Copper nanoparticles obtained by chemical reduction stabilized by micelles of various surfactants

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Abstract. We carried out the synthesis of copper nanoparticles via chemical reduction of micelles stabilized by various surfactants of different nature, such as cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB). We investigated the sustainability of the products of synthesis, i.e. copper nanoparticles stabilized by micelles of various surfactants, after the period of 50 days. Surface morphology and elemental composition of obtained copper nanoparticles were characterized by scanning electron microscopy (SEM).

1. Introduction

The advances in nanoscale entities (particularly, nanoparticles dots) synthesis have gained much prominence in chemistry, physics, medicine, instrument engineering and other fields of science and industry. People planning to use nanoparticles in their field of work usually expect these entities to have properties that are significantly different from large-scale materials. The lower is size of said particles, the greater share of atoms form their surface, therefore, surface energy contribution to total energy increases which may lead to high reactivity, unique optical properties, lower melting temperature etc. Therefore, development of effective methods of synthesis and further study of nanoscale entities (such as nanoparticles) is very important.

Some of the most interesting materials of this type are copper nanoparticles. As a material, copper functional characteristics (such as heat and electric conductivity) are not worse than those of other widely used metals (such as silver or gold), while the price of copper is much lower.

Moreover, slight changes in copper chemical composition, namely its oxidation, turn it from a highly efficient conductor to semiconductor. This feature is unique for copper and finds many practical applications in nanoelectronics, photonics, medicine, instrument engineering, agriculture etc. [1]. Currently, copper nanoparticles gained much prominence as catalysts used in methane conversion and ethanol oxidation. They are an important component of composite materials [2] and synthetic dyes [3, 4]. They are used to produce medical equipment and antibacterial agents and films [5] as well as sensor devices. In electronics copper nanoparticles are used in production of integrated circuits [6],...
Contact layers and electrodes [7], active layers of solar cells, transistors, storage batteries, sensors, capacitors etc.

There are various methods of production of active conductive layers with embedded nanoparticles [8-10]. Some of them are rather widespread, i.e. spin coating method [11, 12], which is often used for serial production. Another method – Langmuir-Blodgett technique [13-15] is usually considered a laboratory technique, so it is less widespread, however, this method allows formation of monomolecular layers of particles with organic surfactant matrix. Another specific feature of this method is its ability to produce multilayered structures with unique and controllable composition of each layer.

Preparation of working nanoparticles solutions for each of these methods can be highly specific and may consists of multiple stages. Development of synthesis methods and further production, modification and study of nanoscale particles remain a very important and difficult task.

Out of all numerous methods of copper nanoparticles production, the most simple and cheap one is nanoparticles synthesis via reduction of copper (II) ions using various stabilizers [16, 17], as this method does not require complex technical performance and allows controlling the size and morphology of obtain products. A specific modification of this method is micelle synthesis using surfactants as stabilizers. Micelles used as «nanoreactors» lead to formation of colloid metal particles and the formed coating serves as a deterrent for metal particles growth which leads to creation of a stable system inside the micelle and prevents oxidation of metal particles [18].

The purpose of this work is to examine a stable of copper nanoparticles for some period of time using a various surfactants.

2. Material and methods

2.1 Chemicals
The following chemicals were used in the process copper nanoparticles synthesis: copper (II) chloride [CuCl$_2$·2H$_2$O] (Mr ≈ 171 g/mol), cetylpyridinium chloride (CPC) [C$_{21}$H$_{40}$ClNO] (Mr ≈ 357.5 g/mol) and cetyltrimethylammonium bromide (CTAB) (Fluka) as a cationogenic surfactants [C$_{19}$H$_{42}$BrN] (Mr ≈ 364.46 g/mol), hydrazine hydrate (HH) [N$_2$H$_4$·H$_2$O] (Mr ≈ 50 g/mol) (Vekton), distilled water [H$_2$O] and aqueous ammonia [NH$_4$OH] UHP 25-5 (Vekton).

2.2 Instruments
Solution mixing during the process of copper nanoparticles synthesis and heating the substrate with copper nanoparticles on silicon substrate was performed using ICA RCT basic magnetic stir bar. Centrifugation of copper nanoparticles (in order to separate them from surfactant) was performed using Elmi CM-70M centrifuge. The morphology of a surface and the chemical composition were determined by means of the scanning electronic microscope (SEM) (Tescan Mira II LMU) in the mode of detecting of secondary electrons (SE) (at 20-30 kV). UV-visible absorption spectra were registered on the spectrophotometer (SHIMADZU UV-2550) in the wavelength range of 500-750 nm. All measurements were made at normal conditions.

2.3 Cetylpyridinium chloride (CPC)
50 ml of aqueous solution of CPC (0.01 M) was divided evenly between two conical flasks. 0.0428 g of copper (II) chloride CuCl$_2$·2H$_2$O was added to the first flask resulting in light blue solution. Then 3 ml of aqueous ammonia NH$_4$OH was added to the flask until pH 11. The color of solution slightly changed. 25 ml of HH was added to the second flask. Dissolution of HH in CPC solution led to heat generation; the colour of resulting solution was light yellow. The solution in the first flask was then poured to the solution in the second flask. The resulting solution was mixed by magnetic stir bar at room temperature (23 °C) with rate of revolution being 500 rpm. The colour of solution changed from light yellow to beetroot red. The solution was mixed for 2 hours.
2.4 Hexadecyltrimethylammonium bromide (CTAB)
50 ml of aqueous solution of CTAB (0.01 M) was divided evenly between two conical flasks. 0.0428 g of copper (II) chloride CuCl$_2$∙2H$_2$O. Then 2 ml of aqueous ammonia NH$_4$OH was added to the flask until pH 11. The color of solution slightly changed. 25 ml of HH was added to the second flask. Dissolution of HH in CPC solution led to heat generation; the resulting solution was transparent. The solution in the first flask was then poured to the solution in the second flask. The resulting solution was mixed by magnetic stir bar at room temperature (23 °C) with rate of revolution being 500 rpm. The colour of solution changed from light yellow to beetroot red. The solution was mixed for 2 hours.

2.5 Preparation of the sample solution for application to the Si substrate
In order to improve visualization of copper nanoparticles on the silicon substrate, the sample was specifically prepared. 1.5 ml of copper nanoparticles solutions obtained in accordance with sections 2.3-2.4 was put into an eppendorf microtube. These solutions were then centrifuged for 5 minutes (without adding water). After that 0.5 ml of centrifuged solution were taken from the surface area and diluted with 0.5 ml of water. The resulting solution was centrifuged afterwards for 5 minutes. This operation was performed three times. The prepared solution containing copper nanoparticles was applied to the Si substrates which were then heated at 100 °C for 5 minutes.

3. Results
3.1 Cetylpyridinium chloride (CPC)
The resulting solution was stirred for 2 hours using thermal magnetic stirrer at 30 °C and 500 rpm. Every 20 minutes the record of the aqueous solution color was made. This color changed from light yellow to brown, which presumably indicates the formation of copper nanoparticles whose presence has been proven spectrophotometrically. Identification of copper nanoparticles in the product of synthesis was performed via UV-visible absorption specturm of the solution (Figure 1(a), curves 1 and 2). UV-visible spectrum has a pronounced absorption peak at 580 nm that is characteristic for copper nanoparticles. In this work we also studied stability of obtained nanoparticles for 50 days after synthesis (Figure 1(a), curve 2). Figure 1(a) shows that over time the absorption peak position has not changed, but it became less pronounced which may be connected with oxidation and chemical changes of nanoparticles in time.

Figure 1(b) shows SEM image of copper nanoparticles obtained at the day of the experiment on the silicon substrate for solution centrifuged in accordance with section 2.5 of this article and for the conventional solution, respectively. Figure 1(b) shows that copper nanoparticles are very visible. Nanoparticles have a spherical round shape with size range varying from 60 to 200 nm.

![Figure 1(a, b)](image-url)

**Figure 1(a, b).** (a) UV-visible spectrum: 1 – spectrum obtained at the day of the experiment; 2 – spectrum obtained after 50 days; (b) SEM image of copper nanoparticles obtained at the day of the experiment.
The chemical (elemental) composition of sample of copper nanoparticles on the substrate was studied by means of SEM. The samples for this study were taken from various places of substrate surface. The results of this study are provided in Table 1.

Table 1. Chemical composition of products of copper nanoparticles synthesis on the Si substrate (all results in weight %).

| Point | C    | Cu   | Result |
|-------|------|------|--------|
| 1     | 83.43| 16.57| 100.0  |
| 2     | 87.18| 12.82| 100.0  |
| 3     | 100.0| –    | 100.0  |
| 4     | 100.0| –    | 100.0  |
| 5     | 100.0| –    | 100.0  |

3.2 Hexadecyltrimethylammonium bromide (CTAB)

The resulting solution was stirred for 2 hours using thermal magnetic stirrer at 30 °C and 500 rpm. Every 20 minutes the record of the aqueous solution color was made. This color changed from light yellow to brown, which presumably indicates the formation of copper nanoparticles, whose presence has been proven spectrophotometrically.

Identification of copper nanoparticles in the product of synthesis was performed via UV-visible absorption spectrum of the solution (Figure 2(a), curves 1 and 2). UV-visible spectrum has a pronounced absorption peak at 588 nm that is characteristic for copper nanoparticles. In this work we also studied stability of obtained nanoparticles for 50 days after synthesis (Figure 2(a), curve 2).

Figure 2(a) shows that over time the shape of absorption spectrum of copper nanoparticles in CTAB solution remained unchanged which indicated that the particles are present in the solution after 50 days. At the same time there is a strong decrease in intensity of absorption bands, which indicates of a decrease in the concentration of nanoparticles in solution. This may be explained by their sedimentation and oxidation. Nanoparticles have various irregular geometric shapes with dimensions from 60 to 200 nm.

Figure 2(b) shows SEM image of copper nanoparticles obtained at the day of the experiment on the silicon substrate for solution centrifuged in accordance with section 2.5 of this article. Figure 2(b) shows that copper nanoparticles are very visible.

![Figure 2(a, b)](image-url)

**Figure 2(a, b).** (a) UV-visible spectrum: 1 – spectrum obtained at the day of the experiment; 2 – spectrum obtained after 50 days; (b) SEM image of copper nanoparticles obtained at the day of the experiment.
The chemical (elemental) composition of sample of copper nanoparticles on substrate was studied by means of SEM. The samples for this study were taken from various places of substrate surface. The results of this study are provided in Table 2.

Table 2. Chemical composition of products of copper nanoparticles synthesis on the Si substrate (all results in weight %).

| Point | C   | N   | O   | Al  | Cl  | Cu  | Br  | Result |
|-------|-----|-----|-----|-----|-----|-----|-----|--------|
| 1     | 48.06 | 18.23 | –   | –   | 7.47 | 9.91 | 16.32 | 100.0  |
| 2     | 62.78 | –   | 4.04 | –   | 5.35 | 9.17 | 18.66 | 100.0  |
| 3     | 85.91 | –   | –   | 11.55 | 2.54 | –   | –   | 100.0  |
| 4     | 100.0 | –   | –   | –   | –   | –   | –   | 100.0  |

4. Discussion
Metal nanoparticles can be produced from micellar surfactant solutions where micelles can be regarded as a sort of nanoreactors allowing to regulate the shape and size of nanoparticles. These systems can form in both ionic and non-ionic surfactant solutions where the surfactant has a diphilic structure: hydrocarbon radicals ($C_{n}H_{2n+1}$, $C_{n}H_{2n-1}$, $C_{n}H_{2n+1}$, $C_{6}H_{9}$ etc.) containing 8-18 carbon atoms form the hydrophobic part while polar groups of various nature form the hydrophilic part. Dissolution of surfactants in water lead to water molecules cross-bonding around the non-polar hydrocarbon radicals which is turn leads to decrease of system entropy. Minimal energy corresponds to concentration specific for each surfactant that is called the critical concentration for micelle formation (CCM). At the same time, ions (molecules) of surfactant begin their spontaneous aggregation to micelles which leads to increase in system entropy. The value of CCM depends on the length and degree of branching of hydrocarbon radical, the presence of electrolytes and organic compounds, solution acidity, hydrophilic-lyophilic balance of surfactant and other parameters.

If the concentration is close to CCM, micelles have spherical forms where polar groups are oriented towards the water medium and hydrophobic radicals are located within the sphere forming a non-polar core. These ionic surfactant micelles are charged due to dissociation of polar groups and attract up to 80 % of counterions which are then connected to micelle surface and can be regarded as a single entity from the kinetic point of view.

It is known that the hydrophobic micelle cell can include up to 33-46 volume % of water (as is the case for sodium dodecyl sulfate). Micelles of ionic surfactants at concentration close to CMC form stable aggregates (average radius is 24-30 Å and more, n ~ 20-100).

Micelles are dynamic systems: the lifetime of a surfactant ion (molecule) within a micelle ranges from $10^8$ to $10^5$. Micelles migrate, collide with each other, collapse and form again. The most important property of micelles which becomes evident after they reached the CCM is their solubilization – spontaneous co-solvation of substances in micelles that have low solubility or do not dissolve in water. Ways of inclusion of substances in ionic micelles vary and depend on the nature of both solubilized compounds and surfactant.

Copper ammonium complexes and hydrazine hydrate are very soluble water. The process of copper ion reduction to nanoparticles within the CTAB and CPC micellar nanoreactors is possible in the presence of water microphases with dissolved copper ammonium complex and hydrazine within hydrophobic micelle core. In this case copper nanoparticles are formed within the hydrophobic micelle core. Their volume is then limited by the volume of water microphases and they are protected from oxidation by external (surface) and internal (core) micelle layers.

5. Conclusions
We have synthesized and studied copper nanoparticles stabilized by various micelles. Cationogenic surfactants (CPC and CTAB) allow to produce particles whose size ranges from 60 to 200 nm despite
the differences in the length of hydrocarbon chain in said surfactants (C\textsubscript{21} and C\textsubscript{19}), respectively. The synthesized nanoparticles have only slight differences in size which can serve as an evidence of close radii of hydrophobic micelle cells produced by a similar type of cationogenic surfactants. Copper nanoparticles produced in CPC solution remain stable even after 50 days have passed since the date of synthesis. The absorption spectrum of such nanoparticles shows that absorption peak retains its intensity and position but starts to broaden. This can be an indicator of formation of other products of copper nanoparticles oxidation. Analysis of absorption spectra of copper nanoparticles procured in CTAB solution also revealed that the spectra retained their form. This shows that the nanoparticles are present in the solution after 50 days. However, the intensity of spectral band significantly decreases which indicates of a decrease in nanoparticles concentration in said solution. This can be explained by nanoparticles sedimentation and oxidation.

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