Morphology and redispersibility of silver nanoparticles prepared by chemical reduction

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T S Lukhmyrina, M S Shestakov, A V Shvidchenko and B A Matveev
Ioffe Institute, Saint Petersburg 194021, Russia

Abstract. In the present work we fabricated and investigated colloidal Ag nanoparticles (NPs). The NPs were synthesized by the chemical reduction method of Ag_2SO_4 using $NaBH_4$ in the presence of different surfactants. Morphological properties of synthesized colloidal Ag-NPs were studied by ultraviolet-visible (UV-vis) spectroscopy and dynamic light scattering (DLS). Average NP size varied in the range from 3 to 15 nm. Redispersibility of dried NPs with various stabilizers was also investigated and recovered that fish oil is effective stabilizer.

1. Introduction

Metal nanoparticles (NPs) demonstrate unique physicochemical properties arising from nanoscale dimension and high surface to volume ratio [1]. This opens path for a wide range of promising NPs applications in the diverse fields of photonics, nanoelectronics, sensing, imaging, information storage and medicine [1,2]. In particular, contact conductive layers formation in microelectronic devices by using sintered NPs is of great interest due to its high conductivity and thermal stability [3]. Low NP melting temperature T_m is crucial in this case. It was shown that due to increased surface-to-volume ratio, the lower the NP size, the lower is T_m [4,5]. Since particle agglomeration causes the system to decrease the NP number and increase its average size, clustering prevention is necessarily, which could be achieved through the adding of surfactant [6].

The exciting application potential of NPs has resulted in a plenty of experimental recipes for their synthesis either in water or in nonpolar organic solvents. The common methods are laser ablation, electron irradiation, biological synthetic and chemical reduction by $NaBH_4$, polyol, tannic acid etc. Among them, chemical methods are the most expedient and cost-effective [7]. In most cases, Ag NPs were stabilized by surfactants, polymeric stabilizers or amphiphilic block copolymers [8]. Despite such a huge variety of synthesis techniques, most of them are experiencing problems with stability and aggregation of NPs, control of morphology, size and size distribution.

In this work, we study the influence of surfactants on the morphological properties of the Ag NPs and the impact of polymeric stabilizers on NP redispersibility.

2. Results and discussion

Silver sulfate (Ag_2SO_4) was used as a precursor. Sodium borohydride ($NaBH_4$) was used as a reducing agent for the reduction of silver ions in relation to Ag atoms. Sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) were used as surfactants, cyclohexane, glycerol and fish oil were used as stabilizers.

In order to investigate the role of the surfactant, Ag_2SO_4 (1.6 mM) and $NaBH_4$ (7 mM) solutions were prepared and for test purposes divided into three equal pairs. Then SDS or AOT were added to one of the solutions as it shown in scheme on figure 1, a. Then in each case $NaBH_4$ solution was added drop by drop into Ag_2SO_4. The NPs formation was confirmed via solution color changing from clear

to yellow and then dark brown [9]. All reactions were carried out at room temperature and maintained for 4 hours. An estimated silver concentration in each solution was 0.2 g per liter.

The colloids were diluted with distilled water to a concentration of 5 mg per liter and exposed to ultrasound treatment. Further, the samples were characterized via ultraviolet-visible (UV-vis) spectroscopy and dynamic light scattering (DLS) (see figure 1). The NPs shape was investigated via optical absorption spectra in the UV and visible ranges that were recorded using "UNICO SpectroQuest UV-2800 spectrophotometer (quartz cuvette; optical path length – 10 mm). The NPs size distribution was obtained via DLS using Zetasizer Nano ZS (Malvern Instruments, UK).

The UV-vis absorption spectrum of each colloid is shown on figure 1, b. The peak position around 390 nm indicates on average NP diameter of 10-15 nm for each colloid [9]. Narrow and symmetric shape of colloid 1 curve indicates on spherical NPs shape with narrow size distribution.

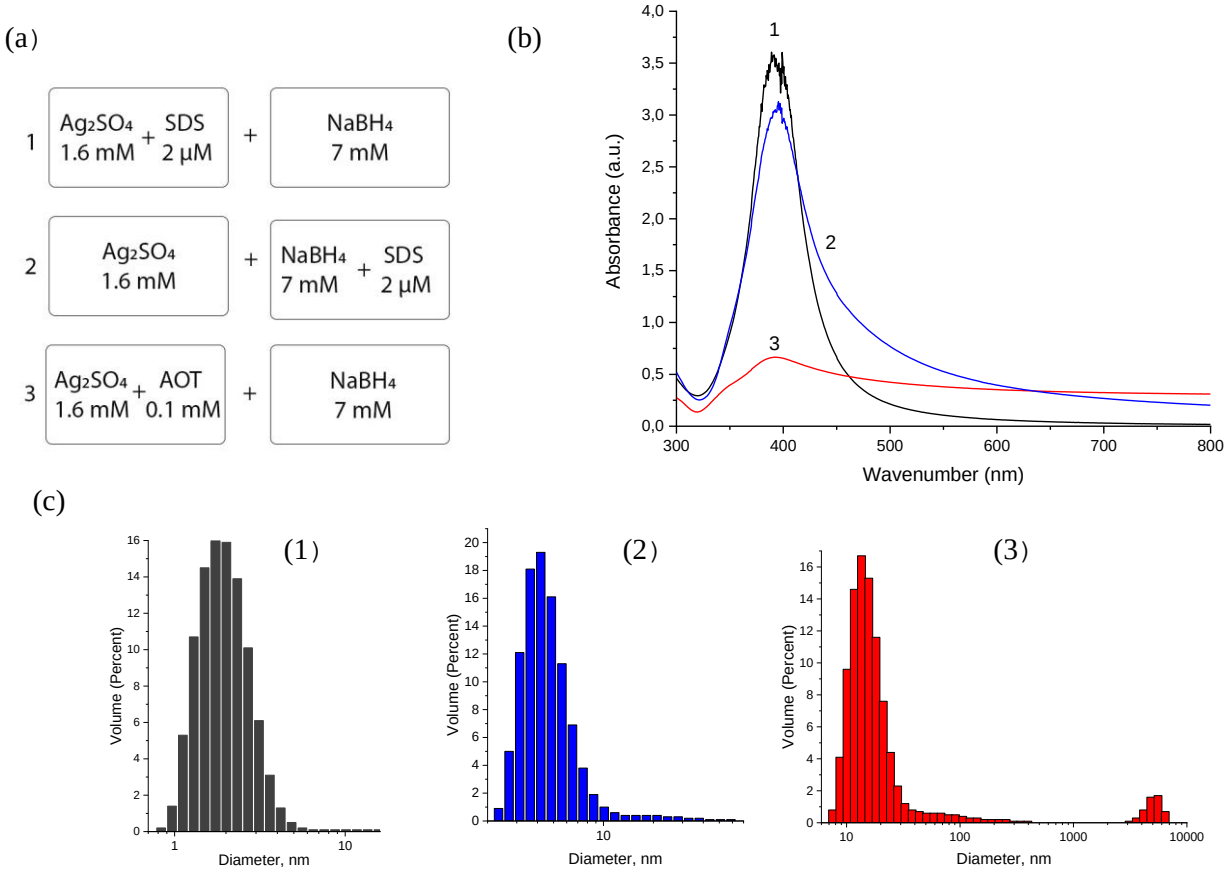

Figure 1. (a) Scheme of reactions, **(b)** The UV-vis absorption spectra of the Ag NPs colloids synthesized in presence of the different surfactants, **(c)** Size distribution of nanoparticles obtained using DLS.

Curves 2 and 3 have highly asymmetric right shoulder and pronounced plateau in long wavelength region (from 500 nm) that indicate on particle agglomeration or aggregation and wide size distribution [9]. Curve 3 has low intensity which commonly indicates on low reaction efficiency.

The size distribution obtained via DLS technique (figure 1 (b)) shows that the average NPs size were 3 and 5 nm in case of colloid 1 and 2 respectively. The distribution is wider in colloid 2 probably because number of SDS molecules in drops are not enough for double molecular layer formation. Average NPs size in colloid 3 turned out to be 15 nm, an additional peak at 3000 nm is clearly associated with aggregation process. This shows that SDS is more efficient surfactant than widely used AOT as it prevents undesirable processes such as agglomeration and aggregation and limits the NPs growth.

It should be noticed that the colloid color was changing in time from dark brown to grey (figure 2) when Ag concentration exceeded 0.5 g per liter in any case. This indicates on NPs agglomeration, that however can be easily removed in SDS stabilized colloids by using ultrasonic mixing.

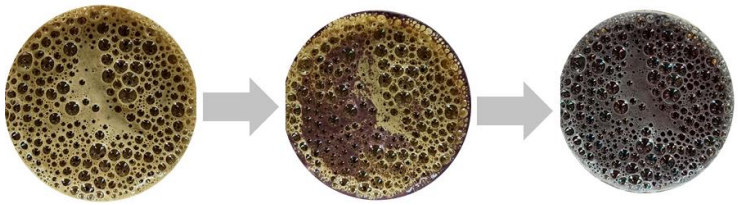

Figure 2. Photos of the colloid with NP concentration more than 0.5 g per liter showing color changing in time

Preparing the conductive paste or ink from NPs require firstly remove them from the mother liquor (for example, by drying) and then redisperse them in the eventual carrier. So, it's important to obtain easily dispersible silver powder. Redispersibility can be improved by adding a stabilizer.

The prepared according to the first recipe [(Ag_2SO_4+SDS)+$NaBH_4$] Ag NP colloid was divided into 4 parts. One of the four stabilizers (none, cyclohexane, glycerol and fish oil) was added in each part. Then all mixtures were dried and dispersed in water.

It was recovered that the first three stabilizers are equal in terms of redispersibility, but the reconstituted colloid with glycerol is more stable in time. The NPs stabilized by fish oil required more continual ultrasonic mixing than the other one but the resulting colloid was extra stable. There is no difference between powders from pure colloid and from mixture with widely used cyclohexane to examine impact of the latest one, infrared absorption spectrum was obtained in figure 3. No cyclohexane peaks were noticed, all peaks corresponded to SDS, that means all cyclohexane evaporated.

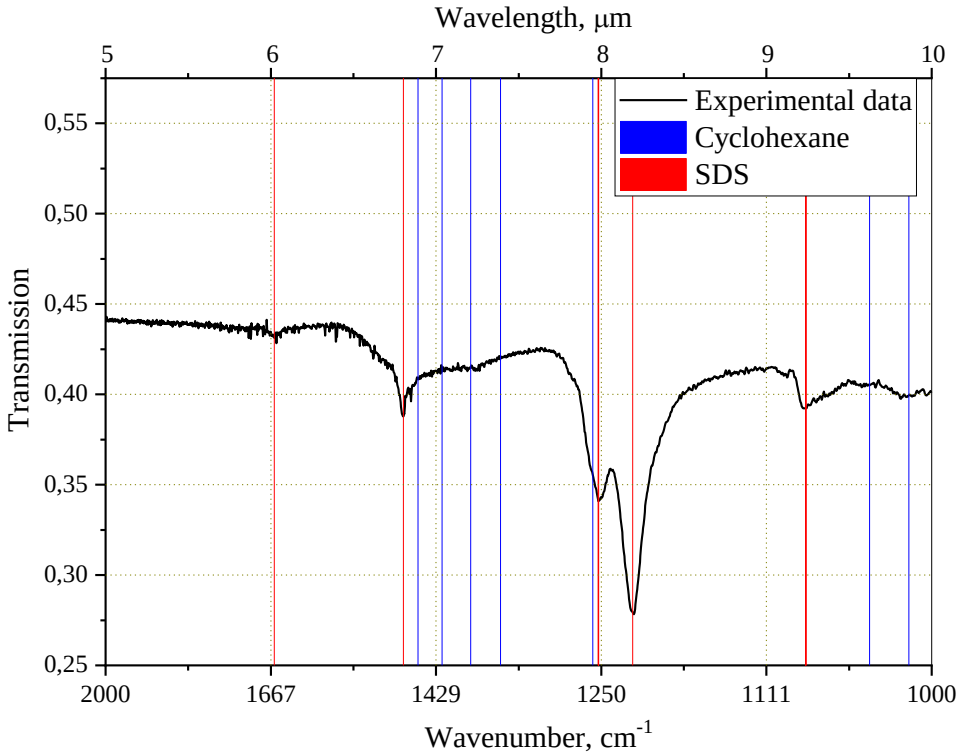

Figure 3. Infrared absorption spectrum of cyclohexane stabilized Ag colloid. Vertical line is peak position for pure cyclohexane **[10]** and SDS **[11]**.

3. Conclusion

The effect of specific surfactants and methods of their application on the morphology of chemically obtained silver NPs was investigated by UV-visible absorption spectra and DLS technique. It was shown that SDS is efficient surfactant in terms of smallest NP size and narrow size distribution providing that it was added to silver salt solution.

Glycerol and fish oil were recognized as the most effective stabilizers, the selection should be made based on the presence of stabilizers in developing ink or pastes.

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