S.J. Thorpe, Int. J. Hydrog. Energy 33 (2008) 5773-5778.

[3] M.G. Kang, T. Xu, H.J. Park, X. Luo, L.J. Guo, Adv. Mater. 22 (2010) 4378-4383.

[4] E.C. Garnett, W. Cai, J.J. Cha, F. Mahmood, S.T. Connor, M.G. Christoforo, Y. Cui, M.D. McGehee, M.L. Brongersma, Nat. Mater. 11 (2012) 241-249.

[5] Y. Fang, H. Wei, F. Hao, P. Nordlander, H. Xu, Nano. Lett. 9 (2009) 2049-2053.

[6] Y. Badr, M.A. Mahmoud, J. Mol. Struct. 749 (2005) 187–192.

[7] B. Sun, X. Jiang, S. Dai, Z. Du, Mater. Lett. 63 (2009) 2570-2573.

[8] G.W. Huang, H.M. Xiao, S.Y. Fu, Nanoscale 6 (2014) 8495-8502.

[9] S. Yao, Y. Zhu, Nanoscale 6 (2014) 2345-2352.

[10] J.J. Zhu, Q.F. Qiu, H. Wang, J.R. Zhang, J.M. Zhu, Z.Q. Chen, Inorg. Chem. Commun. 5 (2002) 242-244.

[11] L. Zhang, P. Zhang, Y. Fang, Anal. Chim. Acta. 591 (2007) 214-218.

[12] S. Green, A. Cortes, G. Riveros, H. Gómez, E.A. Dalchiele, R.E. Marotti, Phys. Stat. Sol. (c) 4 (2007) 340-343.

[13] K. Zhao, Q. Chang, X. Chen, B. Zhang, J. Liu, Mater. Sci. Eng. C. 29 (2009) 1191-1195.

[14] K.K. Caswell, C.M. Bender, C.J. Murphy, Nano Lett. 3 (2003) 667-669.

[15] D. Zhang, L. Qi, J. Yang, J. Ma, H. Cheng, L. Huang, Chem. Mater. 16 (2004) 872-876.

[16] S. Chang, K. Chen, Q. Hua, Y. Ma, W. Huang, J. Phys. Chem. C. 115 (2011) 7979-7086.

[17] J.J. Zhu, C.X. Kan, J.G. Wan, M. Han, G.H. Wang, J.Nano Mat. 2011 (2011) 1-7.

[18] F. Fievet, J.P. Lagier, B. Blin, B. Beaudoin, M. Figlarz, Solid State Ionics. 32 (1989)198-205.

[19] A. R. Siekkinen, J. M. McLellan, J. Chen, Y. Xia, Chem. Phys. Lett. 432 (2006) 491-496.
[20] X. Tang, M. Tsuji, P. Jiang, M. Nishio, S.M. Jang, S.H. Yoon, Colloids Surf. A 338 (2009) 33-39.
[21] X.C. Jiang, S.X. Xiong, C.Y. Chen, W.M. Chen, A.B. Yu, J. Nanopart. Res. 13 (2011) 5087-5101.
[22] Z. Li, A. Gu, M. Guan, Q. Zhou, T. Shang, Colloid Polym. Sci. 288 (2010) 1185-1191.
[23] H. Mao, J. Feng, X. Ma, C. Wu, X. Zhao, J. Nanopart. Res. 14 (2012) 1-15.
[24] W. Zhang, P. Chen, Q. Gao, Y. Zhang, Y Tang, Chem. Mater. 20 (2008)1699-1704.
[25] P. Ramasamy, D.M. Seo, S.H. Kim, J. Kim, J. Mater. Chem. 22 (2012) 11651-11657.
[26] M. Rajamathi, and R. Seshadri, Curr. Opin. Solid State Mater. Sci. 6 (2002) 337-345.