CHEMICAL WET SYNTHESIS AND CHARACTERIZATION OF COPPER-SILVER NANOPARTICLES

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Abstract

AgCu nanoparticles (NPs) of near-eutectic composition were prepared by various route of wet synthesis. Nanoparticles suspended in nonpolar solvents were prepared by solvothermal synthesis from metallo-organic precursors. AgCu colloids in aqueous solution were obtained by hydride reduction of Ag and Cu nitrates under action of different stabilization substances. The different surface stabilizing agents were used. Chemical characterizations of as-synthesized AgCu NPs were done using inductively-coupled plasma-optical emission spectrometry (ICP-OES). The optical properties of nanoparticles were monitored using UV-Vis spectrophotometer. The size of colloid nanoparticles was measured by both dynamic light scattering (DLS) and small angle X-ray scattering (SAXS) method in some extra cases. Zeta potential of AgCu colloids was measured by electrophoretic method. Size and shape of metal core of nanoparticles and morphology of aggregates were investigated by electron microscopy (SEM, TEM and HRTEM), the thermal properties of AgCu nanoparticles were evaluated by differential scanning calorimetry (DSC) and temperature controlled X-ray diffraction method (t-XRD). Mass loss under heating inside inert and air was monitored by thermo gravimetric analysis (TGA). The fraction of organic matter was deduced from ICP-OES analysis and compared to TGA mass loss. The adsorption maxima in UV-Vis region were occurred. Hydrodynamic size of AgCu NPs measured by DLS was compared with the metallic core size obtained by electron microscopy. The morphologies of aggregates were observed as well as the phase transformation (t-XRD) that undergoes at heating to liquid temperature (DSC). The obtained results were compared with respect to perspective use.

Key words: nanoalloy, phase transformation, aggregate, melting.

1. INTRODUCTION

The investigation of nanometer sized particles is intensively pursued because they can have unique properties with respect to their bulk counterparts. Syntheses of metal nanoparticles are currently under view because of their potential application in material science and commercial industries.

The alloy nanoparticles reveal high surface-to-volume ratio. This property affects also phase transformations occurred for these materials. Size effect on the melting temperature of sub micrometer particles is well known for long time [1]. Alloy nanoparticles represent more complex system but theoretical modelling and prediction of NPs phase diagram is also possible [2], [3], [4], [5], [6].

The experimental verification [7], [8], [9], [13] of the theoretical prediction for nanoalloys is great problem because of a need for individual nanoparticle stabilization. The organic compounds can have this function when metal nanoparticles create so called (metal/organic) core-shell system M@O (M - metal, O - organics).

The organic molecule functionalization is highly important and in the case of successfully stabilization control high innovative applications can be possible. Only in that case, for example, the applications of nanoparticles as highly conductive inks [8], in lead free electronics [9], or as catalysis [10] can be possible. Of course the risk of use for environmental treat has to be under view too [11].

AgCu nanoparticles represent the promising system, which can have potential application not only for above mentioned topics.

2. SYNTHESIS

The samples of the Ag-Cu nanoalloy were synthesized in non-aqueous solvents (oleylamine+octadecen) or in methanol and subsequently conversed into water. The weights of metal precursors were such that the compositions of final nanoparticle samples were near eutectic (metal input equivalent to Ag-42 at % Cu in NPs).

Non-aqueous solvent synthesis was done using mixture of solvents 27ml oleylamine+30ml octadecene that was heated in lead-tin solder bath at 230 °C under an inert atmosphere of nitrogen gas. Copper acetylacetonate $Cu(acac)_2$ and silver acetate (resp. silver nitrate) as precursors were dissolved in 3 ml of oleylamine and injecetd into hot solvent mixture. Thus the metal cations of precursors were reduced and the AgCu bimetallic nanoparticles prepared. The product was separated by centrifugation for 20min on a Heraeus Labofuge 400 centrifuge at 6000 rpm and washed by methanol/hexane solution. Nanoparticles were washed three times to remove organic residues and dispersed in hexane using an ultrasonic bath.

The Ag-Cu nanoparticles in water were synthesized by chemical coreduction of silver nitrate and copper (II) nitrate hydrate as metal precursors. The synthesis was done at presence of various nanoparticle surface stabilizer (1,0-phenantroline, polyvinyl alcohol (PVA) or triethylentetraamine). The sodium borohydride as reducing agent was applied in methanol solvent at -45 °C (or at laboratory temperature) under an inert atmosphere of nitrogen. The product was separated by centrifugation for 10 min on a centrifuge at 6000 rpm. The powders were washed by methanol to remove organic-soluble residues by three or more cycles and resuspended in deionized water free of dissolved air gases (Mili-Q deionisation).

3. EXPERIMENTAL RESULTS

Synthetized AgCu nanoparticles were characterized by several methods e.g. inductively coupled plasma-optical emission spectrometry (ICP-OES), UV-Vis spectroscopy, dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM and HRTEM).

The optical properties of dispersion of AgCu nanoparticles (colloids) were monitored by UV-Vis spectroscope Unicam VV4. Maximum of absorption spectrum of AgCu NPs was around 390-420 nm (yellow/brown color colloids).

Some portions of nanoparticles (approx. 2mg) were dried under the vacuum, weighted, dissolved in 2 ml of concentrated nitric acid and diluted by Mili-Q water. Chemical composition of this solution was measured using inductively coupled plasma-optical emission spectrophotometer (ICP-OES) on a Thermo iCAP 6500 Duo. The organic molecules remain on the NP surface (forming AgCu@O) although the samples were repeatedly washed [12]. High portion of organic residues (see **Table 1**) reveal for AgCu@O NPs (see **Fig 1**) prepared in methanol. Structural characterization of synthesised AgCu nanoparticles was carried out by X-ray diffraction (XRD). The electron microscopy of the AgCu NPs prepared in none-polar solvent (see **Fig 2**) reveal single phase face-centered cubic crystalline in some cases, twinned particles, and tend to spinodal decomposition to Ag rich and Cu rich phase.

Table I: Chemical composition of some selected samples of AgCu nanoparticles in dry state prepared in methanol/water.

	total composition			**metal fraction**		
sample	mass% Ag	mass% Cu	organic residues	mass% Ag	mass% Cu	surfactant
OZ_AgCu_4	43.9	7.5	48.6	85.4	14.6	phenanthroline
OZ_AgCu_11	3.5	1.0	95.6	79.	21.0	phenanthroline
OZ_AgCu_9	4.4	2.0	93.7	68.8	31.2	PVA
OZ_AgCu_10	10.8	7.0	82.2	60.8	39.2	PVA

Particle size and distribution were characterised using DLS method on Zetasizer Nano ZS ZEN 3500 DLS instrument at the angle of 173° in a colloidal solution at 25°C, small-angle X-ray scattering (SAXS Rigaku BioSAXS-1000 instrument), and by methods of electron microscopy. The AgCu metal cores of the prepared NPs were mostly in range 5-50nm. Some samples form aggregates with hundreds nm in size and covered by organic residual envelope (see **Fig 1**).

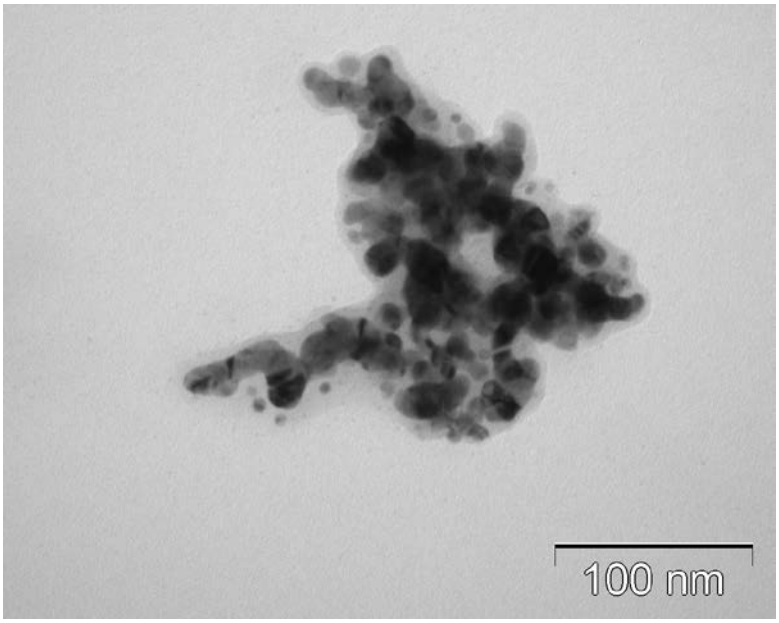

Fig 1: Representative of AgCu NPs aggregate (sample OZ_AgCu_4, effective hydrodynamic size 200nm, average core size 28nm, TEM).

Transmission electron microscopy (TEM) observations were carried out on a Philips CM12 STEM transmission electron microscope operated at 120 kV and a high resolution TEM (HRTEM) JEOL JEM2010 FEG operated at 200 kV with a point resolution of 2.3 Å. Both instruments were equipped with an energy dispersive X-ray (EDX) detector. To prepare samples for TEM, a drop of dilute Ag-Cu colloid suspension was placed on a carbon-coated grid and allowed to dry by evaporation at ambient temperature. The HRTEM and XRD (**Fig 3**) results show that AgCu nanoparticles prepared in none-polar solvent have substitutional f.c.c. crystal lattice. These nanoparticles decompose to copper and silver rich particles during heating and they consequently grow to microparticles (see **Fig 4**).

Thermal properties of AgCu nanoparticles were investigated by differential scanning calorimeter (DSC). The AgCu NPs samples (about 10 mg) were measured in Y_2O_3-coated alumina crucibles covered by a lid. Netzsch STA 409 CD/3/403/5/G instrument was used. Operated conditions were inert atmosphere of flowing (70 cm^3 ml^{-1}) argon Ar6N with the heating rate of 10°C min^{-1} from room temperature to usually 1000 °C. Oxygen free atmosphere was improved at higher temperatures by metallic zirconium trap located in the hot zone of the calorimeter. The bulk spherical drops were occurred after DSC measurement (**Fig 5**).

The phase diagram respecting size of the AgCu NPs was calculated by the CALPHAD method considering surface energy of the bulk Ag-Cu alloy in liquid and solid (fcc) states [6]. The predicted eutectic melting point depression was not experimentally observed when the nanoparticles were heated above the melting point by DSC method. The samples melt at eutectic temperature exactly as bulk AgCu alloy. The spherical microparticles consisting of the eutectic copper and silver rich phases (**Fig 5**) were observed after melting and cooling to ambient laboratory temperature by SEM.

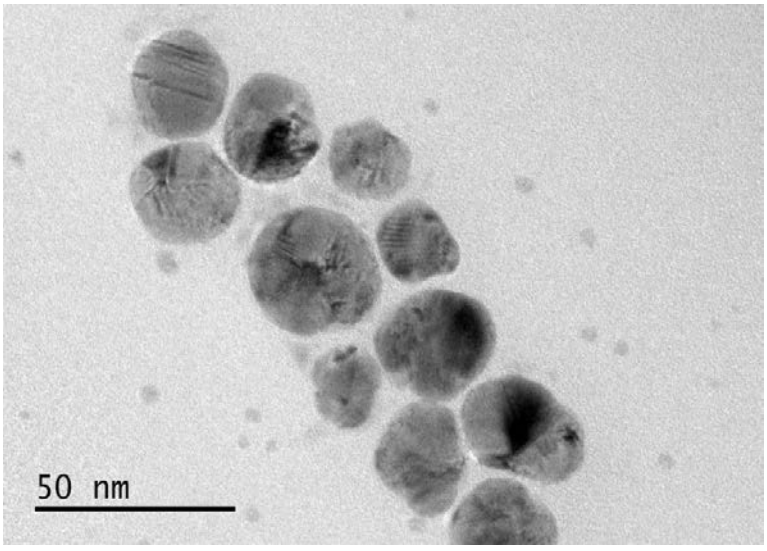

Fig 2: AgCu Nps (sample AgCu2, none-polar solvent synthesis**,** before t-XRD) representing starting state of the sample (TEM).

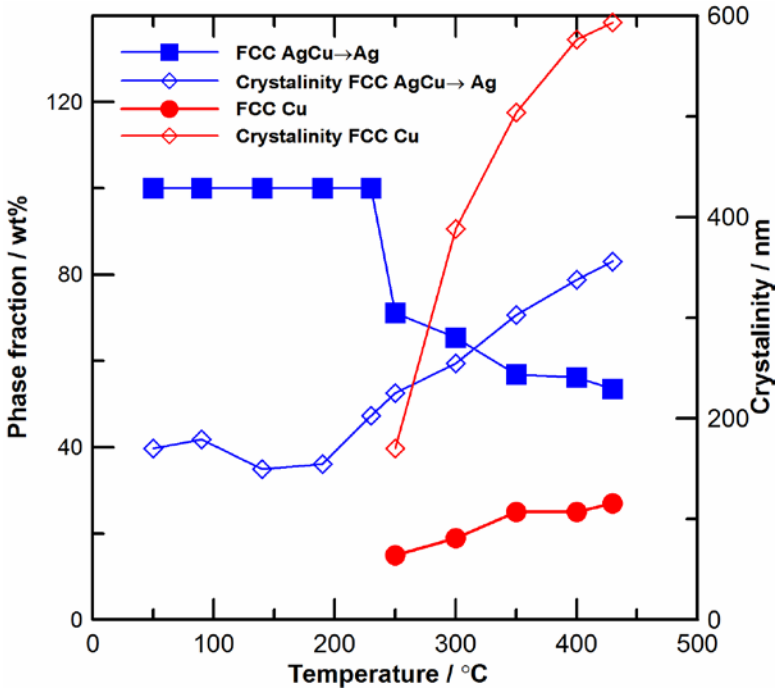

Fig 3: Temperature dependence of phase ratios of FCC copper rich phase (FCC_Cu), FCC silver rich phase (FCC_Ag), and crystallinity (calculated from Sherrer equation).

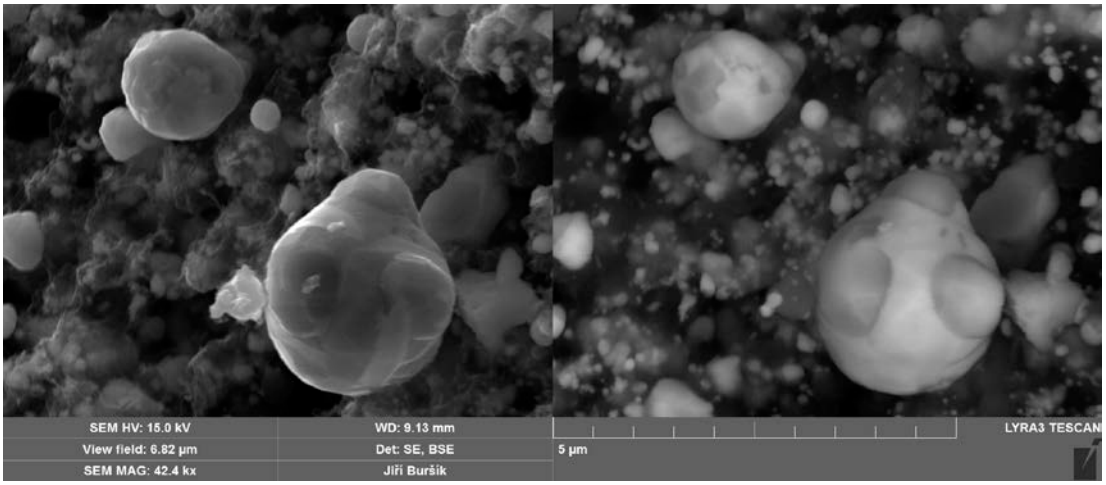

Fig 4: Microstructure (SEM) of the AgCu NPs (sample AgCu47) after heating till 350°C and consequent cooling to room temperature (left and right – different detector).

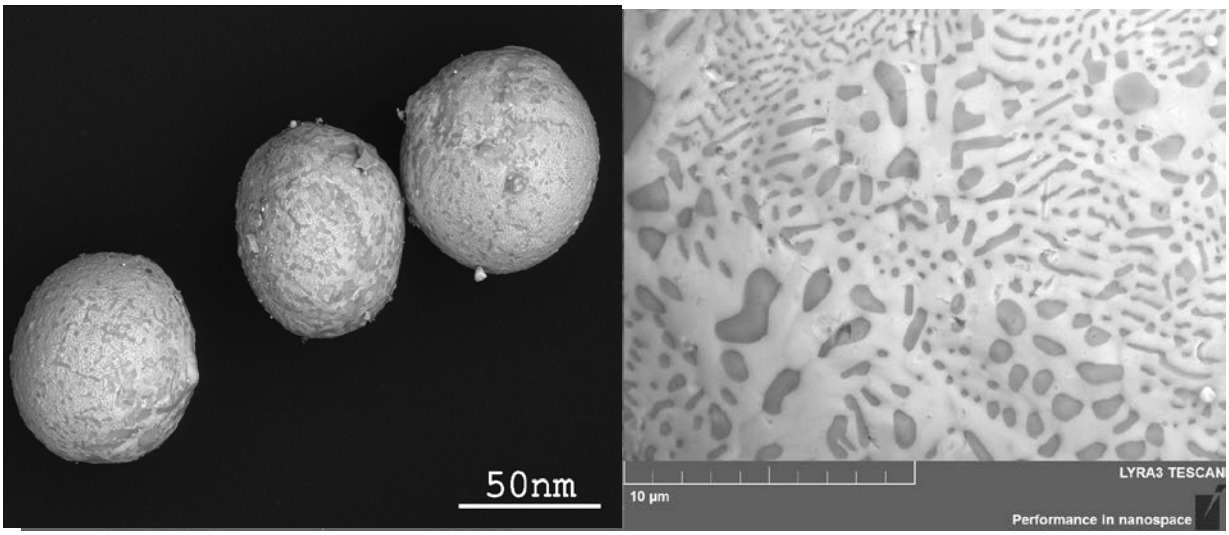

Fig 5: SEM images of AgCu microparticles after DSC measurement. Overview of spherical particles (right) and detail with eutectic microstructure (left).

4. DISCUSSION

The reason for the phenomenon observed can be the metastable state of the nanoparticles but there are also other unknown effects at the nano-scale level that hinder the Cu- and Ag-rich phase separation at low temperatures. The open question is also if the general equilibrium thermodynamics can be used to describe the AgCu NPs system under view.

The electron microscopy of the AgCu NPs prepared in none-polar solvent (see **Fig 2**) reveal single phase face-cantered cubic crystalline (frequently twinned) as occurred also in [6].

5. CONCLUSION

AgCu nanoparticles were prepared by solvothermal synthesis and using sodium borohydride as reducing agent in polar solvent. Colloidal solutions of the nanoparticles in both non-polar solvent and water were

characterized by various methods. The experimentally occurred thermal behaviour of the AgCu NPs was compared with the predicted phase diagram of the AgCu nanoalloy. The aqueous AgCu colloid nanoparticles were used as the starting material for the tests of toxicity.

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