

ELECTROCHEMICAL SYNTHESIS, CHARACTERIZATION AND APPLICATION OF MATRIXLESS METAL NANOPARTICLES

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Abstract

In this work, the development of the novel route of synthesis of metal nanoparticles in aqueous systems (referred to as matrixless nanoparticles) is presented. Nanoparticles are generated in the process of electro-dissolution of metal electrodes in deionized water without any additives apart from dissolved atmospheric carbon dioxide which acts as a source of counterions for generated metal cations. With this approach we were able to obtain silver, copper and gold nanoparticles of a high stability (reaching several years in the case of AgNPs). The synthesis conditions such as duration (from several hours to days) and applied potential were strongly dependent on the chosen metal. Other factors crucial for the synthesis efficiency were: lower temperature ca. 10 – 15 °C due to higher CO₂ solubility and presence of the atmospheric molecular oxygen facilitating the initialization of the electrochemical dissolution of metal electrodes. Characterization of obtained samples was conducted with the use of Transmission Electron Spectroscopy, Single Particle Inductively Coupled Plasma Mass Spectrometry and Dynamic Light Scattering method.

Keywords: Metal nanoparticles, electrosynthesis, zeta potential, nanoparticle size

1. INTRODUCTION

Nanomaterials, such as nanoparticles (NPs), have accompanied humankind for thousands of years. The first known usage of nanoparticles was the addition of gold compounds into the glass matrix resulting in AuNPs formation. [1, 2] Nowadays nanotechnology is a crucial research field for all areas of humans' activity, starting from medicine and cosmetology [3-5] through electronics and photonics [6] to catalysis e.g. in chemicals production, environment protection or oil industry [7, 8]. There are many ways of preparing such systems. The most common ones include: chemical reduction, solvothermal methods, laser ablation or ball milling [9]. However, major challenge in nanoparticles synthesis lies in the ability to control their size distribution and provide their long-lasting stability. The size of synthesized nanomaterials strongly depends on the conditions of the synthesis and can be optimized. Furthermore, in order to prevent the aggregation process, one must introduce stabilizers (e.g. citrates, thiols, polymers [10-12]) at the beginning of the synthesis. However, their presence may be an obstacle for further usage. For instance, because of the toxicity of some stabilizing compounds covering the metallic surface or their interaction with mammalian cells, application of such particles in medicine or cosmetology would be limited [13, 14]. In general, any additional compound in the mixture affects its characteristics, hence the organic stabilizers modify the properties of metallic nanoparticles as well [15, 16].

To address this problem, during our research, the synthesis of matrixless (i.e. without any external additives) silver and copper nanoparticles was examined and optimized. It was also found that the same approach can be used to obtain gold and platinum nanoparticles, although the optimization step is still to be carried out. Prepared samples of nanoparticles were characterized with Transmission Electron Microscopy (TEM), Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS) and Dynamic Light Scattering (DLS) techniques. Moreover, our colloidal samples can be successfully applied as a growth biostimulants for lettuce (*Lactuca sativa* L. var. capitata), but the in-depth description is out of scope of this paper.

2. MATERIALS AND METHODS

2.1 Synthesis of Matrixless Metal Nanoparticles

The only materials used for the synthesis of Matrixless Metal Nanoparticles (MeNPs) were: silver, copper or gold wires (2 mm in diameter, 99.99%, MBB Szklo, Poland), glassy carbon (Sigma-Aldrich) and ultrapure water (Milli-Q System, water conductivity at 25 °C: 0.055 $\mu\text{S}/\text{cm}$). For each metal, the synthesis of nanoparticles was conducted in a two-electrode system using an AutoLab potentiostat (PGSTAT 128N) and controlled via Nova 2.1 software. 10 cm of a metal wire was used as an anode and a glassy-carbon electrode was used as a cathode. Each time, the water-jacketed beaker was filled with 100 mL of ultrapure water and the temperature was set to the desired value (between 15 and 25 °C). The temperature in the cell was controlled using a refrigerated circulator (Polystat, Cole Parmer, Vernon Hills, IL, USA). [17]

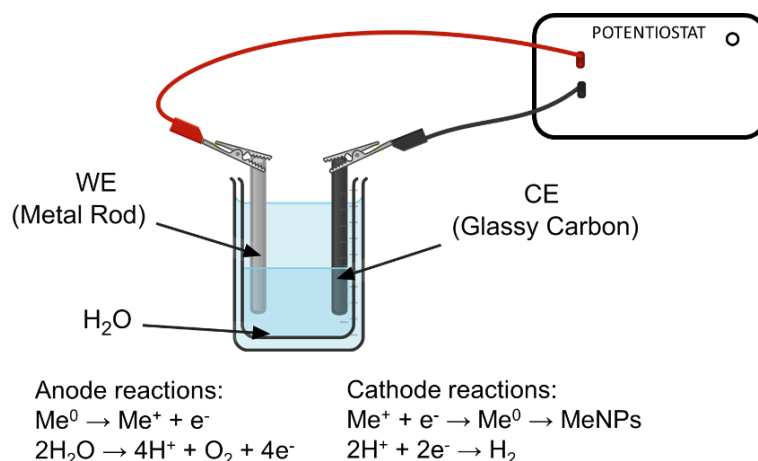


Figure 1 Scheme of electrochemical setup used for synthesis of matrixless metal nanoparticles. Working electrode and Counter electrode are denoted as WE and CE respectively.

In each case, the metal electrode immersed in ultrapure water was electrochemically dissolved under chronoamperometric conditions (the pulse potential between 3.5 and 10 V, duration from 8 to 24 h depending on the metal). Aforementioned conditions (different for each examined metal nanoparticles system) of temperature and potential were selected as the most optimal based on previous experiments carried out in our group. The electrochemically active area of the cathode was kept constant for all experiments and was equal to $11 \pm 0.1 \text{ cm}^2$.

2.2 Characterization of Matrixless Metal Nanoparticles

In order to characterize synthesized metal (Ag, Cu, Au) nanoparticles, the Transmission Electron Microscope (TEM, Libra 120 (Zeiss), Jena, Germany), Single-Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS, NexION 5000, PerkinElmer, US) and Dynamic Light Scattering (DLS, Zetasizer Nano, Malvern Instruments, Malvern, UK) techniques were used.

DLS measurements were carried out at room temperature to determine the hydrodynamic diameter of colloidal MeNPs. Along with the size measurements, the zetasizer apparatus was used to determine a zeta potential of the nanoparticles present in samples which can be associated with the stability of prepared colloidal systems.

For each metal, Transmission Electron Microscopy was used to visualize the size and shape of synthesized metal nanoparticles. As a reference method, SP-ICP-MS was applied to specify the average size of the nanoparticles present in synthesized systems. This method allowed determining the concentration of nanoparticles, as well. Furthermore, in the case of silver nanoparticles, the stability of obtained samples was tested by measuring the AgNPs sizes using TEM and DLS techniques one week and 3 years after the synthesis.

3. RESULTS AND DISCUSSION

First of all it is worth discussing what is the chemical composition of the colloidal nanoparticles samples obtained in our electrochemical setup. Since the process is conducted in ultrapure water, the only ions which can appear in the system are metal cations from anode material, H^+ , OH^- and probably HCO_3^- due to atmospheric carbon dioxide dissolution. As a result, appearing nanoparticles are stabilized by electrostatic repulsion between ions covering their surface. Another question is the composition of NPs themselves. According to experiments performed on samples of silver nanoparticles with Energy Dispersive Spectroscopy [17], obtained particles were mainly composed of metallic cores and only part of them was made of silver(I) oxide rather than reduced metal. Based on this observation, we supposed that remaining systems contained mainly metallic nanoparticles as well, especially those with gold and platinum. However, this issue will be verified in future measurements.

3.1 Determination of nanoparticles' size

Based on TEM images (**Figure 2**) one can see that the nanoparticles obtained from the electrosynthesis are spherical and, in the case of silver nanoparticles, polydisperse. In **Figure 2A**, two main fractions of AgNPs are visible: one of diameter around 20 nm and the other one of 5 nm. In the case of copper nanoparticles, the sample was quite monodisperse and the observed diameter of CuNPs was ca. 3 nm. Based on Figure 2C, one can suppose that a concentration of gold nanoparticles was lower in comparison to AgNPs and CuNPs samples, which can be explained by lower reactivity of corresponding metals used as anodes. The diameters of AuNPs in examined samples were similar and equal to ca. 20 nm.

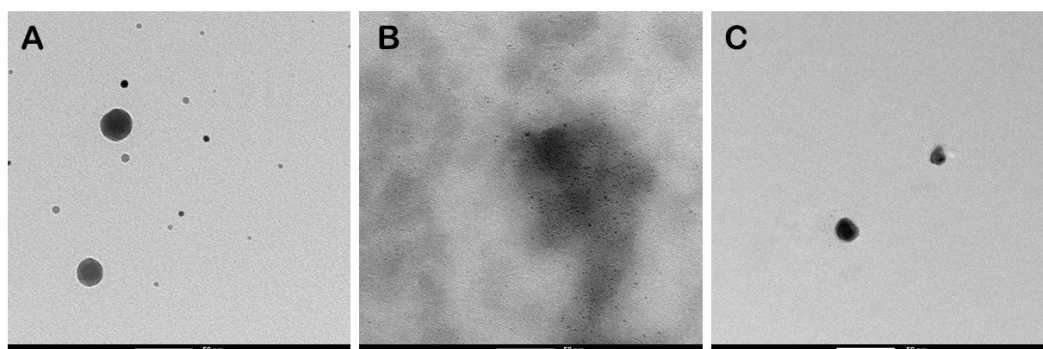


Figure 2 TEM images of matrixless silver (A), copper (B) and gold (C) colloidal nanoparticle systems. The scale shown on images (white line) is 50 nm.

DLS measurements resulted in bigger values of nanoparticles size which is caused by hydrodynamic diameter given by the measurement itself. The Pdl (polydispersive index) was the highest in the case of silver nanoparticles and equal to 0.3. In the case of CuNPs and AuNPs the Pdl values was between 0.1 and 0.2 which meant the low polydispersity of prepared systems.

SP-ICP-MS measurements also did not show the same mean sizes as those determined from TEM images. It was caused by the fact that the ICP-MS method showed the global tendencies within the system, while the TEM depicted only a small part of the sample. On the other hand, because of the relatively high concentration of metal cations present in all of the matrixless samples, nanoparticles of smaller sizes are treated by the SP-ICP-MS as an ionic background. The threshold of detected nanoparticles varies depending on metal present in the sample. In the case of AgNPs the minimal diameter, which could have been observed, was ca. 20 nm while for other metals it was from 10 to 15 nm.

Comparison of average nanoparticles sizes determined with all three techniques applied during the research is presented in **Table 1**.

Table 1 Comparison of the averaged nanoparticles' size (r) in selected samples of aqueous colloidal systems. Characterization performed with the DLS, TEM and SP-ICP-MS techniques.

Metal Nanoparticle System	Conditions of the synthesis	r_{DLS} (nm)	r_{TEM}^* (nm)	$r_{SP-ICP-MS}$ (nm)
Ag	E = 3.5 V, t = 8 h, T = 15 °C	31.5 ± 2.3	ca. 20 and 5	40.2 ± 1.0
Cu	E = 4 V, t = 10 h, T = 15 °C	78.7 ± 1.3	ca. 3	56.4 ± 0.34
Au	E = 10 V, t = 24 h, T = 25 °C	69.5 ± 11	ca. 20 and 13	24.5 ± 0.67

*the most frequently observed size

3.2 Determination of nanoparticles' concentration

Among all available analytical techniques, SP-ICP-MS is the only one that enables to determine nanoparticles' concentration in bulk sample directly during the analysis. However, in some cases it can be problematic to determine the nanoparticles' concentration with a very high accuracy. As it was mentioned in the section concerning MeNPs sizes, if the concentration of cations of a corresponding metal (ionic background) is high, it is more likely for the smallest NPs to be included into the background together with free cations. As a result, since in some cases we obtained nanoparticles of sizes in the "problematic" region (e.g. below 10 nm) the resulting concentrations determined for these samples were probably underestimated. The typical concentrations of nanoparticles observed in the matrixless systems prepared by electrosynthesis described in the section 2.1 are presented in **Table 2**.

Table 2 Comparison of concentration of nanoparticles (c_{NPs}) and cationic background (c_{Me^+}) in matrixless MeNPs (Me = Ag, Au, Cu) samples determined with SP-ICP-MS measurements.

Metal Nanoparticle System	Conditions of the synthesis	c_{NPs} (particles/L)	c_{Me^+} (mg/L)
Ag	E = 3.5 V, t = 8 h, T = 15 °C	$(1.284 \pm 0.047) \times 10^9$	8.49 ± 0.12
Cu	E = 4 V, t = 10 h, T = 15 °C	$(1.171 \pm 0.014) \times 10^9$	$<1 \times 10^{-3}$
Au	E = 10 V, t = 24 h, T = 25 °C	$(4.83 \pm 0.53) \times 10^5$	$(7.83 \pm 0.32) \times 10^{-3}$

Based on the information depicted in **Table 2**, one can see that the synthesis of AgNPs and CuNPs resulted in the samples of fairly high concentration. In the case of AuNPs, the concentration is lower but still satisfactory, given that there are no external reductors and stabilizing agents used.

3.3 Stability of synthesized systems

One way to estimate the stability of metal nanoparticles' systems is to determine the zeta potential of the NPs. The values of zeta potential obtained for selected samples of silver, copper and gold nanoparticles are gathered in **Table 3**.

Table 3 Average zeta potential of matrixless MeNPs (Me = Ag, Au, Cu) samples

Metal Nanoparticle System	Average zeta potential (mV)
Ag	-31.1 ± 3.1
Cu	-31.6 ± 1.3
Au	-23.2 ± 2.1

Since colloidal systems of AgNPs were first to be optimized during the research, this system was chosen for long-period size tests as well. The DLS and TEM measurements were performed 3 years after the synthesis had been conducted. **Figure 3** shows the evolution of the size of silver nanoparticles in the sample prepared under the most optimal synthesis conditions (i.e. temperature equal to 15 °C, time = 8 h, applied potential = 3.5V).

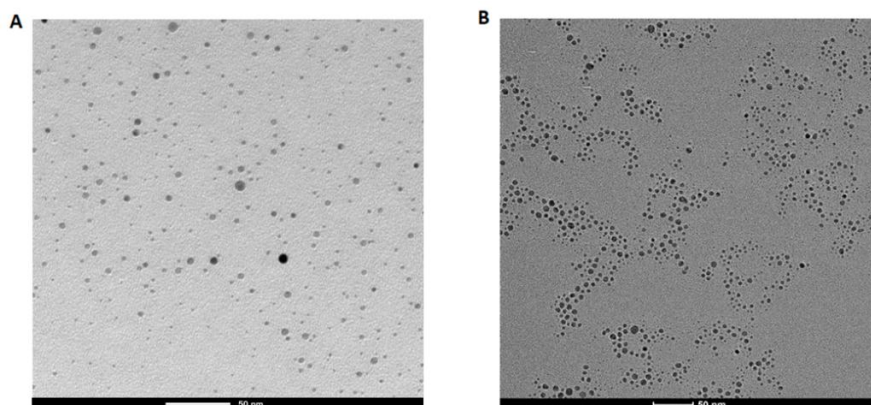


Figure 3 TEM images of silver nanoparticles 1 week after synthesis (A) and 3 years after the synthesis (B). The scale shown on images (white line) is 50 nm.

According to results of the DLS size measurements, the nanoparticles' diameter in the same sample was equal to (65.0 ± 2.9) and (57.7 ± 1.2) nm one week and 3 years after the synthesis, respectively. The size of the AgNPs present in the sample only slightly changed even after 3 years which can be considered as a very satisfying result indicating a surprising stability of nanoparticles without any organic stabilizers. TEM images have also showed comparable sizes of AgNPs both in the freshly-made sample and the 3-year old sample. The in-depth time-dependent size measurements for other metallic nanoparticles are still under investigation.

4. CONCLUSION

In this work we focused on preparation and characterization of metal nanoparticles (Ag, Au, Cu) which did not require any additives such as reductors and external stabilizing agents. In order to obtain such systems the chronoamperometric conditions were applied using two-electrode systems. This approach enabled to obtain colloidal nanoparticle samples dispersed in water. The nanoparticles were characterized by DLS, SP-ICP-MS and TEM techniques which enabled to determine the estimated size, shape, concentration of both nanoparticles and the ionic background as well as zeta potential. Relatively high values of zeta potential

obtained for silver, copper, and gold nanoparticles, suggest good stability of prepared systems which was confirmed by TEM and DLS measurements repeated after 3 years from the time of synthesis in the case of AgNPs. Exceptional stability and lack of organic compounds opens up new possibilities of application of prepared colloidal systems, e.g. in agriculture or catalysis.

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