Effect of Some Experimental Conditions of the Pulsed Plasma in Liquid on the Formation of Nanostructures

Adilet Zakypbekov
Kyrgyz-Turkish Manas University

Wei Xu
Kumamoto University

Niidome, Takuro
Kumamoto University

Alimzhan Kalbekov
Kyushu University

他

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Effect of some experimental conditions of the pulsed plasma in liquid on the formation of nanostructures

Adilet Zakypbekov[1], Wei Xu[2], Takuro Niidome[2], Alimzhan Kalbekov[3] Emil Omurzak[1]
[1]Kyrgyz-Turkish Manas University, Bishkek, Kyrgyz Republic
[2]Kumamoto University, Kumamoto, Japan
[3]Kyushu University, Fukuoka, Japan
Corresponding author email: emil.omurzak@manas.edu.kg

Abstract. *Optimal conditions for the synthesis of copper oxide nanoparticles under the pulsed plasma conditions carried out inside liquid media with different pH values and electrical conductivities were studied. To test the effect of liquid temperature on the composition of synthesized nanoparticles, syntheses were carried out at room temperature (20 ^{0}C) and in a water bath at a temperature of 80 ^{0}C. A 5% aqueous solution of acetic acid (pH=2,41; λ=0,1123 S*l/см*mol (20 ^{0}C); λ=0,5673 S*l/см*mol (80 ^{0}C)), distilled water (pH=7; λ=0,00009 S*l/см*mol (20 ^{0}C); λ=0,00011 S*l/см*mol (80 ^{0}C)) and a 0.02% aqueous solution of sodium hydroxide (pH=11,7; λ=26,48 S*l/см*mol (20 ^{0}C); λ=156,154 S*l/см*mol (80 ^{0}C)) were used. It was found that nanoparticles were synthesized in all samples, and the size and composition of the particles were greatly influenced by the electrical conductivity of the liquid and the composition of the liquid.*

Keywords: Nanoparticles, synthesis of copper, synthesis of copper oxides, pulsed plasma, pH environments.

1. INTRODUCTION

In principle, it is known that nanoobjects can be obtained from almost any macroobjects or molecules. The synthesis of copper nanopowders and their oxides can be achieved using a variety of methods, each offering unique advantages in terms of control over particle size, morphology, purity, and scalability. There are several common methods for synthesizing copper nanopowders and copper oxides that are more efficient than others. For example, copper nanoparticles can be synthesized by reducing copper salts (e.g. copper sulfate, copper chloride) in a solution containing a reducing agent (e.g. sodium borohydride, hydrazine). Control of particle size and morphology can be achieved by adjusting reaction parameters such as temperature, pH, and concentration of reagents [1]; The polyol method involves the reduction of copper salts in a polyol solvent (e.g., ethylene glycol) at elevated temperatures in the presence of a stabilizing agent (e.g., polyvinylpyrrolidone (PVP)). This makes it possible to synthesize monodisperse copper nanoparticles of controlled size and shape [1, 2]; Also, copper nanopowders can be obtained by mechanical grinding of bulk copper in the presence of a grinding agent (for example, surfactants) under conditions of high energy costs. This method offers scalability and control over particle size distribution [1, 3]; It is also possible to electrodeposit copper nanoparticles onto conductive substrates from an electrolyte solution containing copper ions. Control of particle size and morphology can be achieved by adjusting deposition parameters such as applied potential, deposition time, and electrolyte composition [2, 3]; Hydrothermal/solvothermal synthesis Copper oxide nanoparticles can be synthesized under high pressure and high-temperature conditions in aqueous or organic solvents. Control of particle size, crystallinity, and morphology can be achieved by adjusting reaction parameters such as temperature, pressure, reaction time, and precursor concentration [3]; Copper oxide nanoparticles can be synthesized by thermal decomposition of copper-containing precursors (e.g., copper acetate, copper nitrate) at elevated temperatures in the presence of a reducing agent or an inert atmosphere [4]; Also, copper oxide nanoparticles can be synthesized by sol-gel methods by hydrolysis of copper-containing precursors (for example, copper acetate, copper nitrate) in a solvent, followed by gelation and heat treatment. Control of particle size and morphology can be achieved by adjusting precursor concentration, solvent composition, and processing conditions [5].

Although the above methods are effective, they require very low or very high temperatures, require special complex equipment resistant to the pressures created by these temperatures, and a large amount of energy resources to adjust them. In addition to the problems mentioned, some methods require the use of special chemicals and special additional equipment [6, 7]. One of the alternative methods is plasma methods for the synthesis of nanoparticles in liquids. Promising and effectively used methods for producing copper nanoparticles are the method of pulsed laser ablation in liquids [8, 9], the method of plasma electrolysis in liquids [10], the method of plasma electrochemical synthesis in liquids [11, 12], and the method of pulsed plasma synthesis in liquids [13].

In all plasma synthesis in liquid methods, manipulation of electrical conductivity levels in the liquid medium during the synthesis process introduces an important variable that influences the size, morphology and composition of the resulting nanoparticles. Understanding and optimizing these functions is essential to tailor nanoparticles to specific applications. An intriguing aspect of this synthesis process is the

manipulation of electrical conductivity in a liquid environment, introducing a critical parameter that profoundly influences the characteristics of the resulting nanoparticles. Exploring different electrical conductivities adds a level of complexity and versatility to the synthesis process, allowing researchers to tailor the properties of nanoparticles for specific applications [9, 10, 13].

Metals and metal oxides are important technological materials used as catalysts in the chemical industry [1, 2, 5], as well as in electronic and photonic devices [1-3, 6]. Copper nanoparticles and their oxides are used in a wide range of applications such as catalysis [1, 3, 15, 16], gas sensors [2], magnetic storage media [2, 3], batteries, solar energy transformers [5], field emission [6] and antibacterial properties [7, 9]. The particular use of cuprous oxide as a narrow bandgap P-type semiconductor has attracted much attention due to its potential applications in nanodevices such as electronics, optoelectronics, and sensing. It is widely used as a powerful heterogeneous catalyst due to its high activity and selectivity in oxidation and reduction reactions [5]. Copper oxide is also excellently used as an antioxidant, antibacterial and antitumor or anticancer agent. The copper oxide nanoparticle binds to the cell membrane and enters the cell, generating reactive oxygen species (ROS), which causes oxidative stress in the cell. Oxidative stress leads to metastasis, cancer proliferation, apoptosis, DNA damage, cytotoxicity, and dysregulated cell signaling. The free hydroxyl radical generated by the nanoparticles combines with DNA to form 8-hydroxy-2-deoxyguanosine (8-OHdG), causing DNA damage. CuO nanoparticles exhibit antibacterial activity against various bacterial strains such as Staphylococcus aureus, Bacillus circulens BP2, Escherichia coli and P. aeruginosa. Recently, CuO nanoparticles have found applications in cholesterol detection, lactate biosensors, microbial DNA sequencing, and HIV drug analysis. There are specialized CuO nanoparticles such as glucose sensors, hydrogen peroxide sensors, immunosensors, and dopamine sensors for detecting various biomolecules. ROS generated by CuO nanoparticles causes toxicity that leads to cell death. There is research into fighting tumors using nanoparticles due to their antitumor nature. Metal nanoparticles exhibit anticancer activity due to physicochemical properties such as antioxidant effects or the use of external irritants. Free radicals produced by metal nanoparticles kill cancer cells [4].

The synthesis of copper oxide nanoparticles using pulsed plasma in liquids is an interesting area of research, with the pH of the medium and the electrical conductivity of the synthesis playing a key role in determining the size, morphology, surface composition and stability of the nanoparticles. Understanding and controlling these properties are important steps towards harnessing the full potential of these nanoparticles for applications ranging from catalysis and sensing to biomedical and environmental fields. The study of conductivity-dependent synthesis parameters opens up new possibilities for tailoring the properties of copper oxide nanoparticles to meet specific application requirements.

2. MATERIAL AND RESEARCH METHODS

Nanoparticles were synthesized by the method of pulsed plasma in liquid in an installation [14], the diagram of which is presented in the figure (Fig. 1). To find the correct concentration when using acid and alkali to synthesize nanoparticles, the solutions were diluted until the electrodes began to correctly pulse the plasma as they approached. Plasma pulsation was measured using an oscilloscope. The optimal required electrical capacitance for the synthesis of nanoparticles was chosen to be 2 μF; the optimal concentrations and other characteristics are given in the table (Table 1).

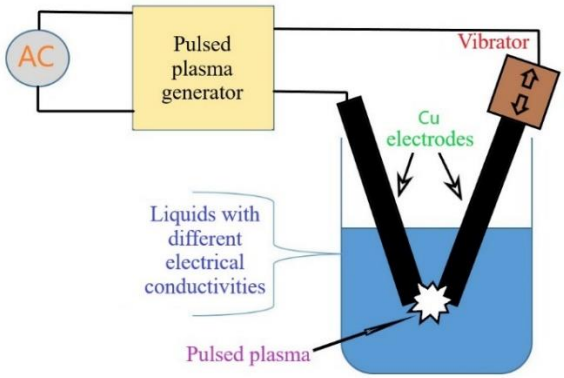

Fig. 1. Installation diagram for producing copper nanoparticles using pulsed plasma in liquid.

Table 1. Optimal characteristics of liquids for the synthesis of nanoparticles.

Temperature [^{0}C]		20	
Liquid	CH_3COOH (5%)	H_2O	NaOH (0,02%)
pH value	2,41	7	11,7
Temperature [^{0}C]		80	
Liquid	CH_3COOH (5%)	H_2O	NaOH (0,02%)
pH value	2,41	7	11,7

Copper wires (99,999 % purity) are used as the anode and cathode; solutions with different electrical conductivities are poured alternately into a heat-resistant glass, and nanoparticles are synthesized within a few hours. Syntheses at high temperatures were carried out in a water bath. When using distilled water, the synthesized nanoparticles are left to settle out of the liquids for some time, then they are separated from the water and dried. When using solutions of acid and alkali, the synthesized nanoparticles are left to settle out of the liquid for some time, then they are separated from the liquid, then distilled water is poured in and the process is repeated until the liquid is cleared of ions. An ion meter was used to test ion purification and only after purification were the nanoparticles dried.

A scanning electron microscope (JEOL, JSM- 7600F, Japan) and a stationary X-ray diffractometer (Rigaku, SmartLab, Japan) were used to determine the size and composition of the synthesized powders.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the synthesized samples at room temperature: a) vinegar solution (5%), b) distilled water, c) sodium hydroxide solution (0.02%); SEM images of the synthesized powders at room temperature: d) vinegar solution (5%), e) distilled water, f) sodium hydroxide solution (0.02%); Particle size distribution of the samples obtained by using the ImageJ program: g) vinegar solution (5%), h) distilled water, i) sodium hydroxide solution (0.02%).

In an experiment carried out at room temperature and in an acidic solution, it turned out that the composition of the synthesized powder was two-thirds copper(I) oxide, and the rest was metallic copper (Fig. 2a). The resulting powder was agglomerated in large quantities (Fig. 2d), but nano-sized sponge- and rod-shaped powders with an average size of 120 nm were also present (Fig. 2g). But in an experiment conducted in distilled water, the opposite was true: the composition of the synthesized powder consists of two-thirds metallic copper, and the rest is copper(I) oxide (Fig. 2b). The resulting powder did not undergo agglomeration (Fig. 2e), and nanosized powders were synthesized in a round shape with an average size of 60 nm (Fig. 2h). And in an experiment conducted in an alkaline environment, the composition of the synthesized powder consists of 78% copper metal, 12% copper(I) oxide, and additionally 10% copper(II) oxide was synthesized (Fig. 2c). The resulting powder was agglomerated in relatively small quantities (Fig. 2f), and nanosized powders were synthesized in needle-like, dendritic and sponge-like shapes with an average size of 80 nm (Fig. 2i).

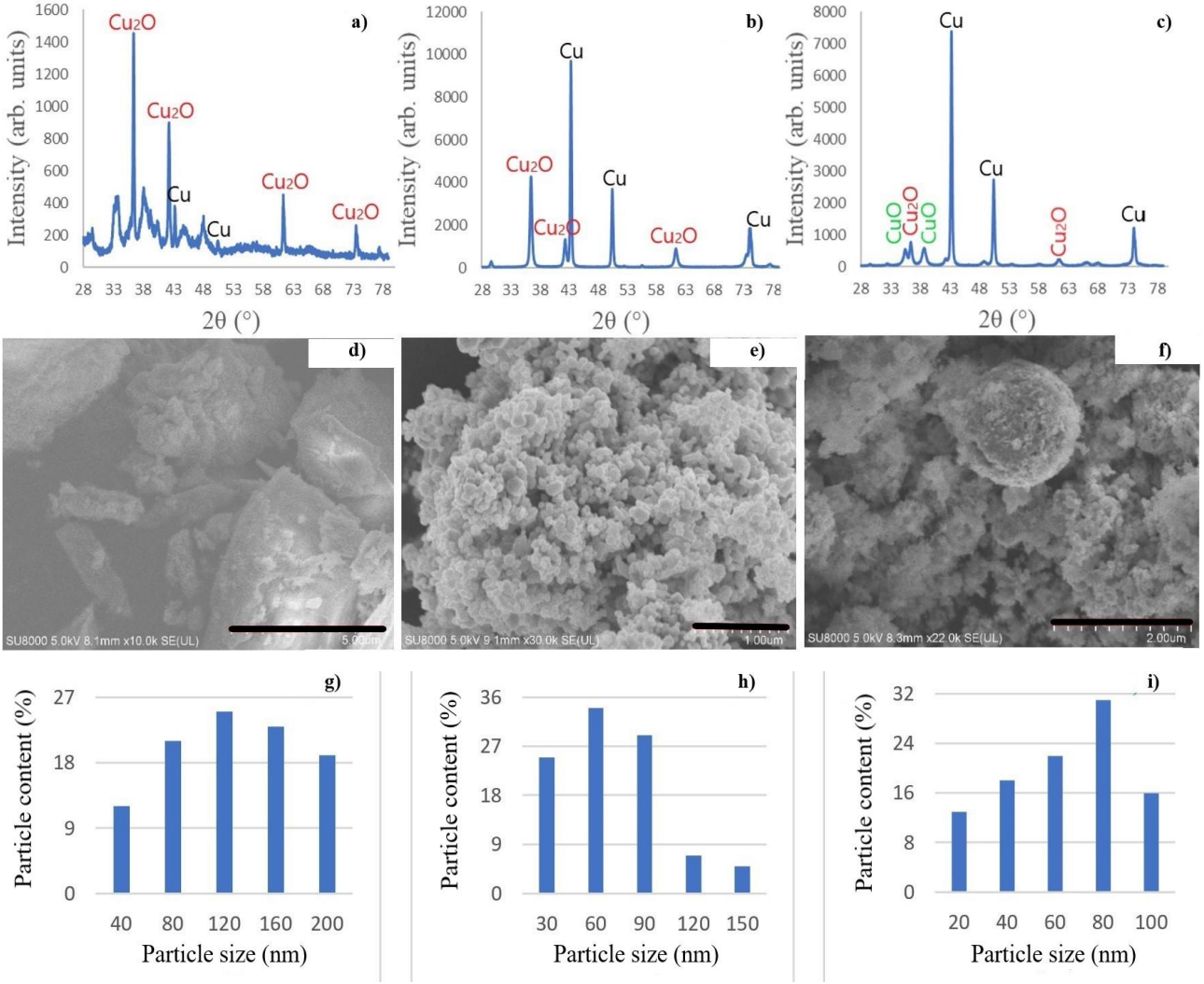

Fig. 3. XRD patterns of the synthesized samples at room temperature: a) vinegar solution (5%), b) distilled water, c) sodium hydroxide solution (0.02%); SEM images of the synthesized powders at room temperature: d) vinegar solution (5%), e) distilled water, f) sodium hydroxide solution (0.02%); Particle size distribution of the samples obtained by using the ImegeJ program: g) vinegar solution (5%), h) distilled water, i) sodium hydroxide solution (0.02%).

In an experiment conducted at a temperature of 80 ^{0}C and in an acidic solution, it turned out that the composition of the synthesized powder consists of almost 60% metallic copper, and the rest is copper(I) oxide (Fig. 3a). The resulting powder agglomerated in large quantities, as at room temperature (Fig. 3d), but there were also nano-sized powders of round and spongy shape that were less than 100 nm in very small quantities (Fig. 3g). And in the experiment conducted in distilled water, the composition of the synthesized powder is not similar to the experiment at room temperature and the powder consists of 79% metallic copper, 16.5% consists of copper(I) oxide and additionally synthesized 4.5% copper(II) oxide, which was not synthesized in the experiment performed at room temperature (Fig. 3b). The resulting powder partially underwent agglomeration (Fig. 3e), and nanosized powders of round and spongy shape with an average size of 60 nm were synthesized (Fig. 3h). And in the experiment conducted in an alkaline environment, the composition of the synthesized powder is almost similar to the experiment at room temperature and consists of 84% copper metal, 13% copper(I) oxide and 3% copper(II) oxide (Fig. 3c). The resulting powder was partially agglomerated in relatively small amounts (Fig. 3f), and nano-sized powders were synthesized in rod and dendritic shapes with an average size of 80 nm (Fig. 3i).

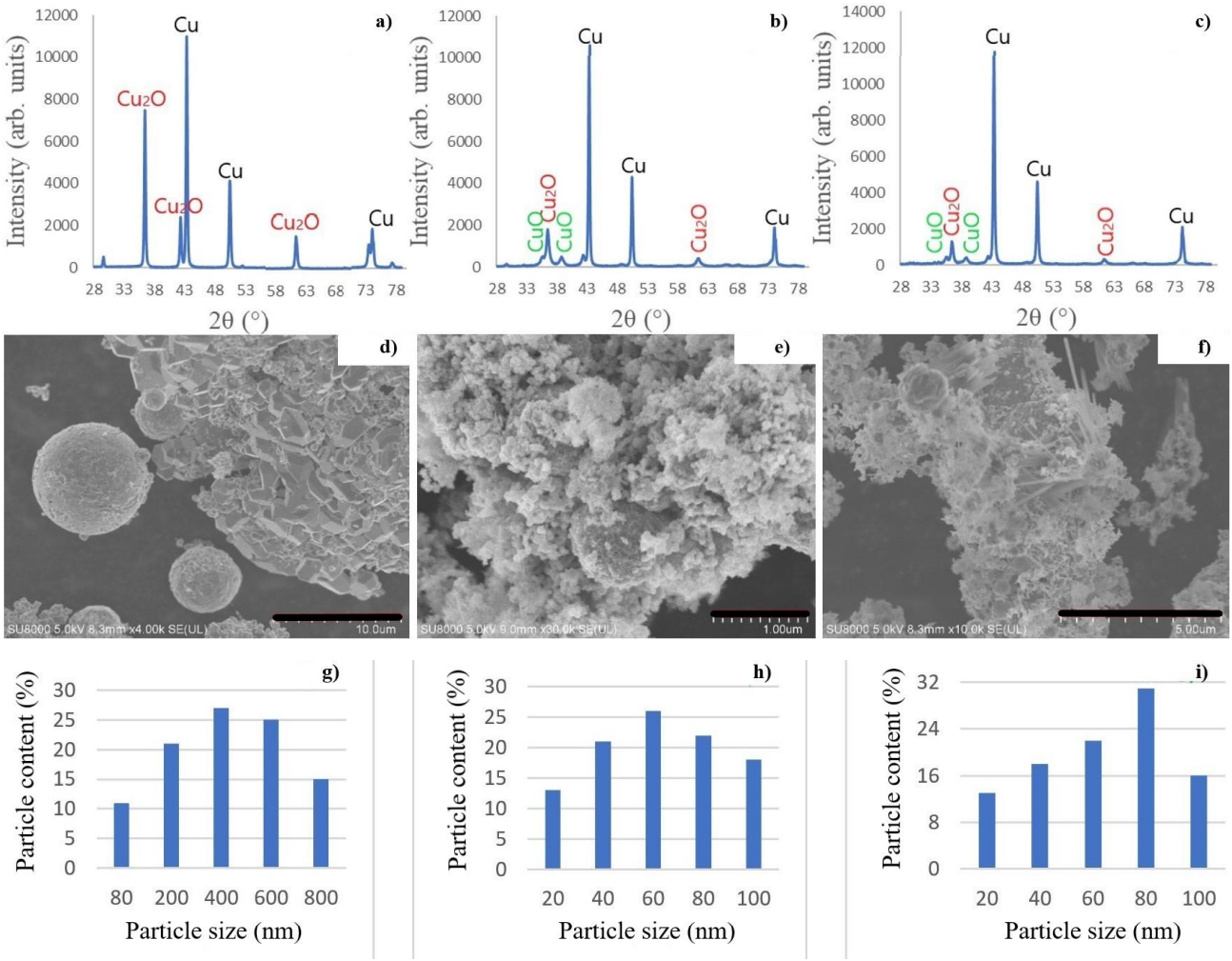

Fig. 4. XRD patterns of the synthesized samples at a temperature of 80 °C: a) vinegar solution (5%), b) distilled water, c) sodium hydroxide solution (0.02%); SEM images of the synthesized powders at a temperature of 80 °C: d) vinegar solution (5%), e) distilled water, f) sodium hydroxide solution (0.02%); Particle size distributions of the samples obtained by using the ImegeJ program: g) vinegar solution (5%), h) distilled water, i) sodium hydroxide solution (0.02%).

Table 2. Characterizations obtained using MDI Jade5 and ImageJ software for nanoparticles synthesized under specific conditions.

Temperature [^{0}C]	20			80		
Liquid	CH_3COOH (5%)	H_2O	NaOH (0,02%)	CH_3COOH (5%)	H_2O	NaOH (0,02%)
Average size of powders (nm)	120	60	80	400	60	80
Cu content (%)	34	63,7	78	58,5	79	84
Cu_2O content (%)	66	36,3	12	41,5	16,5	13
CuO content (%)	0	0	10	0	4,5	3

According to the data obtained using the MDI Jade5 program, in all samples the data on the species characteristics of the content of copper, monovalent, and divalent copper oxides turned out to be equally similar (Table 3).

Table 3. All parameters and characteristics of substances obtained using the MDI Jade5 program.

Substance	Density, g/cm^3	Lattice length, nm	Lattice type	Angles between the sides
Cu	8,95	a = 0,3615, b = 0,3615, c = 0,3615	cubic crystal lattice Fm-3m(225)	α = 90°, β = 90°, γ = 90°
Cu_2O	6,09	a = 0,4260, b = 0,4260, c = 0,4260	cubic crystal lattice Pn-3m(224)	α = 90°, β = 90°, γ = 90°
CuO	5,80-6,10	a = 0,4653, b = 0,3410, c = 0,5108	monoclinic crystal lattice (tenorite) C2/c(15)	α = 90°, β = 99,48°, γ = 90°

Under pulsed plasma conditions, distilled water undergoes electrolysis to form hydrogen (H^+) and hydroxide (OH^-) ions. These ions can participate in redox reactions with copper ions and other particles generated by the plasma. As shown in reactions 1 and 2, hydrogen and oxygen molecules can be synthesized from water molecules.

$$2H_2O \xrightarrow{\text{Electric discharge}} H_2O_2 + H_2 \qquad (1)$$

$$2H_2O_2 \xrightarrow{\text{Decomposition}} 2H_2O + O_2 \qquad (2)$$

Copper ions undergo reduction reactions facilitated by electrons from the plasma, leading to the nucleation and growth of metallic copper nanostructures. At the same time, oxygen-containing compounds formed as a result of water oxidation oxidize copper compounds, which leads to the formation of copper oxides as shown in reactions 3 and 4.

$$4Cu + O2 \xrightarrow{200°C} 2Cu_2O \qquad (3)$$

$$2Cu + O2 \xrightarrow{400°C} 2CuO \qquad (4)$$

As shown in Table 2 and the figures, many powder mixtures contain a greater proportion of copper metal than their oxides. This is explained by the reduction of the oxides with hydrogen, as shown in reactions 5 and 6. In powders containing both copper oxides, it can be noticed that the divalent oxide is always smaller than the monovalent oxide. This can be explained by the fact that the synthesis of divalent oxide requires more energy than monovalent oxide, and less energy is lost to reduce the divalent oxide with hydrogen.

$$Cu_2O + H_2 \xrightarrow{260°C} 2Cu + H_2O \qquad (5)$$

$$CuO + H_2 \rightarrow Cu + H_2O \qquad (6)$$

As shown in reactions 7 and 8, less energy is required to decompose a divalent oxide than a monovalent oxide.

$$2Cu_2O \xrightarrow{1800°C} 4Cu + O_2 \qquad (7)$$

$$4CuO \xrightarrow{1100°C} 2Cu_2O + O_2 \qquad (8)$$

The absence of copper(II) oxide in the experiment with a solution of acetic acid is explained by the fact that acetic acid can only react with copper(II) oxide, as shown in reaction 9. Moreover, it does not react with copper(I) oxide and with metallic copper itself. Sodium hydroxide in solutions is stable during electrolysis and does not react with copper and its oxides, at least in dilute solutions of sodium hydroxide.

$$CH_3COOH + CuO \rightarrow (CH_3COO)_2Cu + H_2O \qquad (9)$$

The best stabilizer turned out to be distilled water because the average particle size is relatively small, and then sodium hydroxide solution, while there was no big difference in the size of particle formation when the temperature of the medium changed. But in a solution of acetic acid, the particles began to agglomerate and a change in temperature, or rather an increase in temperature from 20 ^{0}C to 80 ^{0}C, gave a worse effect. Water molecules are adsorbed on the surface of copper

nanostructures and their oxides, affecting their surface chemistry, stability and reactivity. Hydration effects and the presence of water layers can change the surface properties of copper nanostructures and their oxides, affecting their interaction with surrounding ions or molecules and their catalytic activity. The dielectric properties of water also affect the distribution of electric fields and the behavior of charged particles in the plasma-liquid system. The viscosity and surface tension of water influence bubble formation, cavitation dynamics, and the structure of fluid flow caused by a pulsed plasma discharge. These hydrodynamic effects can influence the distribution of reactants, energy release, and mass transfer processes relevant to the formation of nanostructures. These surface modifications can influence the nucleation, adhesion, and growth processes during the formation of nanostructures and can lead to the formation of surface-modified copper nanostructures and their oxides with desired properties. Sodium hydroxide can also act as a stabilizing agent, preventing agglomeration or controlling the size distribution of copper nanostructures formed under pulsed plasma conditions.

Relatively crystallized nanoparticles were obtained from sodium hydroxide solution. Various types of nanorods are observed in the figures. Not clearly visible nanocrystals are observed in distilled water, but the resulting nanopowders turned out to be stable. The resulting crystals in a solution of acetic acid turned out to be crystalline, but unfortunately, the size turned out to be large.

4. CONCLUSIONS

An experiment was conducted to synthesize nanoparticles using different solutions such as distilled water, acetic acid, and sodium hydroxide under different temperature conditions. To analyze the synthesized nanoparticles, methods such as X-ray diffractometry and scanning electron microscopy were used. The results confirmed that the particles were predominantly in the nano range and were identified as Cu, Cu_2O, and CuO. The study found that distilled water and sodium hydroxide lead to little particle agglomeration and a relatively large portion of the powder consists of stable nanoparticles, while acetic acid leads to particle agglomeration, especially at higher temperatures. The mechanisms of synthesis and the chemical reactions involved in the synthesis process are presented, in particular the reduction of copper ions to metallic copper and the oxidation of copper compounds to form copper oxides. The study made observations regarding the morphology of the synthesized nanoparticles, such as the formation of nanorods in sodium hydroxide solution and larger but different crystals in acetic acid solution.

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