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# SODIUM CITRATE AND POLYVINYLPYRROLIDONE CAPTURED SILVER NANOPARTICLES TRANSFER TO ORGANIC SOLVENTS

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Silver nanoparticles (NPs) have gathered extensive attention due to their properties – chemical stability, good conductivity, catalytic activity, and antimicrobial activity. This makes NPs suitable for potential applications in the development of new technologies in the field of photonics, electronics, medicine, biochemical sensing, and imaging. Nanoprisms have local surface plasmon resonance starting from visible to near infra-red spectrum, broadening the possibilities of their applications. Ag NPs typically are synthesized in aqueous solution but the handling of NPs often requires their dispersion into nonpolar solvents and their mixing with organic compounds. Thus, nanoparticle transfer to organic media is essential for application in the field of emission enhancement due to NPs – organic semiconductor interaction. A shell changing method for NP tranfer was successfully used with a high transfer rate, but rather low stability. The previously proposed sonochemical method for NP transfer from aqueous to organic polymeric media is extended to different organic solvents. The ultrasonic method is suitable to obtain stable NPs in both organic solvent and organic solvent/organic compound solutions, and it can be stored at ambient conditions for at least several months. Transfer efficiency is suficient and NPs remain stable in an organic solvent like chlorobenzene, anisole, dichloromethane. The method has potential in NPs containing thin film preparation because sonication prevents the agglomeration of clusters.

***Keywords:*** *Changes of shell, chemical synthesis, silver nanoprism, transfer to organic solvents.*

## 1. INTRODUCTION

Metal nanoparticles (NPs) have been a very active research object due to the local surface plasmon resonance (LSPR) effect that can be used in various applications, such as sensors, photovoltaic and Raman spectroscopy [1]–[3]. Surface plasmon enhanced fluorescence (PEF) is an important effect to improve the emission properties of the semiconductor. It offers higher emission efficiency and decreased lifetime via the local electric field enhancement effect of the metal nanoparticles induced by its LSPR [4]–[6]. Initially, the emission enhancement was achieved in inorganic semiconductors, but recently more systems consisting of organic semiconductors were tested. It is driven by the growing potential of organic materials in the light-emitting diodes, photovoltaics and solid-state lasers [7], [8].

Nevertheless, metallic nanoparticle – organic compound systems face several issues. Preparation of the nanoparticles with controlled size, shape and distribution, which is essential for emission enhancement, and transferring of nanoparticles in organic solvent could be considered as the most important. Synthesis of specific size and shape of nanoparticles is important because it determines the spectrum of LSPR, which in turn should match the emission spectrum of an organic dye to get the highest enhancement [9]. Metallic nanoparticles most efficiently can be synthesized in an aqueous solution, but organic materials usually cannot be dissolved in water; therefore, metal nanoparticles should be transferred to the organic solvent, like chloroform or toluene. For this reason, the nanoparticle's shell should be changed to one which can disperse the nanoparticle in the organic solvents.

In the literature, there are several methods to disperse the nanoparticles in organic solvents – NP transfer from aqueous solution by shell changing, centrifugation, solvent evaporation and NP powder redispersion in organics [10]–[13], silver nanoparticles can be synthesised directly in an organic solvent like toluene [14], [15]. Despite so many methods, there are still several challenges associated with NP transfer to organic media, like transfer efficiency, repeatability and stability. NP stability in organics is temporal and NP agglomerates in a short period of time – from a few hours to some days.

In this study, a well-described method of NP synthesis in an aqueous solution was used [11], [16]. Nevertheless, most of the syntheses resulted in another size of NPs than expected from literature. The difference is related to the procedure of adding the reducing agent, so the amount, time interval and frequency of the reducing agent were studied in more detail. Synthesised NPs were transferred to organic solutions by two of the most promising transfer methods – shell changing and transfer during sonification. Shell changing transfer method is described in many papers [12] and it gives the best repeatability of the transfer process, but a chemical synthesis of a new shell is required, which complicates the process. Phase transfer during sonification is simple to use, but repeatability is lower, and some degradation of nanoparticles may occur. Ultrasonic method has been used only for one solvent/polymer system and chemical methods have been mostly applied to nanospheres [13]. The possible nanoprism transfer to different organic solvents and organic solvent/organic compound systems with and without the change of shell by using both methods were extended.

## 2. MATERIALS AND METHODS

All the reagents and solvents were used as received without any further purification: $AgNO_3$ (≥99.8 %, Supelco), Polyvinylpyrrolidone (PVP, $M_w$ ~29000, Sigma Aldrich), sodium citrate (USP), hydrogen peroxide solution (30wt%, Sigma-Aldrich), sodium borohydride (NaBH4, ≥98 %, Sigma-Aldrich), deionized water, ethanol (96 %), dichloromethane (DCM, ≥99.8 %, Sigma-Aldrich), chlorobenzene (≥99.8 %, anhydrous, Sigma-Aldrich), 1,2 Dichlorobenzene (99 % Alfa Aesar), anisole (99.7 %, Sigma-Aldrich), toluene (99.8 %, anhydrous, Sigma-Aldrich), Tris-(8-hydroxyquinoline)aluminum (Alq3, 99.995 %, Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB, 99+ %, ACROS Organics™), 2-Aminoethanethiol (99,9 %, Flourochem), oleic acid (99 %, Alfa Aesar), Hydroxylamine hydrochloride (99+ %, ACROS Organics™), methanol (≥99.9 %).

*Synthesis of Silver Nanoparticles in aqueous solution:* Silver nanoprisms were synthesized by borohydride reduction of $AgNO_3$ [11], [16]. Sodium citrate (9.2 mM 5 ml), PVP (0.2 mM 5 ml), $H_2O_2$ (30 wt%, 60 ml) while stirred with magnetic bar at ambient conditions were added to aqueous solution of AgNO3 (0.19 mM 18 ml). Afterwards, $NaBH_4$ (100mM 70–250 ml) was added to obtain NP solutions with different absorption peak and nanoprism size (Fig. 1). A synthesis outcome dependence on added reductant procedure will be discussed further.

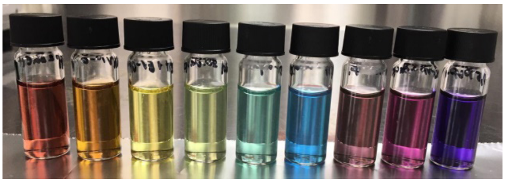

*Fig. 1.* Synthesized Ag NPs aqueous solutions with different nanoprism size.

The absorbance spectra of NPs solutions were measured with spectrophotometer Cary 7000, shape and size of NPs were studied with TEM Fei Technai, Z-potential values and hydrodynamic diameter of NPs were measured by Anton Paar Litesizer™ 500.

## 3. RESULTS AND DISCUSSION

According to the literature, the amount of $NaBH_4$, added to the solution during the synthesis of NPs, defines the size of NP and LSPR wavelength [11], because $NaBH_4$ affects NP shell formation and bounding ability of sodium citrate to Ag NPs [16]. A greater amount of borohydrides promotes citrate bounding to $Ag^0$; thus, NPs are forming faster and the prism size is bigger. If a reduction agent is added in smaller parts, it is possible to obtain smaller nanoprisms.

Nevertheless, during the synthesis it was noticed that the different sizes of NPs could be obtained in a solution by adding the same amount of $NaBH_4$. The difference was in the adding frequency and the period of time between additions of $NaBH_4$. To the best of our knowledge in the literature there is not mentioned the adding procedure impact on size of the NPs. The same amount can be added at once or in several parts. Greater NPs form if $NaBH_4$ solution was added at once. If a small part of $NaBH_4$ is added, silver spherical nanoseeds form in solution, further adding of $NaBH_4$ allows obtaining greater NPs. Thus, the amount and adding frequency of $NaBH_4$ is a crucial factor in the nanoprisms synthesis.

If more than 120 ml $NaBH_4$ solution is added simultaneously, blue NPs solution is obtained, indicating the formation of the greater nanoprisms. Red nanoprism aqueous solution can be obtained by adding 50 ml $NaBH_4$ solution to well stirred $AgNO_3$, sodium citrate, PVP solution immediately after $H_2O_2$ was added. Then 20 ml more $NaBH_4$ solution should be added after 2 min. Another factor affecting synthesis is $NaBH_4$ reaction with water, which can be observed as gas evolution from solution [17]:

$$NaBH_4 + 2\,H_2O \rightarrow NaBO_2 + 4\,H_2.$$

Sodium borohydride solution should be prepared shortly before use and the temperature of the solution should be decreased to inhibit the reaction.

Moreover, external influence also should be considered. Ambient light impacted not only the process of synthesis but also the stability of the NPs. Nanoprism formation delay after reductant addition increased at more intensive ambient light. The period of time between nanoprism formation indicated by solution color changes after reductant addition at the dim light is 2–3 minutes, but at bright light – 30 min, which is mentioned in [11], [12].

Two NPs aqueous solutions were characterised and used for NP transfer to organic media. Optical absorption of selected solvents is shown in Fig. 2. Chosen solvents had red (further referred to as “Red NPs” in the text) and blue (further referred to as “Blue NPs” in the text) colour.

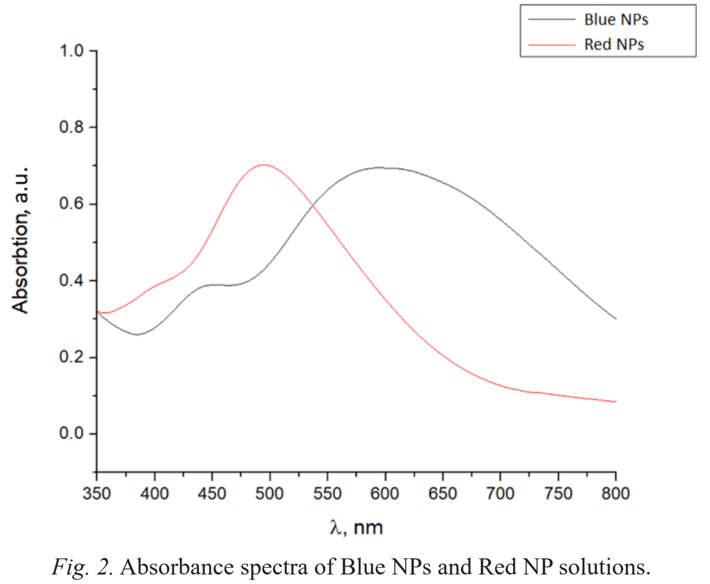


*Fig. 2.* Absorbance spectra of Blue NPs and Red NP solutions.

A hydrodynamic diameter (HD) and Z-potential (ZP) of the investigated NPs are presented in Table 1. The value of ZP for Red NPs solution measured shortly after synthesis is $\xi$ = -10.89 mV indicating instability of the NPs [18]. The stability of Red NPs increases and the ZP value of the solution became $\xi$ -16.51 mV after two weeks stored in the dark. An HD of the NPs increases and FWHM (full width at half maximum) broadens about 2.4 times. The HD of Red NP sample has values in the range from 27.49 to 76.90 nm and the same solutions measured after 14 days had HD values in the range from 26.19 to 146.23 nm. Thus an HD of ~27nm is related to single NP in the solution, but greater HD indicates small cluster formation in the solution. There are no changes in the second peak; thus, there is no NP decomposition. At the same time, a ZP value became more negative, so the stability increased. It could be explained by the formation of more regular NP cluster forms. An HD does not change for freshly synthesized and ultrasound treated NPs stored for 2 weeks, but ultrasound treatment improves ZP values two times. Ultrasound separates NPs from each other and repulsive surface forces become predominant. TEM images are shown in Figs. 3 and 4. Red NPs shortly after synthesis are glued together, what is the reason of the low ZP value. After Red NPs solution sonication for 2h, NPs became very well dispersed and only individual NPs could be seen in the TEM field of view. Ultrasonically separated NPs one from the other and repulsive surface forces overcame attraction surface forces, which held NPs together in agglomerates/clusters. After an additional 1 h in ultrasonic bath degradation of NPs starts and a great number of smaller NPs can be seen, while HD values in the first and second peak do not change.

ZP measurements show good stability of freshly synthesized Blue NPs, but HD values show a reduction of NPs size after 2 weeks. Sonification leaves no impact on Blue NPs ZP, thus, on stability. The ultrasonic treatment leaves no impact on HD of Blue NPs stored for 2 weeks. For all solutions, there are decrement in HD value. Blue NPs shortly after synthesis are well separated and no agglomerates are seen. After sonification of 2 h only individual NPs can be seen on the TEM field of view, similar to the Red NPs. No additional number of smaller NPs was observed after 3 h of sonification; thus, Blue NPs do not require stabilization after synthesis. Still, we suggest 0.5–1 h sonification for Blue NPs, because in the few synthesized aqueous NP solutions slight agglomeration of Blue NPs was observed. There are no spectral changes for most of blue nanoparticles synthesis or they are very seldom, in contrast – Red NP aqueous solution tends to change absorption peak towards the red spectral region and some red solutions change their colour to blue.

**Table 1.** Hydrodynamic Diameter and Z-Potential Values of Red NP and Blue NP Solutions

| Sample | $HD_{1peak}$, nm | FWHM±ΔFWHM, nm | | | $HD_{2peak}$, nm | FWHM±ΔFWHM, nm | | | Z-potential, mV±DmV | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Red NPs | 52.19 | 49.4 | ± | 1.5 | 4.39 | 2.57 | ± | 0.09 | 10.89 | ± | 0.56 |
| Red NPs * | 86.21 | 120.0 | ± | 7.8 | 5.86 | 4.91 | ± | 0.31 | 16.51 | ± | 0.57 |
| Red NPs +2hus* | 52.68 | 48.0 | ± | 1.2 | 5.00 | 3.43 | ± | 0.13 | 18.44 | ± | 0.85 |
| Red NPs +2+1hus* | 54.58 | 53.2 | ± | 2.6 | 5.12 | 3.69 | ± | 0.12 | 20.76 | ± | 1.03 |
| Red NPs in_chlorbenzene | 8.68 | 3.1 | ± | 0.3 | 0.50 | | | | | | |
| Red NPs in DCM | 7.44 | 2.8 | ± | 0.4 | - | | | | | | |
| | | | | | | | | | | | |
| Blue NPs | 52.96 | 54.7 | ± | 3.1 | 2.55 | 3.18 | ± | 0.27 | 21.82 | ± | 1.09 |
| Blue NPs * | 42.33 | 38.3 | ± | 1.1 | 2.62 | 1.89 | ± | 0.08 | 20.53 | ± | 0.99 |
| Blue NPs +2hus* | 41.27 | 39.8 | ± | 2.5 | 2.33 | 2.07 | ± | 0.10 | 23.70 | ± | 1.14 |
| Blue NPs +2+1hus* | 38.34 | 32.3 | ± | 1.6 | 2.33 | 1.76 | ± | 0.08 | 20.65 | ± | 1.02 |
| Blue NPs in DCM | 8.68 | 2.8 | ± | 0.3 | - | | | | | | |
| Blue NPs in anisole | 97.66 | 53.9 | ± | 3.60 | - | | | | | | |

* - measurements performed 14 days after synthesis

TEM data show that NP size in Red and Blue NP solutions fits lognormal distribution (Fig. 5). The mean value of Red NPs is smaller according to the literature data [19], [20]. However, size distribution is affected by a high amount of nanospheres, since nanospheres and nanoprisms have different absorption peaks. A standard deviation of size distribution is rather high indicating a variety of NP size and shape in synthesized solution. Comparison of TEM and HD data shows that thickness of NP shell is roughly 10 nm. Thus such NPs can be used for energy transfer from NPs to surrounding molecules, like luminescent molecules [21], [22] for SRP enhanced luminescence.

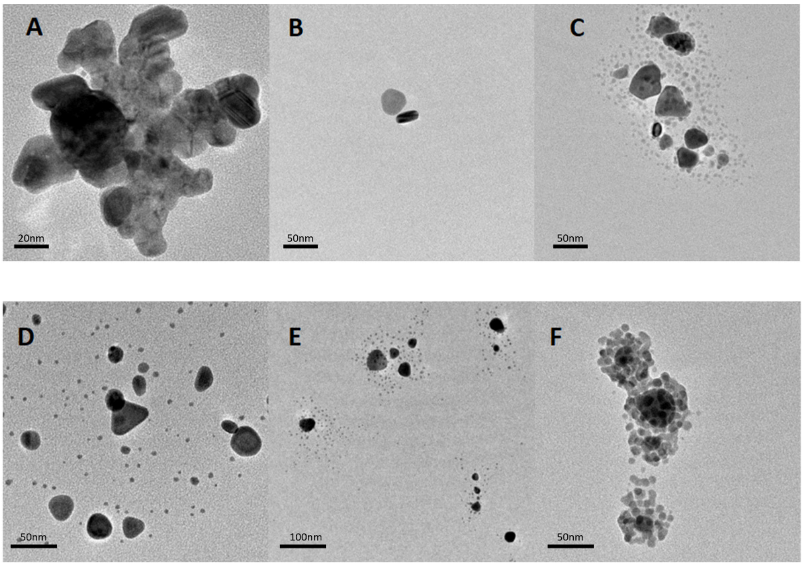


*Fig. 3.* TEM images of Red NPs solution. A – solution shortly after synthesis; B – after 2 h sonification; C – after 2 h+1 h sonification; D – NPs in anisole; E – NPs in chlorobenzene; F – NPs in DCM.

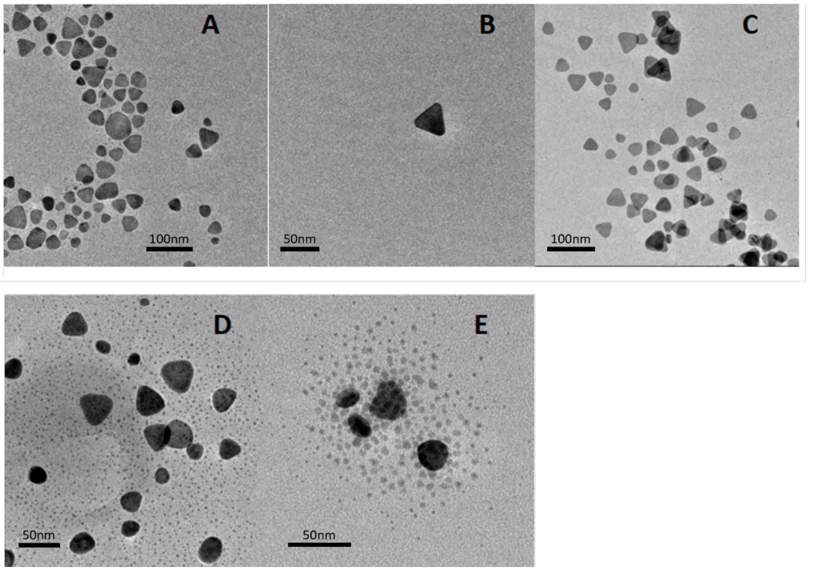


*Fig. 4.* TEM images of Blue NPs solution. A – solution shortly after synthesis; B – after 2 h sonification; C – after 2 h+1 h sonification; D – NPs in chlorobenzene; E – NPs in DCM.

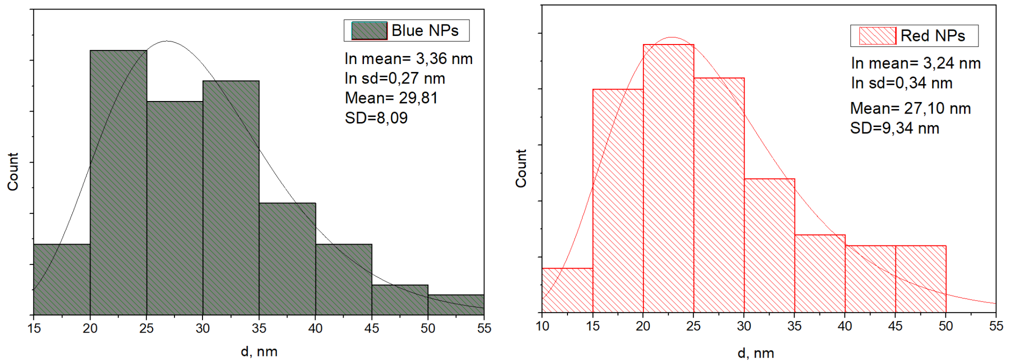


*Fig. 5.* NPs size distribution obtained from TEM data; on the left – Blue NPs, on the right – Red NPs.

*Silver nanoparticles transfer from aqueous to organic solvents:*

In literature, sonochemical method was used to transfer spherical NPs to polymethylmethacrylate (PMMA) dissolved in organic solvent [13]. No other materials were tested, thereby applications of the method were limited. Nevertheless, the transfer efficiency was high. More organic compounds were tested to approve the method. We transferred prismatic NPs to PMMA, polystyrene, polysolfone (Fig. 6).

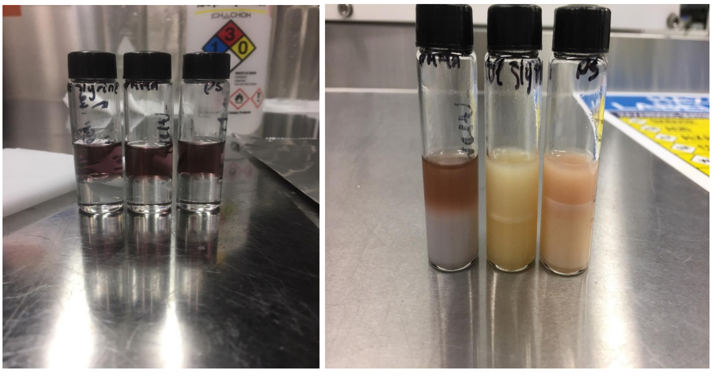

*Fig. 6.* On the left – polymer in DCM and NP aqueous solution; on the right – NP transfer to polymer+DCM solution. Upper layer – aqueous solution, lower layer – NPs –polymer+DCM solution. From left to right – PMMA, polystyrene, polysolfone.

Moreover, NP transfer to organic solvent without organic compound additives would be an even more general approach. In that case, any organic compounds could be dissolved in the metal NP containing solvent afterwards.

The NP transfer to organic solvent was performed. Ethanol of 10ml, which acts as a bounding element, was added to 3ml of synthesized NP aqueous solution. The solution was stirred for ~2–5 minutes, then 3 ml of DCM or another organic solvent (chlorobenzene, anisole) was added. The obtained solution was placed in an ultrasonic bath (37 kHz) for 2–3 h. Aqueous solvent partially or completely discolored indicating the absence of NPs (Fig. 6). After NP transfer process, white precipitate formed that could be complex citrate compounds. Silver is not a component of precipitate, since the same precipitate forms if pure sodium citrate solution in water is used instead of

NPs solution. The precipitate decomposes if solution is stored for 1 week in the dark. A white precipitate forms a segregated layer between the organic and aqueous phase and can have (not always) colour of NP aqueous solution. Figure 6 shows solutions before and after blue NP transfer to organic media. Similar results can be obtained with Red NPs. Precipitate settles between both phases after a few hours. Despite the presented organic solution with visible absorption in visible range after the transfer, the organic phase is colourless when it is separated from aqueous solution and poured to other flask (Fig. 8). Solution with absorption in a visible range is located around the organic phase. The media could be partially transferred NPs, which can be dissolved neither in an aqueous nor in an organic phase. Partially transferred NP is just a suggestion, it is not based on experimental or theoretical results.

NPs in the organic phase are colourless due to the change of the dielectric constant of the solvent [23]. NPs in aqueous solution experience changes before and during ultrasonic treatment: ethanol can change the spectrum before sonication since it acts as a reducing agent in the nanoparticles synthesis [24], [25]. NP solution can change colour during sonification, which indicates the size change or breakup of the nanoprisms. This process can be promoted by sodium citrate reducing properties in an aqueous solution under ultrasonic treatment [26], [27].

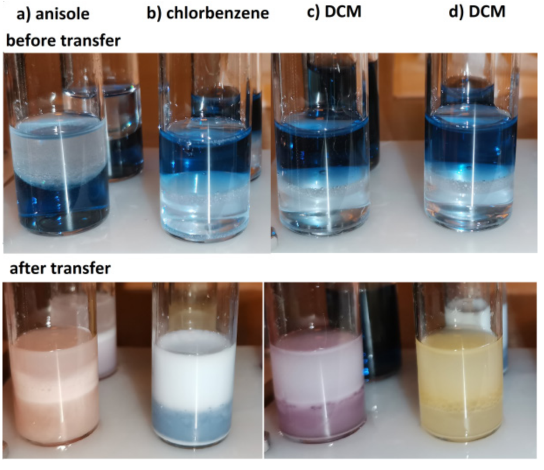


*Fig. 7.* NPs transfer to organic solvents. The upper picture is taken before sonication, bottom – after.

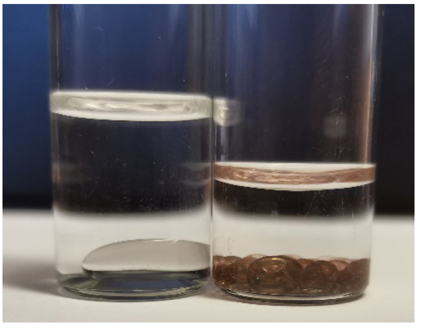

*Fig. 8.* On the left – NPs transfered to DCM before extraction; NPs transfered to DCM after  extraction.

TEM investigation shows a significant number of NPs in organic phase in all used solvents – anisole, DCM and chlorobenzene (Fig. 3 D, E, F and Fig. 4. D and E). In chlorine containing organic solvents nanoparticles fall to pieces. HD measurements do not show a peak at 30–50 nm, only at ~10 nm indicating strong NP decomposition. In anisole, there is a significant amount of small (~10nm) nanoparticles, but the number of nanoprisms overcomes them and no considerable decomposition is observed. HD measurements in anisole were affected by white precipitate and no data could be obtained for red NPs.The ultrasonic method provides stable NPs in organic media but a low transfer rate. Nevertheless, NPs in organic media can be mixed with any organic soluble luminophore, polymer or other material for futher applications.

According to the literature, changing the shell of NPs allows achieving a higher transfer rate [28]. For this reason, synthesized NPs were transferred to organic media (DCM) by changing the shell from sodium citrate + PVP to thiol-termination ligand [16]. Thiol has a great affinity to metallic particles and can easily replace PVP and sodium citrate shells. The synthesis of the ligand is described elsewhere [16]. 1 ml of thiol-termination ligand solution was added to 2 ml of aqueous NP solution. The solution was vigorously stirred, then it was left at room temperature for 1 h. Afterwards, 2 ml of DCM were added, then the solution was stirred until NP transfer to organic media was obvious. After the exchange of shell NPs in organic media solution colour corresponds to the initial aqueous solution. Organic solution became yellow after 12 to 24 hours. TEM investigation showed that prisms sticked together (see Fig. 9), which made changes in SPR wavelength. NPs stability in organic media did not exceed one week, resulting in NP agglomeration and precipitation. The shell that allows dispersing NPs in organic media is oily; thus, the thickness of the shell is large. Litesizer 500 measurements show a very high value of HD exceeding 1 mm, while TEM data do not show considerable changes in NP size. Such NPs can be used for NP introduction into organic media. Despite low stabillity, NPs with changed shell can be successfully used shortly after phase change for nanoparticles containing organic thin film preparation with application in different field, like light emission enhancement.

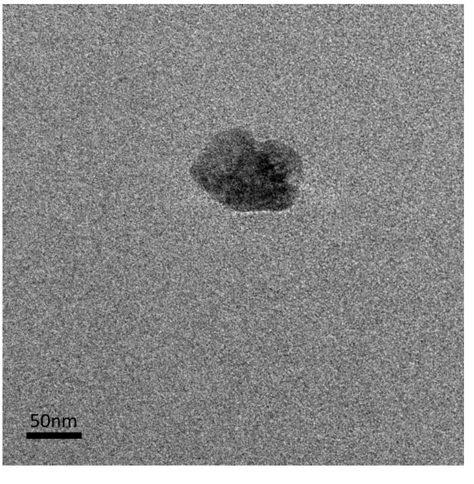


*Fig. 9.* Ag nanoparticle with changed shell.

## 4. CONCLUSION

In this study, silver prismatic nanoparticles with PVP + sodium citrate shell were synthesized. The size of NPs can be changed by varying added amount and frequency of $NaBH_4$. Ultrasound treatment separates NPs in an aqueous solution and increases their stability. Obtained nanoparticles can be transferred to organic media, like DCM, chlorobenzene using the sonochemical method or shell replacing. The second method is more effective for NP transfer to organic media, but it is more difficult. The introduction of NPs in organic media should be done shortly after NP transfer to organic solvent due to the low stability of the NPs. Transfer of NPs to organic media by the ultrasonic method is easier and NPs remain stable for a month at ambient conditions. NPs can be dispersed in a solution volume using an ultrasonic bath. It could be an advantage for organic material containing NP thin film preparation, where there are problems with NP clumping and inhomogeneous dispersion within a volume of a thin film.

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