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Electrochemical Method for Synthesis of Cu, Cu_2O, and CuO Nanoparticles

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Abstract– This article examines several methods for synthesizing copper nanoparticles in solutions using electrochemical reduction. A number of conditions for nanoparticle synthesis are discussed. In particular, studies devoted to the use of different solvents and electrolytes, as well as the investigation of the influence of electrolysis conditions, have been examined. For instance, nanoparticle size can be controlled by adjusting voltage and current strength. The role of stabilizers was also considered; the use of different stabilizers allowed for control over the size and shape of nanoparticles. The influence of the electrolyte pH was studied, revealing its significant impact on the size, morphology, and thermal stability of copper particles. At low pH values $(pH = 5)$, Cu nanoparticles with large sizes and complex shapes are formed. Innovative approaches were proposed, such as using DNA as an electrolyte for nanoparticle synthesis, highlighting the importance of electrolyte selection in determining particle morphology and size.

Key words– copper, synthesizing, electrochemical method, nanoparticles, electrochemistry.

I INTRODUCTION

One of the methods that can be used in the synthesis of Cu, Cu_2O, CuO nanoparticles is the electrochemical method. The electrochemical method has attracted significant attention due to its unique advantages, such as simplicity, direct pathway, low-temperature operation, high current yield, and is an important step towards environmentally friendly methods. For the synthesis of nanoparticles, cyclic voltammetry, potentiostatic, galvanostatic, and pulsed current methods were used, as well as various electrochemical methods [1-11].

The size, shape, and properties of copper nanoparticles synthesized by the electrochemical method are influenced by the following factors:

Solution concentration: Higher solution concentration leads to larger nanoparticle size.

Current: Increasing the current enhances the nanoparticle deposition rate, resulting in a reduction in their size.

Temperature: Elevated temperature increases the nanoparticle deposition rate, also leading to a reduction in their size.

Solvent: The nature of the solvent can influence the shape and size of nanoparticles. For example, in water, copper nanoparticles typically have a spherical shape, while in methanol or acetonitrile, they may have rod-like or needle-like shapes.

Examples of copper nanoparticle synthesis by the electrochemical method.

In the study [12], a cell with copper electrodes and copper sulfate was used. The process involved electrolysis followed by the deposition of Cu nanoparticles on the cathode (Figure 1). The authors synthesized copper nanoparticles in an aqueous solution of copper sulfate. Electrolysis was conducted at a voltage of 15 V and a current of 6 A for 30 minutes. The obtained particles were crystalline and had a spherical shape with a size of 24 nm. Observations of some larger nanoparticles revealed the presence of Van der Waals clusters of smaller objects.

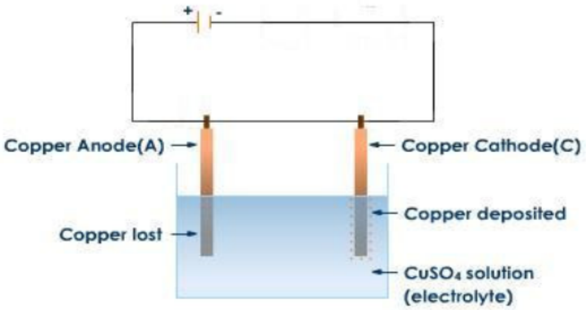

Fig. 1: Deposition of copper nanoparticles on the cathode.

The use of various electrolytes and solvents:

In the study (13), various solvents and electrolytes, including water, acetonitrile, and methanol, were utilized for the synthesis of CuO nanoparticles with different morphologies. Electrolysis was performed using a copper anode and a platinum cathode under different conditions. The authors synthesized copper oxide nanoparticles in an aqueous solution of sodium hydroxide in the presence of various solvents. Sodium hydroxide served as the electrolyte in the electrolytic reactions. Electrolysis was carried out at a voltage of 1.25 V and a current of 100 mA for 2 hours. The resulting nanoparticles ranged in size from 2 to 36 nm. The shape of the nanoparticles depended on the nature of the solvent: in water, they formed clusters, in methanol - a spherical shape, and in acetonitrile (ACN) - honeycomb-like clusters. During electrolysis, $Cu+$ and $OH-$ ions were generated at the anode and cathode, resulting in the formation of CuO_2 and Cu_2O precipitates. Subsequent thermal treatment at 900^oC for 1 hour led to the formation of CuO. Particles obtained in the presence of the water-ACN solvent had the smallest average particle size among the others. CuO nanoparticles obtained in the presence of an aqueous-acetonitrile solvent, upon thermal treatment at 300^oC, showed particle sizes ranging from 5 to 30 nm, while upon thermal treatment of CuO at 900^oC, the particle size ranged from 2 to 36 nm.

In study (14), the authors employed the electrochemical method for synthesizing CuO nanoparticles in an organic environment. A copper metal sheet served as the anode, while a platinum sheet served as the cathode. The solvent used was tetrahydrofuran (THF) with the addition of acetonitrile (ACN) in a ratio of 4:1. Tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPAB), or tetrabutylammonium bromide (TBAB) were used as stabilizers. The current density was set at 10 mA/cm^2. As a result of electrolysis, CuO nanoclusters stabilized by TEAB, TPAB, or TBAB were obtained. The nanoparticles exhibited irregular shape and non-uniform distribution. The authors noted that the use of stabilizers during synthesis allows for the control of nanoparticle size. It was also observed that the cluster size decreases with increasing current density. Thus, the electrochemical method proves to be an effective and versatile approach for synthesizing CuO nanoparticles. The utilization of stabilizers enables control over nanoparticle size and shape. In contrast to previous studies where the synthesis of CuO nanoparticles was conducted in an aqueous environment, in the study [21], synthesis was carried out in an organic medium. This allowed for improved nanoparticle dispersion and reduced agglomeration. Additionally, in the work [14], an inert material was used for the electrode. This helped to avoid contamination of nanoparticles with copper oxidation products formed at the anode.

In study (15), the authors synthesized CuO nanoparticles via electroreduction in a nitrogen atmosphere. A copper sheet served as the anode, while a platinum sheet served as the cathode. The electrolyte used was a solution of tetrabutylammonium bromide (TBAB) in a mixture of acetonitrile and tetrahydrofuran (4:1). Upon applying a current density of 6 mA/cm^2, 95% of copper oxide clusters stabilized by TBAB were synthesized.

During the application of electrical current, the anode slowly dissolves, leading to the formation and subsequent passivation of active TBAB particles. The size of the clusters decreases with increasing current density.

SEM analysis revealed that copper oxide nanoparticles exhibit irregular shape and uneven distribution. This is due to the partial solubility of the surfactant in the solvent under these experimental conditions.

XRD analysis showed that the nanoparticles have a crystalline structure. The sharp peaks obtained indicate the monoclinic structure of the CuO nanoparticles, which was found to be highly crystalline in nature. XRD analysis showed that the synthesized nanoparticles had impurities. Bromine (Br) is present in trace amounts due to the addition of TBAB. The average particle size was calculated using the Debye-Scherrer formula and was 9.56 nm.

The result of HRTEM analysis showed that the copper oxide nanoparticles have a spherical shape and a size of 5–10 nm, which shows good similarity with the grain size calculated by XRD methods. The authors performed antibacterial testing for antibacterial activity on CuO nanoparticles and showed that copper oxide nanoparticles acted as excellent antibacterial agents for both Gram-positive and Gram-negative bacteria.

Effect of Electrolyte pH.

In [16], the authors studied the effect of electrolyte pH on the properties of Cu nanoparticles obtained by the electrochemical method. An oxalic acid solution was used as an electrolyte, the pH of which was maintained using sodium hydroxide. Two copper electrodes maintained a current of 0.1 A for 2 hours at 25^oC, and stirring was carried out with a magnetic stirrer. After electrolysis, the resulting nanoparticles were centrifuged, washed with distilled water, dried in air at 90^oC and calcined at 150^oC. As a result, nanoparticles with sizes ranging from 20 nm to 7 μm were obtained. As a result of electrolysis, Cu nanoparticles with different sizes, shapes and properties were obtained depending on the pH of the electrolyte. At pH = 5, Cu nanoparticles had a microrod-like structure with a length of 500-7000 nm and a diameter of 150-250 nm. They consisted of a mixture of 67% $Cu(OH)_2$ and 33% CuC_2O_4. At pH = 6.5-9.5, Cu nanoparticles had a microspherical shape of various diameters. They consisted of $Cu(OH)_2$. At pH = 12.5, Cu nanoparticles had a cylindrical shape with a length of 50-150 nm and a diameter of about 10-20 nm. They consisted of pure $Cu(OH)_2$. Thus, it was found that the pH of the electrolyte has a significant effect on the properties of Cu nanoparticles obtained by the electrochemical method. The size and shape of Cu nanoparticles depend on the pH of the electrolyte. At low pH values (pH = 5), Cu nanoparticles with large sizes and complex shapes are formed. At high pH values (pH = 12.5), Cu nanoparticles with small sizes and simple shapes are formed. The composition of Cu nanoparticles also depends on the pH of the electrolyte. At low pH values (pH = 5), Cu nanoparticles contain a mixture of $Cu(OH)_2$ and CuC_2O4. At high pH values (pH = 12.5), Cu nanoparticles consist of pure $Cu(OH)_2$. The properties of Cu nanoparticles, such as surface area, thermal stability and porous structure, also depend on the pH of the electrolyte. At high pH values (pH = 12.5), Cu nanoparticles have the largest surface area and are thermally more stable than particles produced at other pH values.

Thus, the study shows that electrolyte pH significantly affects the size, morphology and thermal stability of copper nanoparticles, which provides opportunities for the controlled synthesis of nanoparticles with desired properties.

In (17), researchers proposed using DNA as an electrolyte to synthesize copper nanoparticles by anodic oxidation. This process involved the use of copper and platinum as the anode and cathode respectively, with copper acting as the dissolving electrode. In this process, the bulk of the metal is oxidized at the anode, and metal cations migrate to the cathode. Negatively charged DNA molecules move towards the anode and bind to metal cations, stabilizing in the form of DNA-copper complexes.

Innovative approaches.

The experiments used DNA from calf thymus as a supporting electrolyte and stabilizer of copper clusters. A copper sheet (99.9%) (2 cm × 1 cm) was used as the anode and a platinum sheet (2 cm × 1 cm) was used as the cathode. Electrolysis was carried out in a plexiglass electrochemical cell at a voltage of 4 V for an hour. After electrolysis, the formed DNA-Cu metal complexes were removed from the cell.

Initially, the resulting nanoparticles were amorphous in nature, but after irradiation with an electron beam they were transformed into discrete nanoparticles of various sizes. Visually, the sample was divided into three regions (a, b, c), with particle sizes ranging from 20–50 nm in region a, 10–20 nm in region b, and 5–10 nm in region c.

The choice of DNA as an electrolyte is explained by its negative charge due to the presence of phosphate groups. When a voltage is applied, the negatively charged DNA molecules orient and move towards the positive electrode, while the oxidized copper ions move towards the negative electrode. This interaction results in the formation of DNA-copper complexes in the electrolyte or on the electrode. The use of DNA as an electrolyte made it possible to obtain nanoparticles with an amorphous structure.

This method represents a unique approach to the synthesis of copper nanoparticles, demonstrating the importance of electrolyte selection in determining nanoparticle morphology and size.

Influence of electrolysis conditions.

In electrochemical synthesis, the size of copper nanoparticles can be reduced by increasing the voltage (18).

Increasing the applied voltage generally increases the rate of reduction of copper ions to copper atoms, which can result in the formation of smaller nanoparticles. This is because at higher voltages, nucleation occurs faster than growth, resulting in the formation of more smaller particles. However, it is important to note that excessively high voltage can also produce by-products or cause particle agglomeration, which can negate the benefits of size reduction. The exact voltage required to produce copper nanoparticles of a certain size depends on the specific electrochemical process conditions, including electrode materials, electrolyte composition, and temperature. An average particle size of 21.55 nm was obtained using a potential difference of 27 V (19).

The electrochemical method for the synthesis of copper nanoparticles has demonstrated significant versatility and efficiency in a number of studies. Important parameters in this process are the type of electrolyte, voltage, current, process duration and stabilizers used. The electrochemical method is a simple and less labor-intensive method with maximum purity of nanoparticles (20). In addition, the electrochemical process is environmentally friendly and opens up new possibilities for the synthesis of metal nanoparticles. The electrochemical method is considered suitable for use in the development of new medical drugs. Although the electrochemical method has a number of advantages, this method also has a number of disadvantages, namely: the reaction that occurs can lead to the attachment of a layer (double layer) to the outside of the electrode, which increases the resulting resistance and reduces the current. (21).

II CONCLUSION

Use of various electrolytes and solvents:

A study (13) showed the effect of different solvents on the size of CuO nanoparticles. Water-ACN obtained in the presence of a solvent have the smallest average particle size among the others. In work (14), the synthesis was carried out in an organic medium, which improved dispersion and reduced particle agglomeration.

Influence of electrolysis conditions:

The size of the nanoparticles can be controlled by varying the voltage and current. For example, in work (19), increasing the voltage to 27 V led to a decrease in the average particle size to 21.55 nm.

The role of stabilizers:

The use of various stabilizers, as shown in works (14) and (15), made it possible to control the size and shape of nanoparticles.

Effect of Electrolyte pH: (16) investigated the effect of electrolyte pH on the properties of Cu nanoparticles, showing that pH has a significant effect on particle size, morphology, and thermal stability. At low pH values (pH = 5), *Cu* nanoparticles with large sizes and complex shapes are formed.

Innovative approaches: A study (17) proposed the use of DNA as an electrolyte for the synthesis of nanoparticles, which is a unique approach demonstrating the importance of electrolyte selection in determining particle morphology and size. The use of DNA as an electrolyte makes it possible to obtain nanoparticles with an amorphous structure.

Antibacterial activity: Some of the synthesized *CuO* nanoparticles showed antibacterial activity.

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