Polymer-stabilized copper nanoparticles and their application for catalytic water purification

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Abstract. A study was conducted on the synthesis of copper nanoparticles via chemical reduction of copper sulfate with tert-butylamine borane in aqueous solutions using various polymer stabilizers: polyvinylpyrrolidone (PVP) and Pluronics (F-68, F-127). In situ UV–visible spectroscopy revealed that the polymer stabilizer's nature critically affects the kinetics of nanoparticle formation, as well as their stability and optical properties. It was shown that systems with PVP exhibit gradual formation of stable nanoparticles with characteristic plasmon absorption peaks at 360–370 nm and 580–610 nm, whereas the use of Pluronics leads to rapid aggregation and sedimentation of larger particles. The synthesized copper nanoparticles are of significant interest for the development of advanced catalytic systems for water purification from persistent organic pollutants, including photocatalytic degradation under visible light and catalytic reduction of toxic anions.

1 Introduction

Modern environmental problems and challenges associated with high anthropogenic pressure on the aquatic environment require the development of new effective approaches to wastewater treatment. Removal of persistent organic pollutants (pesticides, pharmaceuticals, industrial dyes) and toxic anions is one of the most important tasks for controlling pollution of aquatic ecosystems. Nanoscale materials, due to their unique physico-chemical properties, open up new possibilities for solving these problems. Copper-containing nanoparticles demonstrate a particular potential for use in this field owing to their prominent catalytic activity, their ability to generate reactive oxygen species, and their economic availability.

A key aspect of the practical application of copper-containing nanoparticles in water purification technologies is the development of controlled synthesis methods that ensure the production of particles resistant to oxidation and aggregation with preset characteristics. The chemical reduction method in aqueous solutions in the presence of polymer stabilizers allows the preparation of nanoparticles with controlled size and morphology. In this study, the synthesis of copper-containing nanoparticles was carried out by reducing copper sulfate with tert-butylamine borane in the presence of polyvinylpyrrolidone (PVP) and Pluronics (F-68, F-127). Special attention was given to the investigation of nanoparticle formation kinetics

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using in situ UV–visible spectroscopy, which enabled the identification of key stages in the process—from the reduction of copper ions to nanoparticle nucleation and growth.

The nanoparticles obtained have the potential to be used to develop environmentally friendly water purification technologies, including photocatalytic decomposition of organic pollutants under the influence of visible light and catalytic reduction of toxic anions. This research contributes to solving urgent problems of environmental protection and pollution control, as well as to the development of sustainable water treatment technologies.

2 Materials and methods

Copper nanoparticles were obtained using the chemical reduction method described previously [1].

The reaction system consisted of aqueous solutions of a copper salt ($CuSO_4$), a polymer stabilizer, and a reducing agent. The polymer stabilizers employed were polyvinylpyrrolidone (PVP) with a molecular weight of 3.6 ´ 10^4, as well as Pluronics F-68 and F-127. Tert-butylamine borane (TBAB) was used as the reducing agent.

The final concentrations of the starting components in the reaction systems are given in Table 1. All reagents used in the synthesis were applied without further purification. Distilled water was used to prepare the solutions. The synthesis was carried out under normal conditions.

Table 1. Concentrations of the starting components in the reaction system.

№	Polymer	Polymer concentration, base-mol/L	$CuSO_4$ concentration, mol/L	Reduction agent concentration, mol/L
1	PVP	0.02	0.0025	0.0075
2	PVP	0.005	0.0025	0.0075
3	F-68	0.02	0.01	0.03
4	F-127	0.02	0.01	0.03

The electronic spectra were recorded in situ during the synthesis using a PE-5400VI spectrophotometer (Ecroschem, Russia). Selected sample aliquots were placed in a glass cuvette with an optical path length of 10 mm. Absorption spectra were analyzed using SC5400 software (Ecroschem, Russia) and MS Excel (Microsoft, USA).

3 Results and discussion

3.1 Characteristics of the synthesized products

3.1.1 Visual characteristics of the synthesized products

During the synthesis of nanoparticles, 10–15 minutes after the addition of the reducing agent, the color of the samples turned yellow. Samples with PVP changed color a few minutes earlier than those with Pluronics. After 15–20 minutes, the samples developed a dark brown color (earlier in the presence of PVP, slightly later with Pluronics). Visibly observable suspensions of particles, characteristic of colloidal systems, were formed. After 45 minutes, samples with PVP acquired a dark purple hue, whereas in samples containing Pluronics, large almost black particles formed, floating in the transparent liquid and quickly settling to the bottom of the test tube. Samples prepared with PVP showed no visible changes over the course of 24 hours.

3.1.2 Electron spectroscopy of the synthesized products

The electronic spectra of the samples prepared in the presence of PVP were studied in detail. Low concentrations made it possible to closely monitor the entire synthesis process.

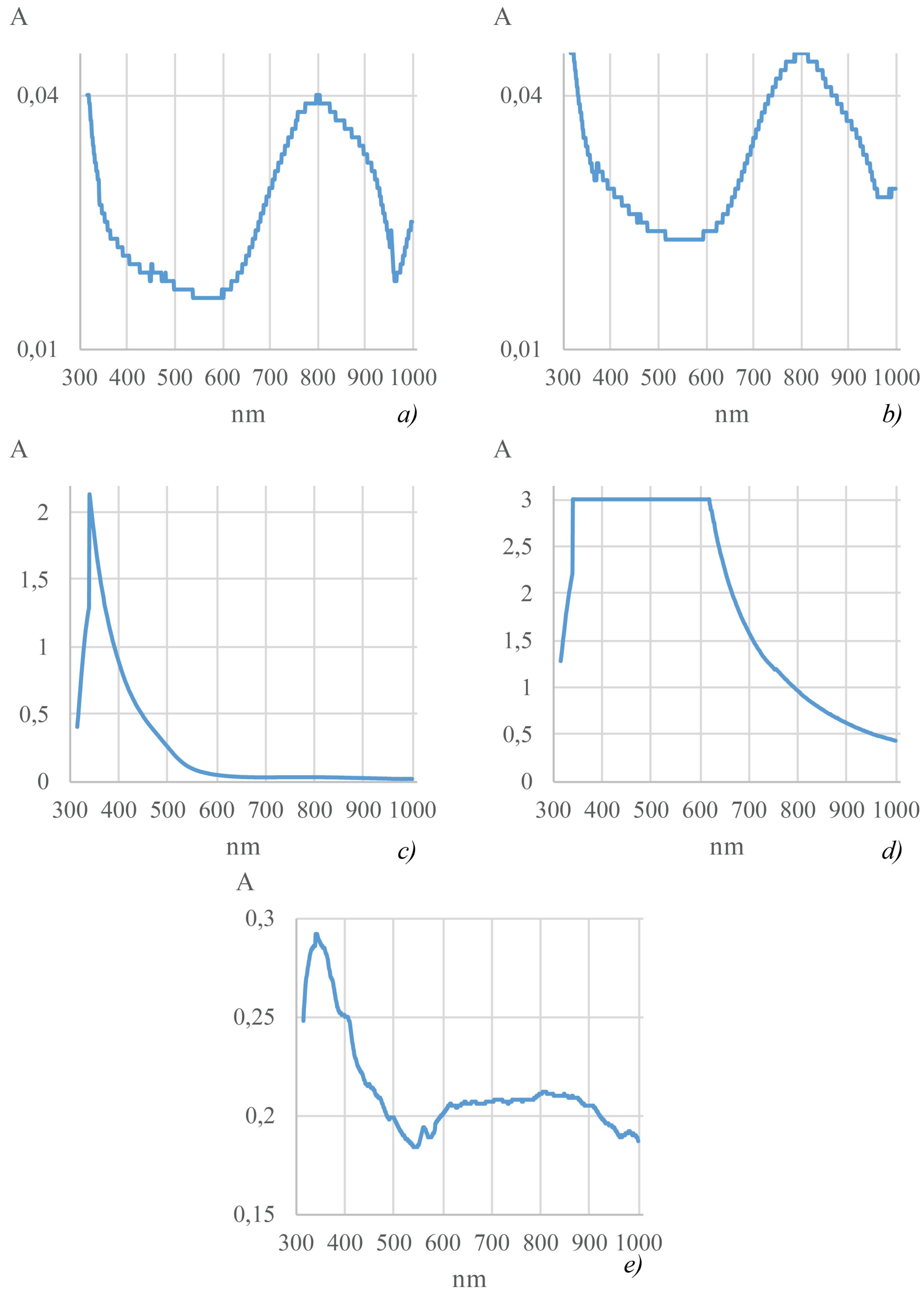

Fig. 1. Electronic spectra of sample No. 1 at the beginning of the synthesis (a), 5 minutes (b), 10 minutes (c), 30 minutes (d), and 90 minutes (e) after the addition of the reducing agent.

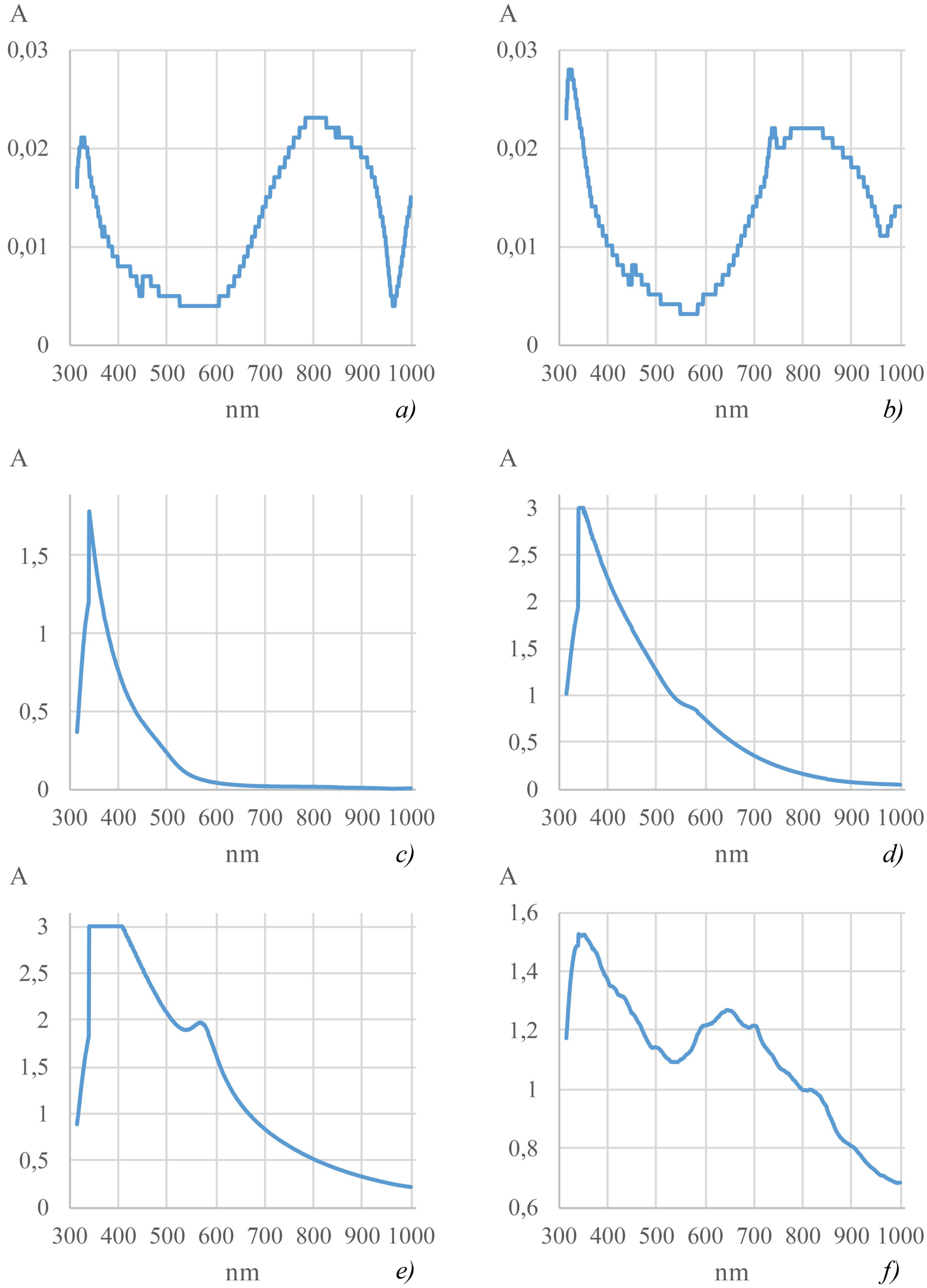

Fig. 2. Electronic spectra of sample No. 2 at the beginning of the synthesis (a), 5 minutes (b), 10 minutes (c), 15 minutes (d), 20 minutes (e), and 90 minutes (f) after the addition of the reducing agent.

In the presence of PVP, immediately after the addition of the reducing agent, the spectra showed a broad absorption maximum centered around 800 nm (Fig. 1a, 2a), which persisted for 5–10 minutes (Fig. 1b, 2b) and corresponds to the spectral signature of Cu^{2+}. In the case of sample No. 2, an immediate formation of a subtle peak around 360 nm was observed, which either indicates the formation of very small copper nanoparticles [2] or, more likely in this case, corresponds to an intermediate stage of nanoparticle formation—partial reduction of copper ions and the formation of short-lived Cu^{+}–PVP complexes [3].

Ten minutes after the start of the synthesis, the spectra exhibited a distinct, intense absorption maximum centered around 360 nm (Fig. 1c, 2c), indicating the formation of very small copper nanoparticles [3].

Fifteen minutes after the addition of the reducing agent, an absorption peak began to form around 580 nm in the spectra of sample No. 2 (Fig. 2d), indicating the formation of larger Cu^{0} particles, which became more intense over time (Fig. 2e) [4].

In sample No. 1, due to the higher concentration of the initial reagents, the absorption intensity in the wavelength range from 360 to 700 nm exceeded the measurement capacity of the available equipment without additional treatment (Fig. 1d). Therefore, to capture the spectral profile of the subsequent stages of synthesis, the sample was diluted with distilled water at a ratio of 1:9.

After 90 minutes, both samples exhibited an intense peak at 360–370 nm, corresponding either to small copper nanoparticles or Cu_2O (Fig. 1e, 2f). In sample No. 1, a weak peak around 580 nm persisted. In the second sample, this peak shifted to a longer wavelength region, with a maximum around 610 nm.

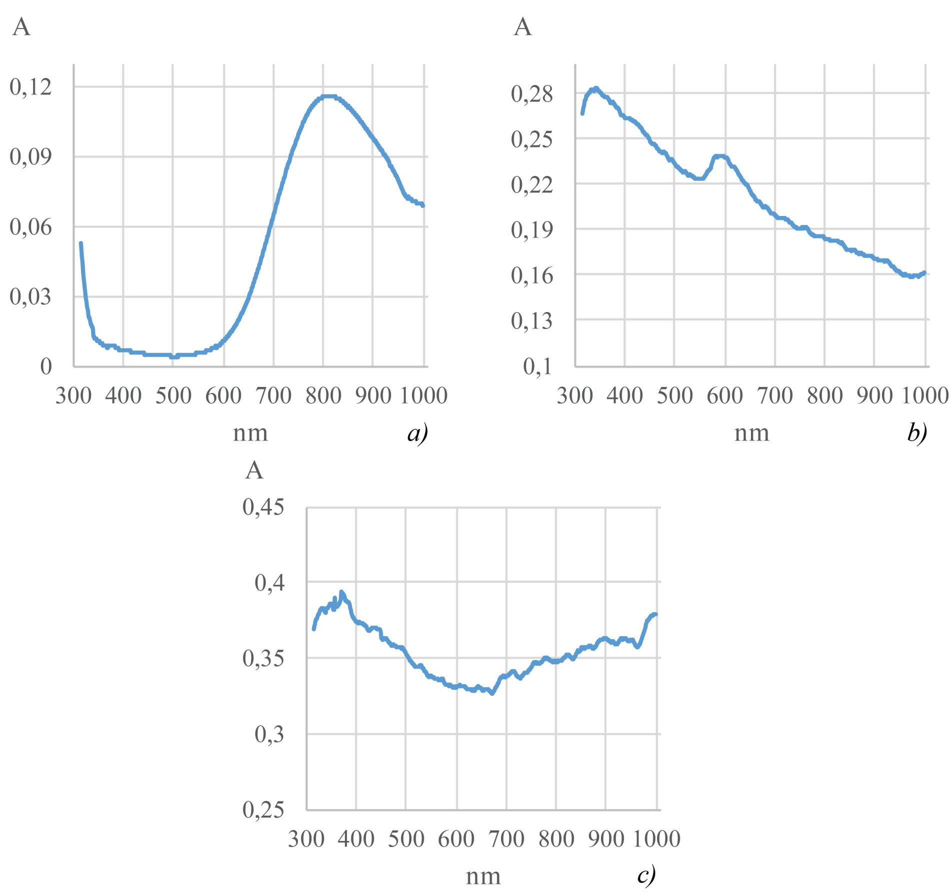

Fig. 3. Electronic spectra of sample No. 3: at the beginning of the synthesis (a), after 25 minutes, diluted 1:9 (b); and of sample No. 4 after 25 minutes (c).

Pluronics F-68 and F-127 are triblock copolymers consisting of a central polypropylene oxide block and terminal polyethylene oxide blocks. The formation of organized structures in the bulk solution occurs spontaneously when the polymer concentration reaches a certain critical value—the critical aggregation concentration (CAC). The main contribution to the association forces comes from the increase in the system's free energy due to the aggregation of the hydrophobic parts of the molecule and the release of water molecules. In aqueous solutions, polymolecular aggregates are formed. Due to rapid precipitation and lower stability, systems containing Pluronics F-68 and F-127 were studied in less detail.

At the initial stage (within the first few minutes after the addition of the reducing agent), a broad peak around 810 nm appeared in the electronic spectra (Fig. 3a), confirming the presence of copper ions in the system [5].

The absorption values in the samples quickly reached the sensitivity limits of the spectrophotometer. Twenty minutes after the addition of the reducing agent, the spectrum became uninformative due to high absorption values. Upon dilution (1:9) of the sample containing Pluronic F-68, two absorption peaks were observed in the electronic spectrum (Fig. 3c). The first peak was around 355 nm, and the second at 585 nm. This pattern is assumed to reflect the formation in the system of both very small copper particles (peak at 355 nm) and larger particles and aggregates (peak at 585 nm). Analysis of the diluted sample containing Pluronic F-127 showed a different pattern (Fig. 3d). The absorption values remained within a fairly narrow range across the studied spectrum, showing only a small peak around 370 nm. It is assumed that larger particles in the presence of Pluronic F-127 settled more quickly, not entering the sample, as the critical micelle concentration and CAC for this polymer are significantly lower. Although sols did not form in the Pluronic systems (precipitates occurred), there were no signs of metal oxidation in these precipitates during the observed period, indicating that the polymer chains reliably protect the surface of the copper nanoparticles.

Based on visual and spectroscopic analysis, it was established that polyvinylpyrrolidone provides significantly more effective stabilization of copper nanoparticles compared to Pluronics. In PVP systems, the gradual formation of stable nanoparticles with characteristic plasmon peaks at 360–370 nm and 580–610 nm is observed, whereas the use of Pluronics leads to rapid aggregation and sedimentation of larger particles. Thus, the nature of the stabilizer critically influences the synthesis kinetics and the morphology of the resulting copper nanoparticles.

3.2 Copper nanoparticles in catalytic water purification

The use of copper-containing nanoparticles in catalytic water purification is one of their most promising applications, extending beyond simple bactericidal treatment. Acting as highly active catalysts, they initiate and accelerate chemical reactions that break down persistent pollutants.

Copper nanoparticles can be used in photocatalytic water purification. When a nanoparticle absorbs a photon of light, an electron–hole pair is generated, with the hole (h^+) capable of directly oxidizing organic pollutant molecules on the particle surface. Additionally, hydroxyl radicals are formed in this process, which can break down complex organic molecules (pesticides, dyes, pharmaceuticals) into CO_2 and water [6]. Compared to other photocatalysts (e.g., TiO_2), copper has a narrower band gap, which enhances the utilization of visible light from the solar spectrum, making the water purification process more energy-efficient and cost-effective [7].

For the degradation of highly persistent organic pollutants (phenols, complex pesticides, industrial dyes), catalytic oxidation with hydrogen peroxide can be used, which does not depend on light. When hydrogen peroxide is added to water, copper nanoparticles catalyze its decomposition. As a result, instead of slow natural breakdown, the catalytic reaction rapidly generates hydroxyl radicals.

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In addition to oxidation, reduction processes can also be used for water purification. Copper nanoparticles are capable of enhancing the efficiency of reduction reactions, which is important for combating contamination by toxic anions. For example, copper can catalyze the reduction of nitrates (NO_3^-) to harmless N_2 or, at least, to NO_2^- and NH_4^+, which are easier to remove [8]; carcinogenic Cr^{6+}, which is highly toxic, can be reduced to the less hazardous and less mobile Cr^{3+} [9].

In general, as a component of catalytic systems, copper-containing nanoparticles open the way to the creation of effective technologies for water purification from persistent organic pollutants, reducing environmental risks. Their ability to work effectively both in Fenton reactions (in the dark) and in photocatalysis (under light) makes them a key element in the development of new-generation water purification techniques aimed at solving the problems of microscopic contaminants that are difficult to deal with using traditional methods. The efficiency of these processes indirectly depends on the optical characteristics of the nanoparticles, since the intensity and position of plasmonic absorption peaks are determined by the size, morphology, and stability of the nanoparticles. This study showed that the use of polymer stabilizers makes it possible to obtain systems resistant to aggregation and oxidation with controlled optical properties, which is a fundamental basis for the development of new catalytic systems for various water purification technologies.

4 Conclusion

The Conducted research showed the effectiveness of the chemical reduction method using polymer stabilizers for the synthesis of copper-containing nanoparticles. It was found that the nature and concentration of the polymer stabilizer have a significant effect on the kinetics of synthesis, stability, and optical properties of the resulting nanoparticles. Nanosystems obtained in the presence of PVP demonstrated the greatest stability, which was confirmed by both visual observations and electron spectroscopy data. It should be noted that it was electron spectroscopy that made it possible to trace in detail the stages of nanoparticle formation, (from copper ions to stable colloidal systems with characteristic plasmonic peaks).

The obtained copper nanoparticles have significant potential for creating new water purification technologies. In particular, they can be used in the processes of catalytic purification of water from persistent organic pollutants and toxic anions. Their high catalytic activity in oxidation and reduction reactions, as well as their ability to work effectively under the influence of visible light, make them a promising material for creating energy-efficient and economical systems to combat water pollution.

Further research should be aimed at optimizing synthesis conditions, controlling particle size and morphology to increase their catalytic activity and water purification efficiency.

References

1. G.Yu. Ostaeva, V.V. Grushina, E.A. Eliseeva, I.Yu. Isaeva, I.V. Morenko, A.A. Litmanovich, The Effect of the Properties of the Anion on the Process of Formation of a Copper Sol upon Reduction in a Solution of Poly(N-vinylpyrrolidone). Polym. Sci. Ser. B **63**, 737-744 (2021). https://doi.org/10.1134/S1560090421060208
2. M. G. E. S. Journals, Synthesis and characterization of copper nanoparticles: application, in field of oxidation of aromatic hydrocarbons cerium(IV) sulphate under microwave irradiation. Green Chem. Technol. Lett. (2015). https://doi.org/10.18510/GCTL.2015.112

3. O.P. Keabadile, A.O. Aremu, S.E. Elugoke, O.E. Fayemi, Green and Traditional Synthesis of Copper Oxide Nanoparticles—Comparative Study. Nanomat. **10**(12), 2502 (2020). https://doi.org/10.3390/nano10122502
4. G.-Y. Yao, Z.-Y. Zhao, Q.-L. Liu, X.-D. Dong, and Q.-M. Zhao, Theoretical calculations for localized surface plasmon resonance effects of Cu/TiO_2 nanosphere: Generation, modulation, and application in photocatalysis. Sol. Energy Mater. Sol. Cells.. **208**, 110385 (2020). https://doi.org/10.1016/j.solmat.2019.110385
5. I.L. Soroka, A. Shchukarev, M. Jonsson, N.V. Tarakina, P.A. Korzhavyi, Effect of synthesis temperature on the morphology and stability of copper(i) hydride nanoparticles. CrystEngComm, **15**, 8450-8460 (2013). https://doi.org/10.1039/C3CE41303A
6. S.C. Baral, P. Maneesha, S. Datta, K. Dukiya, D. Sasmal, K.S. Samantaray, V.K. BR, A. Dasgupta, S. Sen, Enhanced photocatalytic degradation of organic pollutants in water using copper oxide (CuO) nanosheets for environmental application. JCIS Open. **13**, 100102 (2024). https://doi.org/10.1016/j.jciso.2024.100102
7. F. Bayat, S. Sheibani, Enhancement of photocatalytic activity of CuO-Cu_2O heterostructures through the controlled content of Cu_2O. Mat. Res. Bullet. **145**, 111561 (2022). https://doi.org/10.1016/j.materresbull.2021.111561
8. M. Hong, Q. Wang, J. Sun, C. Wu, A highly active copper-nanoparticle-based nitrate reduction electrocatalyst prepared by in situ electrodeposition and annealing. Sci. Total Environ. **827**, 154349 (2022). https://doi.org/10.1016/j.scitotenv.2022.154349
9. T.O. Ajiboye, O.A. Oyewo, R. Marzouki, D.C. Onwudiwe, Photocatalytic Reduction of Hexavalent Chromium Using $Cu_{3.21}Bi_{4.79}S_9$/g-C_3N_4 Nanocomposite. Catalysts. **12(10)**, 1075 (2022). https://doi.org/10.3390/catal12101075