

EFFECT OF AMINES ON THE SILVER NANOPARTICLES FORMATION AT ROOM TEMPERATURE

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ABSTRACT. Silver nanoparticles, Ag NPs, play an important role in modern technology. Their antimicrobial and catalytic properties are employed in many different fields of research – catalysis, electronics, microbiology and environmental protection. Such major involvement requires cost effective methods for synthesis of stable Ag NPs if they are applied in large scale. Here, we present an environmentally friendly method for preparation of silver nanoparticles at room temperature in the presence of amines. Two types of amines were employed in the synthesis – monoethanolamine (MEA) and triethanolamine (TEA) as a catalyst for the reduction of silver ions to Ag NPs. The resulting nanoparticles were characterized by UV-VIS spectrophotometry and scanning electron microscopy (SEM). Information about their size and morphology was obtained and was used for comparison of the effect of the amine on the process of Ag NPs formation.

Keywords: Ag NPs, nanomaterials, synthesis, amines

ВЛИЯНИЕ НА АМИНИ ВЪРХУ ПРОЦЕСА НА ФОРМИРАНЕ НА СРЕБЪРНИ НАНОЧАСТИЦИ ПРИ СТАЙНА ТЕМПЕРАТУРА

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РЕЗЮМЕ. Сребърните наночастици, Ag NPs, заемат важно място в съвременните технологии. Техните антимикробни и каталитични свойства се използват в много различни научни разработки в областта на електрониката, микробиология и опазването на околната среда. Широката им област на приложение налага необходимостта от разработването на икономически изгодни методи за синтез на стабилни Ag NPs, с цел те да се прилагат в големи мащаби. В това изследване представяме екологосъобразен метод за получаване на сребърни наночастици при стайна температура в присъствието на амин. Два вида амини (моноетаноламин (MEA) и триетаноламин (TEA)) се използват при този синтез, те действат като катализатори при редукцията на сребърни йони до сребърни наночастици. Получените наночастици са охарактеризирани с UV-VIS спектрофотометрия и сканираща електронна микроскопия (SEM). Получена информацията за техните размер и морфология е използвана за сравнение на ефекта на двата катализатора в процеса на образуване на Ag NPs.

Ключови думи: сребърни наночастици, наноматериали, синтез, амини

Introduction

Nanosized particles and nanomaterials have attracted the interest of scientific community due to their unique properties – optical, electronic, and electrochemical (Liz-Marzán, 2006). What makes them really unique is the fact that their characteristics differ from those of the bulk materials and are size-dependant due to the quantum confinement effect. Therefore, the properties of nanomaterials can be tuned just by tuning particles' size without changing the chemical composition (Duan et al., 2000). Silver is one of the popular metals used for production of nanoparticles. Antimicrobial properties of silver ions have been well-known for long time. Silver nanoforms also show such an activity, moreover nanoparticles are much more convenient for applications such as antimicrobial textile, sterile bandages and other commercially available products based on nanosilver (Perera et al., 2013). Other applications are based on its metal conductivity and optical properties. It is applied in modern electronics and optical devices (Natsuki et al., 2011). Silver nanoparticles and materials based on them are important means for disinfection of potable water as an alternative of

chlorine treatment, which leads to formation of carcinogenic by-products and derivatives (Ülküra E et al., 2005; Panacek et al. 2006; Abdel-Aziz et al., 2014).

Synthesis of uniform and stable silver nanoparticles with controllable size is also a difficult task. The optimum synthetic method should address all of the above-mention problems and additionally it should be able to yield nanoparticles with no extraneous chemicals that can potentially alter the particle's optical properties and surface chemistry. In the literature there are various methods for synthesis of silver nanoparticles (AgNPs) (Swathy B., 2014). Many of them are based on the reduction of Ag⁺ ions in water solution. Chemical reduction typically includes reducing agent like polyols, NaBH₄, N₂H₄, sodium citrate and N,N-dimethylformamide. In order to prevent the aggregation of AgNPs, the suspension is stabilized by capping agents such as sodium dodecyl sulphate (SDS), polyvinyl pyrrolidone (PVP), tri-sodium citrate (Jones et al., 2014). Some of the chemical reduction reactions can be carried out at room temperature. However, most of them need elevated temperatures for a higher reaction rate. Nanoparticles' morphology strongly depends on the reaction

temperature. For example, flower-like silver nano architecture with size of the particles 20 nm is formed in the presence of ascorbic acid at room temperature (Kimling J. et al., 2006). The other classic method involves sodium citrate as a reducing and capping agent at high temperature under reflux (Turkevich et al., 1951). Silver nanoparticles have been synthesized in the presence of supercritical carbon dioxide (SCCO₂), from silver nitrate used as a starting material, PVP as a stabilizer of silver clusters, and ethylene glycol as a reducing agent and solvent. Polyvinyl pyrrolidone not only protected the nanosized silver particles from aggregation, but it also promoted nucleation. The silver nanoparticles synthesized by SCCO₂ are smaller and possess higher monodispersity than those produced under the same conditions by the conventional heating methods. As a result, the nanosilver had lower toxicity and higher stability, and the particles were all spherical with mean diameters in the range of 2–5 nm (Jones et al., 2014).

Environmental applications of AgNPs, such as water disinfection (Pradeep A. T., 2009), dyes degradation, gas sensing etc., require stable, non-aggregable and in many cases non-hydrophobic nanoparticles. Surfactants are typically used to protect NPs from aggregation; however, the capping molecules on the surface of NPs block the mass transport and electron transfer and thus reduce their activity (Li D. et al., 2012). In addition, recovery of the AgNPs from the reaction medium is difficult and expensive. The immobilization of AgNPs on solid surfaces or incorporation in solid matrix provides stability and thus facilitates the reuse of NPs. AgNPs have been immobilized on different solid surfaces such as glass slides, silica nanofibers (Wong, C. et al., 2015), coated magnetic particles, carbon nanotubes (Yan et al., 2011) and thiol functionalized polymer-carbon nanotubes composite.

In this paper, we present the formation of silver nanoparticles obtained at room temperature using modified citrate method. It consists of addition of amines (MEA and TEA) which catalyse the reduction of silver ions by sodium citrate thus lowering the reaction temperature.

Experimental part

Chemicals

AgNO₃ (purity >99.8%) was purchased from Teokom Ltd (Bulgaria), tri-sodium citrate dehydrate (Na₃Cit • 2H₂O; for analysis), and hexadecyltrimethylammonium bromide (CTAB; ≥99.0%) - from MERCK & CO., INC. Monoethanolamine (ethanolamine, MEA; pure p. a.) and triethanolamine (TEA; pure p. a.) were obtained from POCH™ (Poland). All reagents were used without further purification. All the solutions were made using double distilled water.

Synthesis of AgNPs

Solution of silver nitrate in double distilled water (d.d. H₂O) was stirred on magnetic stirrer at room temperature. A solution of CTAB with different concentrations (5.10⁻⁴, 1.10⁻³, 2.10⁻³ M) was added drop wise to the AgNO₃ solution and the mixture was stirred for 20 minutes. Then 20 ml Na₃Cit solution (2.10⁻³ M) was added drop wise. After that 3 ml solution of 4.10⁻⁴ M MEA (or TEA) was injected into the reaction mixture. A pale

reddish colour appeared. Aliquots of reaction mixture were taken at 15th and 30th minutes and their spectra were recorded. The amounts of reagents are given in Table 1.

Table 1.
Experimental condition for samples preparation

sample	CTAB, [M]	MEA, [M]	TEA, [M]
1	5.10 ⁻⁴	4.10 ⁻⁴	0
2	1.10 ⁻³	4.10 ⁻⁴	0
3	2.10 ⁻³	4.10 ⁻⁴	0
4	5.10 ⁻⁴	0	4.10 ⁻⁴
5	1.10 ⁻³	0	4.10 ⁻⁴
6	2.10 ⁻³	0	4.10 ⁻⁴

*The AgNO₃ and Na₃Cit solutions were in concentrations 2.10⁻³ M

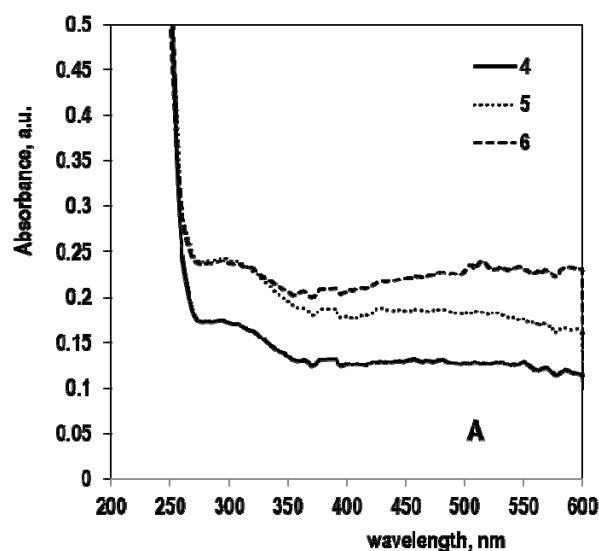
Materials characterization

UV-Vis spectral analysis of the obtained silver nanoparticles (AgNPs) was performed. They revealed peaks characteristic for them. The nanosized structures were also observed by scanning electron microscopy (SEM).

Results and discussions

Ag NPs were formed in aqueous solution by reduction of silver ions with sodium citrate. Addition of amine as a catalyst provides an alternative pathway of the reaction and allows it to proceed at lower temperature, which is an essential advantage of this procedure. Hexadecyltrimethylammonium bromide (CTAB) was used as surfactant and stabilizing agent to prevent Ag NPs from aggregation.

In order to investigate the effect of the amine in the process on silver nanoparticles formation, we tested two types of amines – monoethanolamine (MEA) and triethanolamine (TEA). The Ag NPs formation within 30 minutes was monitored by UV-Vis spectroscopy. The UV-Vis spectra of reaction mixture of Ag NPs (samples 4-6), obtained by TEA catalyzed reduction at 15th and 30th minutes are shown on Fig. 1A and Fig. 1B, respectively.



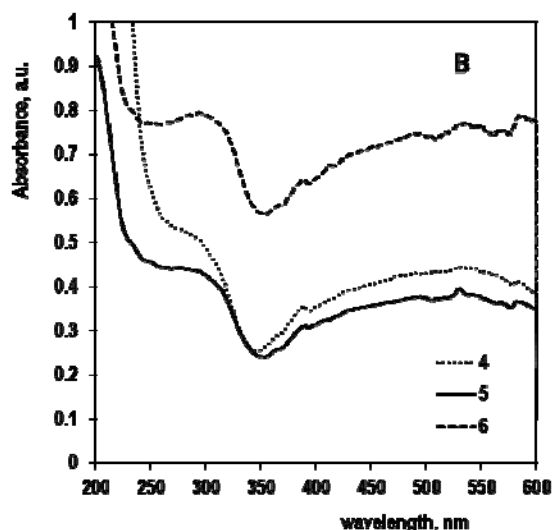


Fig. 1. UV-Vis spectra of samples 4 - 6 with TEA as catalyst and different concentration of CTAB, taken at 15th minute (A) and at 30th minute (B).

The spectra of all the samples showed two well pronounced peaks, which intensities increase with the time. The peak at 270-280 nm can be attributed to the Ag-precursor, formed between silver ions and surfactant molecule, Ag⁺-CTAB complex. The longer-wavelength peaks at 480-580 nm are due to Ag NPs and give rise from nanoparticles with diameter of 100-200 nm (Fig. 1) (Agnihotri et al., 2014). This is also consistent with results shown on Fig. 2A and 2B, where the spectra of MEA-catalysed reaction mixtures are given.

Another parameter investigated in this study is the concentration of the surfactant CTAB. It was observed that the higher is its concentration, the higher is the rate of formation of the Ag NPs in both series of samples (1-3) and (4-6). Moreover, the higher concentration of CTAB leads to slight red shift of the band maximum and the increase in the intensity of both peaks (~280 nm and ~480 nm) in the spectra (Fig. 1A, 1B and Fig.2A, 2B).

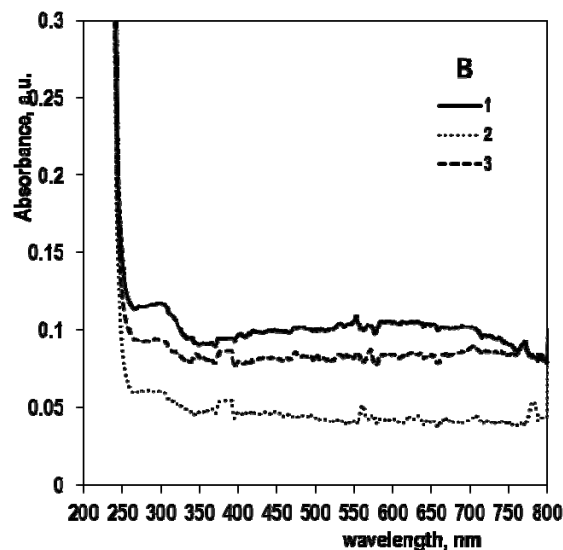
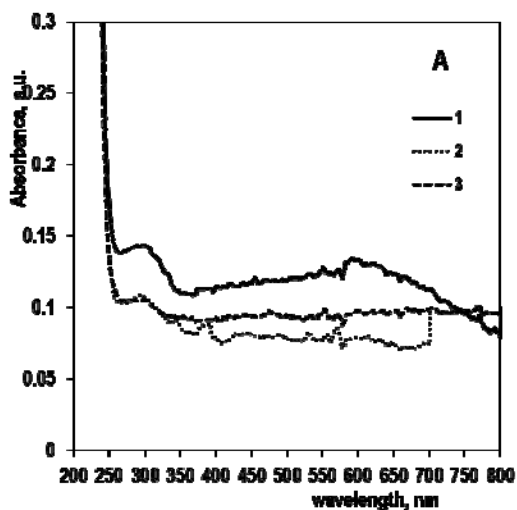


Fig. 2. UV-Vis spectra of samples 1 - 3 with MEA as catalyst and different concentration of CTAB, taken at 15 min (A) and 30 min (B)

The results from the UV-Vis spectra of the obtained Ag NPs were summarized and the data for the wavelength maxima are given in Table 2. It can be seen that the peaks for samples 1-3 are centred at 510-520 nm, while for samples 4-6 the maximum appeared at around 480 nm. It is well known that decreasing of the NPs size is associated with blue shift of the UV-Vis band. Thus, the reaction carried out in the presence of TEA leads to formation of smaller Ag NPs than that in the presence of MEA. Additionally, when the concentration of CTAB increases bigger Ag NPs are formed, as the peak shifts towards higher wavelengths.

Table 2.
The maximum wavelength determined from the UV-Vis spectra

sample	1	2	3	4	5	6
λ_{max}, nm	510	515	520	480	480	490

In order to shed some light on the effect of the catalysts (MEA and TEA) we compared the spectra of Ag NPs obtained at 30th minute with the same concentration of CTAB (5.10^{-4} M). On fig.3 are shown the UV-vis spectra of the reaction mixtures containing TEA and MEA as catalysts.

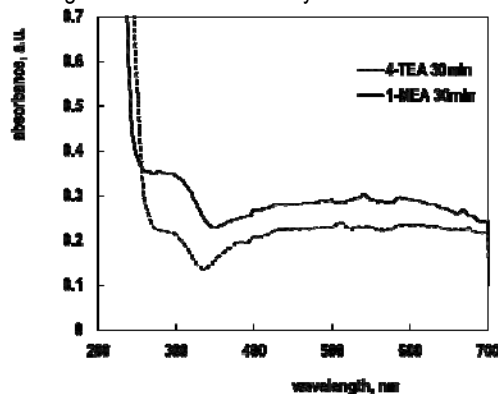


Fig. 3. UV-Vis spectra of AgNPs taken at 30 min from the reaction mixture with different catalyst - TEA and MEA and the same concentration of CTAB - 5.10^{-4} M

As we compare the spectra (Fig. 3) of Ag NPs, formed by MEA and TEA catalysed reaction for the same reaction time, we can observe that the MEA produced NPs are bigger in size (have maximum at higher wavelengths). The structures of both compounds are shown on Fig. 4. MEA is primary amine which generally makes it more reactive than TEA, which is a tertiary amine. Both molecules contain hydroxyl group(s) that are involved in similar chemical reactions.

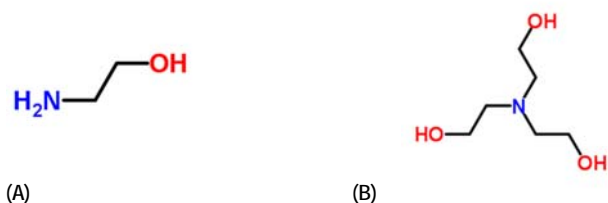


Fig. 4. Chemical structure of the catalysts monoethanolamine MEA (A) and triethanolamine TEA (B)

There is a proposed mechanism for the catalytic action of the amines in the literatures. It involves the addition of proton from the water molecule thus releasing hydroxyl ion. The hydroxyl ions oxidize the OH group in the citrate and free electron is generated in the process. Since the TEA is stronger base than MEA it is supposed to be more active catalyst (Natsuki et al., 2011).

The data from the SEM analysis corresponds well with the data from UV-Vis spectra. The SEM images of Ag NPs are shown on Fig. 5. The average size of the silver nanoparticles is about 200-250 nm.

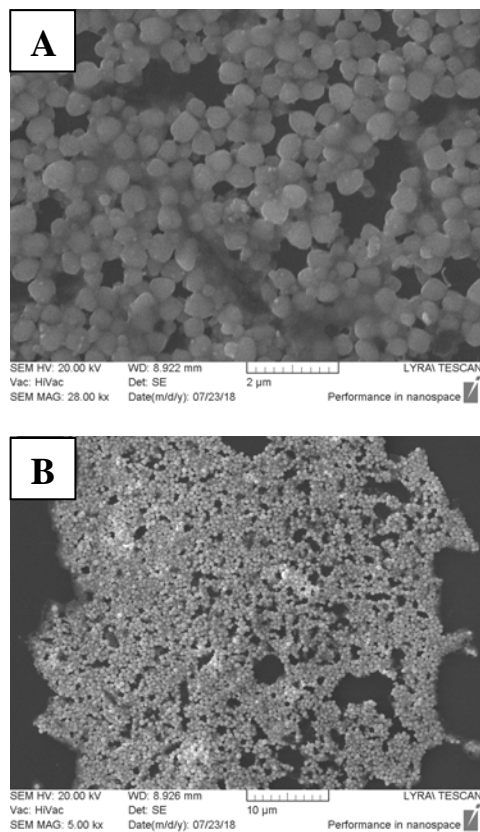


Fig. 5. SEM images at different magnification (A) and (B) of Ag NPs obtained in the presence TEA.

Conclusions

In this study a low temperature synthesis of silver nanoparticles was described and the effect of two amines was investigated. It was demonstrated that both amines (TEA and MEA) can produce Ag NPs at room temperature. This is of great impact since a large scale production of Ag NPs can be achieved only by cost effective methods which don't require heating of the mixture and energy consumption.

The reaction was conducted in water media without using expensive and toxic organic solvents. This method will be suitable for preparation of materials that will be used in water treatment and environmental protection.

The low reaction temperature is crucial for the formation of nanocomposite materials involving the reduction of silver ions adsorbed onto natural zeolite surface. It is necessary to maintain room temperature otherwise we risk desorption of silver ions at elevated temperatures. This method will allow the preparation of the desired nanocomposite material.

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