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Antisolvent-induced encapsulation for extraction/preconcentration of silver nanoparticles

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Abstract

In this research work a simple and very fast antisolvent-induced encapsulation procedure was developed and applied for extraction and preconcentration of silver nanoparticles from diluted aqueous solutions. Organic solvent (1.0 ml) was added to a solution of silver nanoparticles capped with starch (2.0 ml) for formation of a homogeneous solution. To the mixture solution, suitable amount of ammonium sulfate (0.30 g) was added and the solution was vigorously shaken until the salt was completely dissolved. Then 1.0 ml of organic antisolvent was added, after which it was separated into two clear phases by centrifugation at 3000 rpm for 5 min. The influences of effective parameters such as salt (type and amount), organic solvent, and its volume were studied and optimized.

Keywords: Antisolvent-induced encapsulation; Preconcentration; Silver nanoparticles; Diluted aqueous solutions; Organic antisolvent; Starch

1. Introduction

The rapid increase in the production and applications of nanomaterials (NMs) leads to release of NMs into the environment. Noble metal nanoparticles have attracted increasing interest due to their size- and shape-dependent optical and electronic properties, which are expected to have wide applications in optics, microelectronics, sensors, catalysis and so on [1-3].

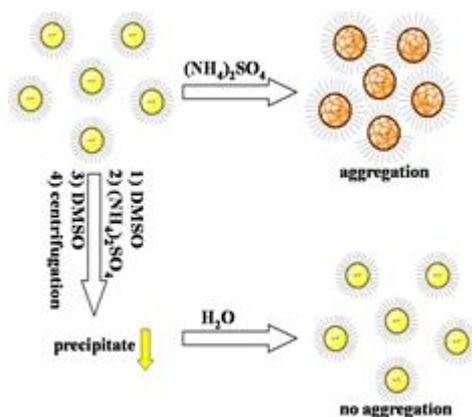
Separation methods for noble metal nanoparticles from diluted aqueous solutions are always attracting considerable attention due to the increasing industrial need and limiting sources. Some sample separation methods have been reported for the extraction of noble metal nanoparticles from diluted aqueous solutions [2-10]. Because of the extremely low concentration of noble metal nanoparticles and the complex matrixes, a simple, fast, more efficient, and cost-effective separation method is essential for extraction and preconcentration of noble metal nanoparticles from diluted aqueous solutions.

It has been suggested that antisolvent procedure can be used as extraction and clean-up steps in sample preparation. In this method, a secondary solvent known as antisolvent or precipitant is added to the solution. Antisolvent is miscible with the solvent but immiscible or slightly miscible with the solute. When an antisolvent is added to a solution with a solute to be separated, the original solubility of the solute in the solution is reduced due to supersaturation driving force, so the solute is crystallized and precipitated. The main advantages of antisolvent in the field of separation and purification are: rapidity, low cost, high enrichment factor, high extraction recovery, simplicity of operation, and ambient temperature may be employed. Antisolvent method was developed for the extraction of highly water-soluble compounds such as pharmaceutical products and biomaterials in industrial processes [11-22].

In this study a simple, rapid, and inexpensive antisolvent-induced encapsulation method has been developed for extraction and concentration of silver nanoparticles from diluted aqueous solutions. This

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procedure provides an antisolvent-induced encapsulation of AgNPs into coating shells [23,24]. The effects of several important parameters influencing the extraction efficiencies of silver nanoparticles (AgNPs) were investigated. The mechanism of this encapsulation is depicted in Scheme 1. However, to our knowledge, there is no report for separation/concentration and dispersion of AgNPs from aqueous solutions using antisolvent-induced encapsulation method.



Scheme 1

2. Experimental

2.1. Chemicals

Ethanol (99.5%), acetonitrile (99.0%), ammonium sulfate (>99.5%), sodium chloride, starch, silver nitrate, and sodium hydroxide (99.0%) were supplied from Merck. Dimethyl sulfoxide (>99.5%) was supplied from Roth.

2.2. Preparation of silver nanoparticles

A modified procedure similar to that previously reported was used to prepare silver nanoparticles [25]. Briefly, the silver nanoparticles (AgNPs) were synthesized in a one-step reduction process in an aqueous solution. All reactions were carried out in oxygen free water under nitrogen. In a typical preparation, a 400 μ l aliquot of a 0.05 M AgNO₃ aqueous solution was added into 100 ml of an aqueous solution containing 0.15 wt % of the soluble starch and vigorously stirred for 1 h. The pH of resulting solution was adjusted to 8.0 by adding 0.1 M NaOH solution. Under this experimental condition, the initial reaction mixture was colorless and the growth of the AgNPs was monitored at different time intervals using UV-vis absorption spectroscopy. After about 1 h the solution turned light yellow, which indicated the initial formation of the AgNPs. The mixture was maintained at 50 °C for 24 h (water bath, MB 402, Belgium) and the color of the reaction solution became yellow.

2.3. Apparatus

Absorption measurements was carried out on a Varian Bio-300 spectrophotometer using a quartz cell with an optical path of 1 cm. X-ray diffraction (XRD) pattern was collected with an automated Philips X'Pert X-ray diffractometer with Cu K α radiation (40 kV, 30 mA) for 2 θ values over 10-80 $^{\circ}$. The sample grid for transmission electron microscopy (TEM) image was prepared by placing a drop of aqueous AgNPs dispersion onto the copper grid coated with a thin amorphous carbon film and subsequently evaporating water naturally overnight at ambient condition. The morphology and size distribution of the AgNPs were determined by a Philips CM200-FEG TEM at an operating voltage of 200 kV. The morphology of capcules was observed by scanning electron microscopy (SEM), FE-SEM, Hitachi S4160 (Japan) under an acceleration voltage of 15 kV. The centurion scientific centrifuge (K280R, UK) was used for centrifuging. Materials were prepared by mass using a balance (Sartorius, model CPA225D, Germany) with an uncertainty of ± 0.1 mg. The pH measurements were made with a 780 pH meter (Metrohm, Switzerland) equipped with a combine Ag/AgCl glass electrode.

2.4. Antisolvent-induced encapsulation procedure

In each antisolvent-induced encapsulation experiment, an aliquot (2 ml) of solution of AgNPs capped with starch was placed in a 10-ml volumetric flask. Dimethyl sufoxide (DMSO, 1.0 ml), as stabilizer, was added. The mixture was shaken and a homogeneous phase was formed instantaneously. To the homogeneous phase, 0.30 g of ammonium sulfate, as coating, was added and the solution was vigorous shaken until ammonium sulfate was completely dissolved and a clear homogeneous phase was observed. In order to phase separation, 1.0 ml of DMSO, as antisolvent, was added and vial was shaken for a few minutes. As a result, the immediate formation of a white precipitate and phase separation were observed. The solution was transferred to a test tube and separation of the phases was accomplished by centrifugation at 3000 rpm for 5 min. Then the solid phase was precipitated in the bottom of test tube. The aqueous solution was discarded and the precipitate resuspended in water.

3. Results and discussion

3.1. AgNPs characterization

Figure 1 shows the UV-vis absorption spectra obtained at different time intervals after mixing AgNO₃ aqueous solution with soluble starch aqueous solution at 50 °C. Formation of AgNPs in the colloidal solution was monitored from their absorption spectra as the small noble metal particles reveal absorption band in the UV-vis spectral region due to surface plasmon resonance (SPR) [25]. The process of reduction of the Ag⁺ ions using the starch was slow, yielding a broad absorption band

centered at about 414 nm until 1 h of reaction, which was assigned to the SPR of AgNPs. The intensity of the SPR band increased systematically with the increase of reaction time, to reach a maximum after about 24 h. Thereafter, the intensity of the SPR band did not change. The reduction of Ag⁺ ions with starch aqueous solution at 50 °C leads to the formation of AgNPs that are stable in solution for several months. This indicates that the soluble starch serves as both reducing and protecting agent.

X-ray diffraction (XRD) pattern of AgNPs powder is shown in Figure 2. The pattern exhibits peaks at 2 θ angles of 38.17, 44.21, 64.32, and 77.12 that correspond to the (111), (200), (220), and (311) crystal planes of a cubic lattice structure of AgNPs, respectively [26]. From the full-width at half-maximum of diffraction peaks, the average size of the AgNPs has been calculated using the Debye-

Scherrer equation [27]. The calculated average size of AgNPs was around 23 nm.

A typical TEM image of the AgNPs is displayed in Figure 3a. In general, the nanoparticles are isotropic in shape. As we anticipated from the absorption data, the characteristic spherical AgNPs are observed with a relatively narrow particle size distribution (10-35 nm range). These results illustrate the synthesis of Ag nanoparticles through reduction of Ag⁺ ions inside the nanoscopic soluble starch templates. The hydroxyl groups act as passivation contacts for the stabilization of the AgNPs formed inside these templates. A histogram of the AgNPs size distribution is also presented in Figure 3b. The average nanoparticles diameter observed is 22.1 nm (standard deviation, SD=3.2 nm) and more than 96% of the AgNPs are in the size range from 10 to 30 nm, indicating a relatively high monodispersity of the AgNPs formed in the system.

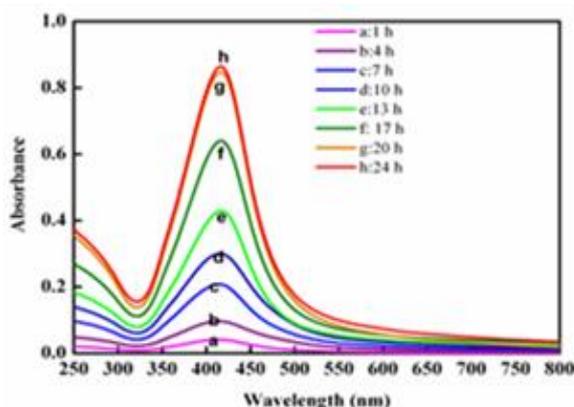


Figure 1. Temporal evolution of UV-visible absorption spectra after addition of AgNO₃ solution into soluble starch solution at 50 °C.

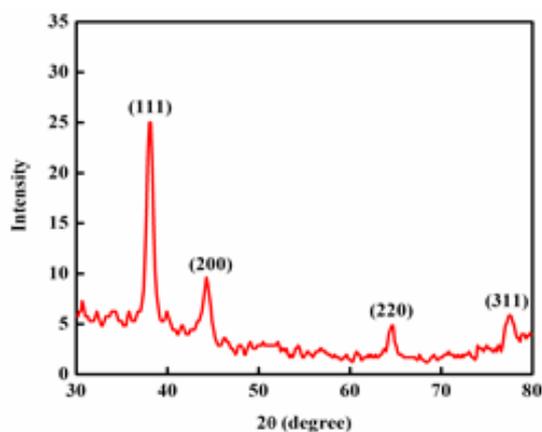


Figure 2. X-ray diffraction pattern of the starch-stabilized Ag nanoparticles.

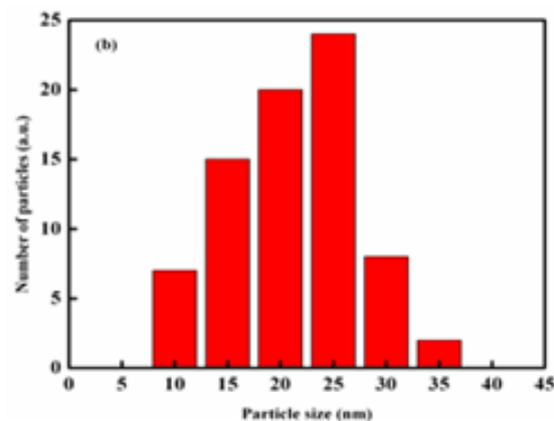
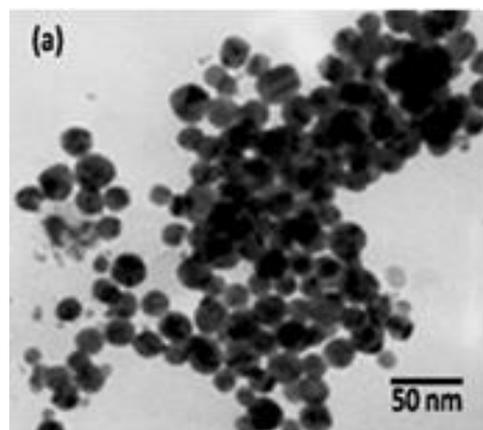


Figure 3. (a) Typical TEM image of the AgNPs stabilized by soluble starch solution, (b) Histogram of the Ag nanoparticles size distribution.

3.2. Extraction of AgNPs

In the assay, it was found that the process is different while reagents were added in different order. Therefore, three different analytical processes were designed. In method 1, coating (ammonium sulfate) was first added into the AgNPs solution and allowed to DMSO added into the mixed solution. In method 2, 2.0 ml of DMSO was first added into the AgNPs solution and allowed to coating was added into the homogeneous solution. In method 3, 1.0 ml DMSO was added into the AgNPs solution then ammonium sulfate was added into the homogeneous solution followed by addition of 1.0 ml of DMSO. In method 1, it was found that AgNPs aggregation occurred as evidenced by an instantaneous color change from yellow to brown (Figure 4). The chemisorbed $(\text{NH}_4)_2\text{SO}_4$ would displace starch from the surface of the AgNPs [28-30]. In method 2, due to very low solubility of ammonium sulfate in AgNPs-DMSO solution precipitation of ammonium sulfate was observed. Consequently the method 3 was chosen for subsequent experiments (Figure 5).

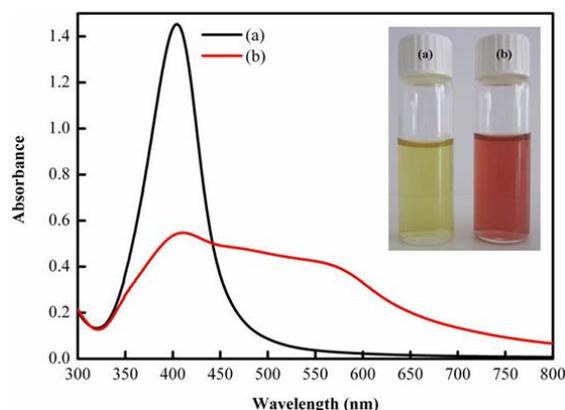


Figure 4. Absorption spectra of AgNPs (a) in the absence of $(\text{NH}_4)_2\text{SO}_4$, (b) in the presence of $(\text{NH}_4)_2\text{SO}_4$. Experimental conditions: volume of AgNPs 2 mL, $(\text{NH}_4)_2\text{SO}_4=0.3$ g.



Figure 5. Photograph of (b) 2 ml of AgNPs+2 ml of DMSO, (c) 2 ml of AgNPs+1 ml of DMSO +0.3 g $(\text{NH}_4)_2\text{SO}_4$, (d) 2 ml of AgNPs+1 ml of DMSO+0.3 g $(\text{NH}_4)_2\text{SO}_4$ +1 ml of DMSO, (e) solution (d) after centrifugation, (f) the solid phase of (e) after resuspension in 3 mL of water.

3.3. Effect of organic solvent as stabilizer and antisolvent

The choice of an appropriate stabilizer and/or antisolvent is essential for the proposed method. The solvent has to meet certain requirements such as miscibility with aqueous phase, good solvent for starch capped AgNPs, and reduction of solubility of coating. Based on these considerations DMSO, ethanol and acetonitrile were tested. The results show that DMSO exhibited the highest extraction efficiency when compared with the other solvents. DMSO molecules stabilize AgNPs by chemisorption onto the surface of AgNP and protect it from aggregation and sedimentation. AgNPs are well dispersed in the homogeneous AgNPs solution-DMSO phase (Figure 6). This may be due to more solubility of starch in DMSO than other solvents [31,32].

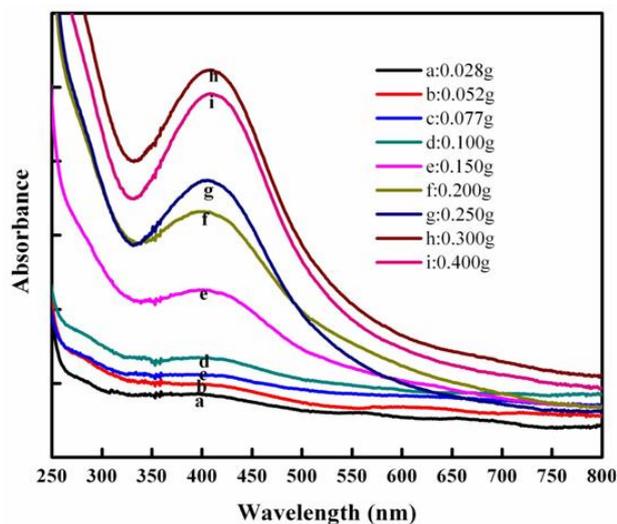


Figure 6. Effect of amount of ammonium sulfate on the extraction of AgNPs. Experimental conditions: volume of AgNPs 2 ml, volume of stabilizer 1 ml, volume of antisolvent 1 mL (the spectrum was taken after the separation of AgNPs by encapsulation and resuspension of nanoparticles in water).

3.4. Effect of coating and its amount

In order to find appropriate coating different salts including, ammonium sulfate, sodium chloride, and sodium carbonate were performed as coating. It was found that except for ammonium sulfate, other salts did not show phase separation and crystal growth. Based on the above results, ammonium sulfate was chosen as appropriate coating.

In order to investigate the effect of amount of ammonium sulfate on the extraction of AgNPs, varied amounts of ammonium sulfate (0.0280–0.4000 g) were added to the DMSO-AgNPs solution. It is evident from Figure 6 that the optimum ammonium sulfate concentration for the extraction of AgNPs and the phase separation was considered to be 0.3000 g. The ammonium sulfate layer surrounding AgNPs imparts chemical

resistance, prevention properties of the encapsulated inorganic particles in aggregative environments [33]. AgNPs act as templates for coating crystal growth and AgNPs are completely coated with a thick coating layer (Figure 7).

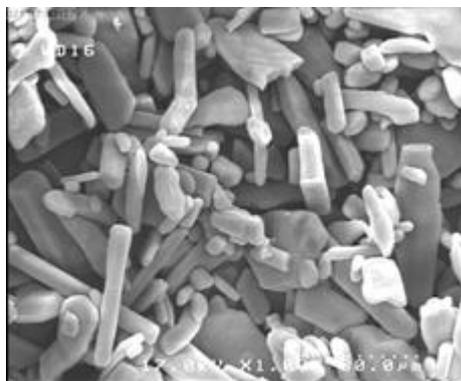


Figure 7. SEM picture of AgNPs powders obtained after antisolvent-induced encapsulation produced at the following conditions: 2 ml of AgNPs, volume of stabilizer=1 ml of DMSO, $(\text{NH}_4)_2\text{SO}_4=0.3$ g, volume of antisolvent=1 ml of DMSO.

3.5. Effect of DMSO as stabilizer

In order to prevent aggregate and color change of AgNPs from yellow to brown, a stabilizer could be used. It is possible to prevention of ammonium sulfate-induced aggregation by adsorbing of DMSO onto the surface of AgNPs. This could be done by initially addition of DMSO followed by addition of coating [34] In order to obtain the best extraction efficiency; different volumes of DMSO (0.25, 0.5, 0.75, 1.0, 1.5, 2.0 ml) were added. Figure 8 shows the curve of the extraction efficiency of AgNPs versus volume of DMSO. By increasing the volume of DMSO up to 1.0 ml, the extraction efficiency increases. Increasing DMSO volume more than 1.0 mL causes a small decrease in the extraction efficiency. The possible reason is due to the more reduction of solubility of ammonium sulfate. Therefore, 1.0 ml was found to be optimum for the following experiments.

3.6. Effect of DMSO as antisolvent

The level of supersaturation depended on the solvent-antisolvent ratio [22]. In order to create supersaturation and consequently to reduce the solubility of salt (the addition of antisolvent rapidly reduced the solubility of coating by binding free water [15]), different volumes of DMSO in the range 0.25~2.0 ml was subjected to the same procedure. The results are shown in Figure 9. The results indicate that the analytical signal increased significantly as the volume of DMSO was increased, and it reached its maximum value at a volume of 1.0 ml. When DMSO volume is greater than 1.5 ml, the extraction profile approach a plateau or even begins to decrease. On the basis of these results, 1.0 ml DMSO was chosen in the subsequent experiments.

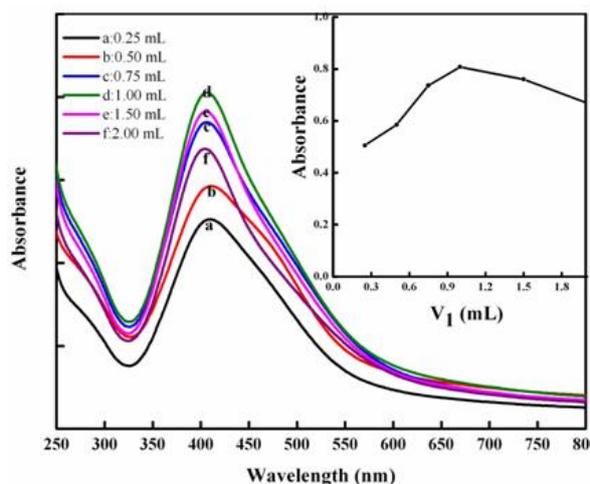


Figure 8. Effect of volume of stabilizer. Experimental conditions: volume of AgNPs 2 ml, volume of DMSO as antisolvent 1 ml, amount of $(\text{NH}_4)_2\text{SO}_4$ 0.3 g (the spectrum was taken after the separation of AgNPs by encapsulation and resuspension of nanoparticles in water).

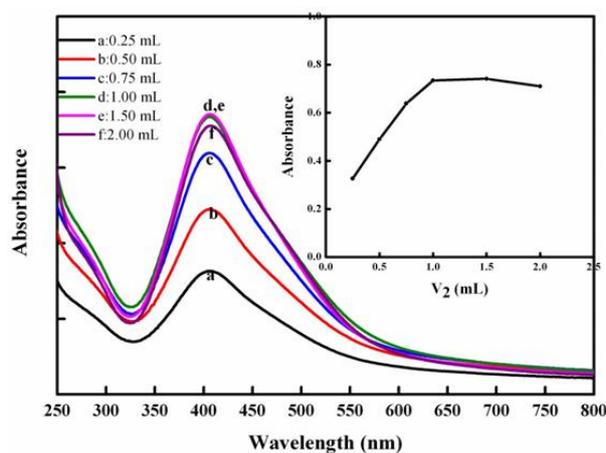


Figure 9. Effect of volume of antisolvent. Experimental conditions: volume of AgNPs 2 ml, volume of DMSO as stabilizer 1 ml, $(\text{NH}_4)_2\text{SO}_4=0.3$ g (the spectrum was taken after the separation of AgNPs by encapsulation and resuspension of nanoparticles in water).

References

- [1] Y. Yang, S. Liu and K. Kimura, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **290** (2006) 143.
- [2] M. Rossier, F.M. Koehler, E.K. Athanassiou, R.N. Grass, B. Aeschlimann, D. Gunther and W.J. Stark, *J. Mater. Chem.* **19** (2009) 8239.
- [3] J. Liu, J. Chao, R. Liu, Z. Tan, Y. Yin, Y. Wu and G. Jiang, *Anal. Chem.* **81** (2009) 6496.
- [4] H. L. Huang, H. P. Wang, G. T. Wei, I.W. Sun, J. F. Huang and Y. W. Yang, *Environ. Sci. Technol.* **40** (2006) 4761.
- [5] C. W. Isaacson, C. Y. Usenko, R. L. Tanguay and J. A. Field, *Anal. Chem.* **79** (2007) 9091.
- [6] Y. C. Chang and D. H. Chen, *Gold Bull.* **39** (2006) 98.

- [7] J. Liu, R. Liu, Y. Yin and G. Jiang, *Chem. Commun.* (2009) 1514.
- [8] J. Benavides, O. Aguilar, B. H. Lapizco-Encinas and M. Rito-Palomares, *Chem. Eng. Technol.* **31** (2008) 838.
- [9] N. Gaponik, D. V. Talapin, A. L. Rogach, A. Eychmüller and H. Weller, *Nano Lett.* **2** (2002) 803.
- [10] X. Wang and Y. Chen, *Mater. Lett.* **62** (2008) 4366.
- [11] P. E. Jentoft and R. J. Robinson, *Anal. Chem.* **26** (1954) 1156.
- [12] Y. P. Jimenez, M. E. Taboada and H. R. Galleguillos, *Fluid Phase Equilibr.* **284** (2009) 114.
- [13] A. Borissova, Z. Dashova, X. Lai and K. J. Roberts, *Crystal Growth & Design*, **4** (2004) 1053.
- [14] D. A. Berry, S. R. Dye and K. M. Ng, *AIChE J.* **43** (1997) 91.
- [15] W. Hyung, Y. Kim, C. H. Chung and S. Haam, *Powder Technol.* **186** (2008) 137.
- [16] C. M. Pina, L. Fernandez-Diaze, M. Prietoc and S. Veintemillas-Verdaguer, *J. Crystal Growth.* **222** (2001) 317.
- [17] W. Liu, Y. Hou, W. Wu, S. Ren, Y. Jing and B. Zhang, *Ind. Eng. Chem. Res.* **50** (2011) 6952.
- [18] T. Panagiotou, S. V. Mesite and R. J. Fisher, *Ind. Eng. Chem. Res.* **48** (2009) 1761.
- [19] C. P. Mark Roelands, S. Jiang, M. Kitamura, J. H. ter Horst, H. J. M. Kramer and P.J. Jansens, *Crystal Growth & Design*, **6** (2006) 955.
- [20] A. Borissova, Z. Dashova, X. Lai and K. J. Roberts, *Crystal Growth & Design*, **4** (2004) 1053.
- [21] H. X. Zhang, J. X. Wang, Z. B. Zhang, Y. Le, Z. G. Shen and J. F. Chen, *Int. J. Pharm.* **374** (2009) 106.
- [22] C. Desai, S.A. Ntim and S. Mitra, *J. Colloid Interf. Sci.* **368** (2012) 115–.
- [23] R.F. Fakhrullin and R.T. Minullina, *Langmuir*, **25** (2009) 6617.
- [24] M. Fujiwara, K. Shiokawa, M. Araki, N. Ashitaka, K. Morigaki, T. Kubota and Y. Nakahara, *Cryst. Growth. Des.* **10** (2010) 4030.
- [25] H. Huang and X. Yang, *Carbohydr. Res.* **339** (2004) 2627.
- [26] X. Wang and Y. Chen, *Mater. Lett.* **62** (2008) 4366.
- [27] A. Goudarzi, G. Motedayen Aval, S.S. Park, M.C. Choi, R. Sahraei, M. Habib Ullah, A. Avane and C.S. Ha, *Chem. Mater.* **21** (2009) 2375.
- [28] Y. Lin, C. Chen, C. Wang, F. Pu, J. Ren and X. Qu, *Chem. Commun.* **47** (2011) 1181.
- [29] Y. Zhang, B. Li and X. Chen, *Microchim Acta.* **168** (2010)107.
- [30] Y. Yuan, J. Zhang, H. Zhang and X. Yang, *Analyst.* (2012) DOI: 10.1039/C1AN15875A.
- [31] F. Zhong, W. Yokoyama, Q. Wang, C. F. Shoemaker, Rice Starch, Amylopectin, and Amylose, *J. Agric. Food Chem.* **54** (2006) 2320.
- [32] J. A. Han and S. T. Lim, *Carbohydrate Polymers*, **55** (2004) 265.
- [33] A. S. Kumbhar and G. Chumanov, *Chem. Mater.* **21** (2009) 2835.
- [34] A. Albanese and W. C. W. Chan, *ACS. NANO.* **5** (2011) 5478.

جداسازی پیش-تغلیظ نانوذرات نقره به کپسولی شدن القا شده با ضد حلال

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چکیده:

در این کار تحقیقاتی روشی سریع و ساده بر پایه کپسولی شدن القا شده با ضدحلال برای استخراج و پیش-تغلیظ نانوذرات نقره ارائه شده است. حلال آلی (۰,۱ میلی لیتر) به محلول نانوذرات نقره پایدار شده با نشاسته افزوده شد. به مخلوط حاصل مقدار معینی از سولفات آمونیوم (۰,۳ گرم) اضافه و محلول تاحل شدن کامل نمک همزده شد. سپس یک میلی لیتر ضدحلال آلی به محلول اضافه شد. به کمک سانتریفیوژ (۳۰۰۰ دور بر دقیقه، ۵ دقیقه) محلول حاصل به دو فاز شفاف تبدیل شد. اثر پارامترهای مختلف مانند (نوع نمک و مقدار آن)، حلال آلی و حجم آن بررسی و بهینه شد.

کلمات کلیدی: کپسولی شدن القا شده با ضدحلال، پیش-تغلیظ، نانوذرات نقره، محلول آبی رقیق شده، ضدحلال آلی، نشاسته.