

PLASMA SYNTHESIS AND TREATMENT OF COPPER-BASED NANOPOWDERS

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Abstract

Cu-based nanoparticles with different morphologies were prepared via submerged electrical discharge of bulk copper and graphite electrodes in a CuCl₂ aqueous solution. The synthesized material was subjected to laser-induced modification. The influence of discharge parameters and electrode composition on the morphology and composition of final products were investigated by transmission electron microscopy (TEM), X-ray diffractometry (XRD), and UV-Vis spectroscopy. It was found that core-shell nanoparticles were formed by the treatment of a CuCl₂ aqueous solution by the arc pulsed discharge with a pulse duration of 4 ms and a peak current of 10 A. Irradiation of nanoparticles in an aqueous solution by a pulsed Nd:YAG laser at 532 nm was shown to cause the shape change and size reduction of the particles. The possible formation mechanism of Cu-based nanoparticles is proposed.

1. Introduction

For any application of nanoparticles to be commercially viable, low-cost production methods must be developed. A low-temperature and non-vacuum synthesis of nanoparticles via discharge in liquid (submerged discharge) provides a versatile choice for economical preparation of various nanostructures in a controllable way. An arc discharge in liquid nitrogen has firstly been reported as a cost-effective technique for the production of carbon nanotubes in 2000 by Ishigamy et al. [1]. Since that time, many efforts have been made to develop this method. Sano et al. proposed to submerge electrodes in water instead of liquid nitrogen [2, 3]. They reported synthesis of carbon onions [2, 3] and single-walled carbon nanohorns (SWNHs) [4, 5]. In the latter case, carbon nanoparticles were produced via discharge in water method with the support of gas injection. Parkansky et al. reported the synthesis of nanoparticles via a pulsed arc submerged in ethanol. Ni, W, steel and graphite electrodes were used [6, 7]. The particle composition varied from carbon to pure metal including various intermediate combinations of these materials. Bera et al. employed an arc-discharge in a palladium chloride solution method to produce carbon nanotubes decorated with *in situ* generated Pd nanoparticles [8]. It is important that the synthesized material contained no chlorine.

Numerous studies focused on the synthesis of metal-containing carbon nanocapsules (CNCs) via submerged discharge method [3-5, 9, 10]. Due to the carbon sheets surrounding the metal core, the CNCs are protected from the environment and from degradation. The carbon coatings mean that nanoparticles are biocompatible and stable in many organic media. Thus, carbon encapsulated nanoparticles are candidates for bioengineering application, high-density data storage, magnetic toners for the use in photocopiers [11, 12]. The metal contain-

ing carbon nanostructures were prepared by using the electrode from mixture of graphite and metal precursor [10, 13]. Recently, Xu et al. demonstrated a possibility to synthesize Ni-, Co-, and Fe-containing CNCs by an arc discharge between carbon electrodes in aqueous solution of NiSO_4 , CoSO_4 , and FeSO_4 , respectively [14]. In contrast to the data reported by Bera et al., the synthesized material consisted of O and S due to SO_4^{2-} ionic precursors in the solution. Since the metal core-forming material was supplied by liquids, the production rate of CNCs was limited by the salt concentration [8]. This restriction may cause a limit to apply the submerged discharge method to large-scale production of CNCs.

In this paper, Cu-based nanoparticles were prepared via submerged discharge of bulk copper and graphite electrodes in a copper chloride (CuCl_2) aqueous solution. Thus, the material of copper electrode, as well as Cu from the solution, was supposed to be incorporated into the resulting nanoparticles. The effect of discharge parameters and electrode composition on the morphology and composition of final products was investigated. Additionally, synthesized material was modified by laser irradiation. The changes in the morphology and composition of nanoparticles were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV-Vis spectroscopy.

2. Experimental

2.1. Synthesis of nanoparticles

The experimental setup for nanopowder synthesis is schematically shown in Fig. 1. It consisted of four main components: a power supply system, electrodes, a cell (glass beaker), and a chilling loop. A pulsed discharge was generated between copper and graphite electrodes being immersed to a depth of 3 cm in 100 ml of aqueous solution of CuCl_2 (0.001 M). A graphite rod (diameter of 6 mm) and a copper bar (2 mm x 4 mm cross section) were used as electrodes. An optimum distance between the electrodes was kept constant at 0.3 mm to maintain a stable discharge. The discharge was initiated by applying a high-frequency voltage of 3.5 kV. The power supply system gives the possibility to maintain several different types of pulsed discharge. One of them is the arc discharge and the second is a spark discharge. Both direct current (dc) and alternating current (ac) pulsed discharges were generated with repetition rates of 100 and 50 Hz, respectively. Current $I(t)$ was recorded during the discharge as a function of time by means of an oscilloscope. The peak current of the arc discharge was 10 A with a pulse duration (full width at half maximum; FWHM) of 4 ms. The peak current of the pulsed spark discharge was 60 A with a pulse duration (FWHM) of 30 μs .

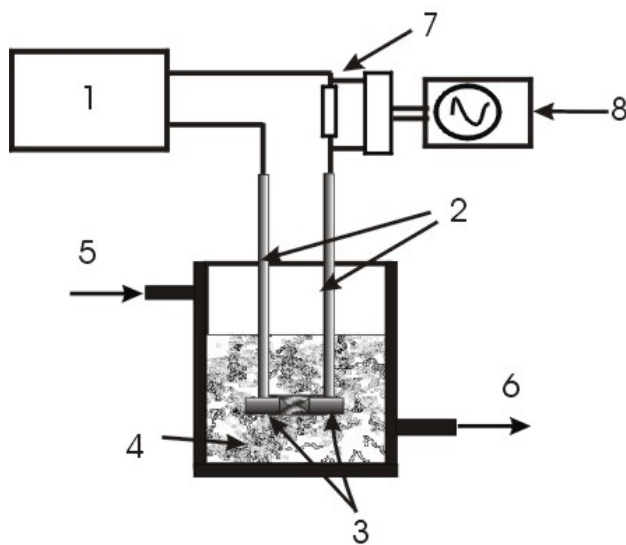


Fig. 1. Schematic diagram of the setup for nanopowder synthesis by submerged discharge method; (1) power supply; (2) electrode holders; (3) electrodes; (4) liquid; cooled water (5) in and (6) out; (7) current sensor; and (8) oscilloscope.

2.2. Laser induced modification

After completion of the discharge, 5 ml of thus obtained suspension was subjected to laser-induced modification. The solution in an cuvette was illuminated for 3 min by the output of the second harmonic (532 nm) of a Nd:YAG laser (LOTIS TII, LS2134) operating at 10 Hz. The laser irradiation fluence was 0.2 J/cm^2 .

2.3. Physical characterization of nanoparticles

Most of the synthesized products were obtained as suspended powders. Two kinds of the samples were studied: suspensions and dry powders. The suspended nanoparticles were investigated by UV-Vis spectroscopy and TEM. These samples were prepared by discharge treatment of CuCl_2 solutions for 1 min. Two milliliters of suspension were used for the measurement of absorption spectra. The spectra were recorded by an UV-Vis spectrometer (Carry-500 Scan) in a range of 200-800 nm.

The suspended nanoparticles were characterized by transmission electron microscopy (TEM) for their size and morphology. A small quantity of liquid was removed from the top of the Petri dish using a pipette and transferred to an amorphous carbon coated Cu grid used for TEM. Transmission electron microscopy was performed using a LEO 906E (LEO, UK, Germany) microscope operating at 120 kV.

Five milliliters of each suspension were used to be modified by laser irradiation. Laser-induced morphology changes of suspensions were investigated by TEM and UV-Vis spectroscopy.

Powder samples were obtained by discharge treatment for 10 min. After a short pre-sedimentation time (ca. 1 min), solid deposits sunk at the vessel bottom. To separate the suspended nanopowder from the sediment, the discharge-treated liquid was carefully poured in a Petri dish excepting last 10 ml with a solid sediment. The remained liquid was allowed to evaporate at room temperature for several days. The residue was collected after the liquid evaporated and examined by XRD. The composition of synthesized samples and their crystal-line structure were characterized by using X-ray diffraction at CuK_α (D8-Advance, Brüker, Germany). Semi qualitative analysis was performed with Diffrac Plus EVA in combination with PDF-2 database and Diffrac Plus TOPAZ.

3. Results and discussion

Six types of nanoparticle suspension were prepared under different discharge parameters. The synthesis parameters are summarized in Table 1. We can see that the weight change of each electrode was generally higher, when a spark discharge was generated. The anode consumption rate was higher than that of cathode irrespective of discharge type and electrode material. However, in contrast to the literature data [15], there was no cathode gain in weight. As a general trend, the nanopowder synthesis rate was higher for spark discharge than that of arc discharge. It may be explained by the difference in current value [16].

For both arc and spark discharges, it was found that the synthesis rate was higher when copper was acting as an anode. There is a discrepancy between nanopowder synthesis rate and material consumption rate. The values of discrepancy D listed in Table 1 were calculated as follows

$$D(\%) = \frac{R_{syn}}{R_{Cu} + R_C} \cdot 100. \quad (1)$$

Here R_{syn} is the synthesis rate of nanopowder, R_{Cu} is the consumption rate of copper electrode, and R_{C} is the consumption rate of the graphite electrode. The discrepancy D depended on discharge parameters. For ac-discharges, the value of discrepancy was higher for a spark discharge than that for an arc discharge. For dc-discharges, this trend remained if the polarity of electrodes was taken into account. It is worth noticing here that the discrepancy between the material consumption rate and the nanopowder synthesis rate may be caused not only by separation of sediment fraction but by the reaction of carbon atoms with water resulting in the production of gaseous compounds [3]. This coincides with the fact that the largest discrepancy (more than 80%) was observed in the sample with the largest graphite electrode consumption rate (sample 3).

Table 1. Summary of nanopowder synthesis parameters.

№	Type of discharge; peak current, pulse duration	Electrodes material	Electrode consumption rate, (R_{Cu} and R_{C}), mg min^{-1}	Synthesis rate, (R_{Syn}), mg min^{-1}	Discrepancy between the synthesis rate and material consumption (D), %
1	ac ¹⁾ spark; 60 A, 30 μs	Cu	6.7	5.9	49
		C	4.8		
2	ac arc; 10 A, 4 ms	Cu	1.2	2.5	34
		C	2.6		
3	dc ²⁾ spark; 60 A, 30 μs	Cu (cathode)	4.7	2.1	81
		C (anode)	6.1		
4	dc spark; 60 A, 30 μs	Cu (anode)	6.6	6.9	38
		C (cathode)	4.6		
5	dc arc; 10 A, 4 ms	Cu (cathode)	1.1	1.9	47
		C (anode)	2.5		
6	dc arc; 10 A, 4 ms	Cu (anode)	2.8	3.3	33
		C (cathode)	2.1		

¹⁾ Alternating current pulsed discharge.

²⁾ Direct current pulsed spark discharge.

The aqueous solutions of CuCl_2 were discharge-treated for only 20 s to obtain yellowish suspensions. The transparency of the suspensions decreased with time during the discharge treatment. The liquids turned to dark yellow after treatment by ac-discharge for 10 min. The suspensions resulting from dc-discharge treatment were conspicuously darker when the C electrode was acting as an anode. The nanoparticle suspensions produced by spark and arc discharges were dark brown and dark grey, respectively. It might be due to the presence of relatively large amount of carbon particles in suspension (see Table 1). The dc-discharge treated solutions were olive-green when Cu was used as the anode electrode. Yellow or green colour of suspension may indicate the oxidation of copper nanoparticles [17]. The presence of Cu_2O nanoparticles was further confirmed by XRD analysis. No changes in colour were observed after laser irradiation of suspensions.

Figure 2 shows the absorption spectra of as prepared (a) and laser irradiated (b) suspended nanopowders synthesized by discharge treatment of an aqueous solution of CuCl_2 (2) for 1 min. The spectra were corrected to the contributions of solvents. The optical density increased with decreasing wavelength. Generally, the optical density of suspensions prepared by spark discharge was higher than that of suspension prepared by arc discharge. This is consistent with the fact that the nanoparticle production rate was higher when the solution was treated by a spark

discharge. In a spectral range of 200–500 nm, the optical density of the samples 1, 4, and 6 was higher than that of samples 2, 3, and 5. This seems to suggest that the main parameter in determining the optical properties of suspensions was concentration of Cu-based nanoparticles. For samples number 1 and 4, a weak absorption peak was observed at a very short wavelength. According to the literature data [18, 19], a surface plasmon peak at a wavelength of 289 nm may be attributed to the presence of very small separated Cu nanoparticles (<4 nm). Though TEM examination confirmed the presence of small nanoparticles in sample 1, there were no nanoparticles with diameter less than 4 nm in sample 4. Moreover, there were no copper nanoparticles in sample 1 as revealed by the XRD (see below). More likely, the existence of a weak absorption peak at 280 nm implied the formation of liquid byproducts.

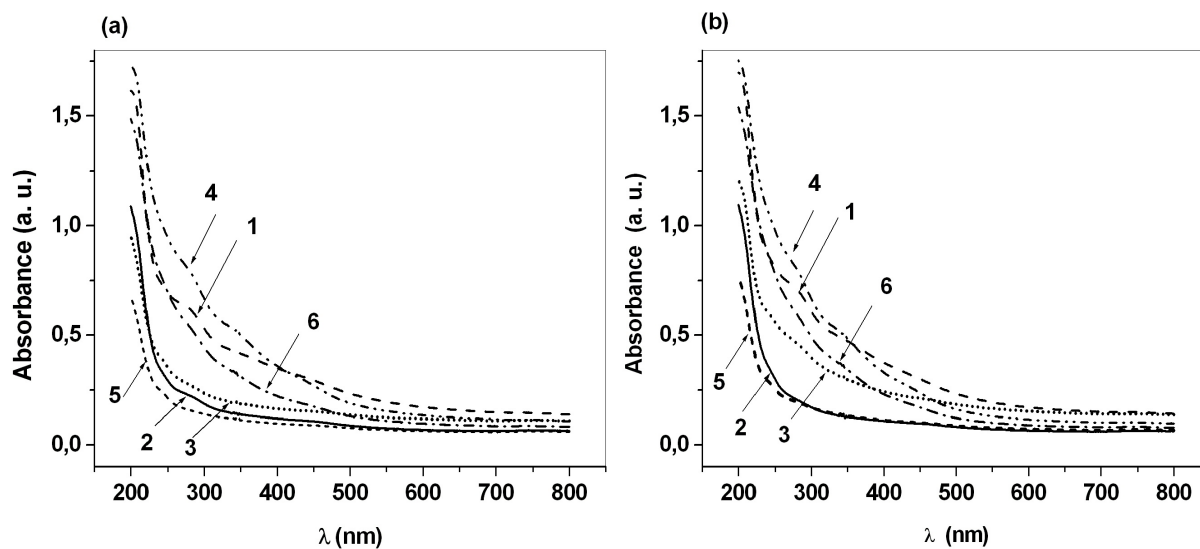


Fig. 2. Absorption spectra for the as-prepared (a) and laser modified (b) suspended nanoparticles produced by ac- (1, 2) and dc- pulsed discharges (3-6). The following electrode pairs were used: Cu and C for the ac-spark (1) and ac-arc (2) discharges; Cu as a cathode electrode and C as an anode electrode for the dc-spark (3) and dc-arc (5); Cu as an anode electrode and C as a cathode electrode for the dc-spark (4) and dc-arc (6).

We did not observe a surface plasmon band around 570 nm in the absorption spectra. The absence of the plasmon band can be explained by copper oxidation on the particle surface [18]. This suggestion was further confirmed by XRD analysis (see below). The suspensions exhibited the same colours after laser irradiation, but absorption intensity increased for samples 3 and 1 and to a less extent for sample 5, as illustrated in Fig. 2b. TEM analysis revealed the morphological similarity of irradiated samples 1, 3, and 5 (see below).

Figure 3 depicts the corresponding TEM images for the suspensions shown in curves 1-6 of Fig. 2. Parts (a) and (b) represent the TEM views of the as-prepared and irradiated samples, respectively. Three distinct structures were observed: dark small spherical particles, dark particles surrounded by gray shell, and gray flake-like structures with diffuse contours. The small dark particles with a diameter of 2-5 nm were observed in samples 1, 2, 3, and 5 (marked with black ellipses in Fig. 3). Some dark particles, appreciable when using ac spark discharge for synthesis, were bigger than 20 nm, indicating coalescence. The nanoparticles synthesized by ac arc discharge (sample 2) were surrounded by the arrowed gray regions, which were probably carbon shells, as shown in Fig. 3a. As we did not have any direct evidence that the shells consisted of carbon, these nanostructures will be referred to as core-shell nanoparticles. The core-shell nanoparticles were also observed in a colloid prepared by a dc

arc discharge between the copper cathode and the graphite anode (sample 5). We can see that core-shell nanoparticles ranged from 20 to 50 nm in diameter, while the cores within the nanoparticles varied from 8 to 25 nm. The cores were non-spherical. They seemed to be composed of small particles clustered together. The flake-like structures with diffuse contours were 50 nm in size. They were observed in all samples. Samples 4 and 6 consisted mostly of a structure with diffuse contours. On the basis of the above observations, the ac arc discharge and dc arc discharges with copper anode electrode seem to be more suitable for synthesis of nanoparticles with core-shell structure.

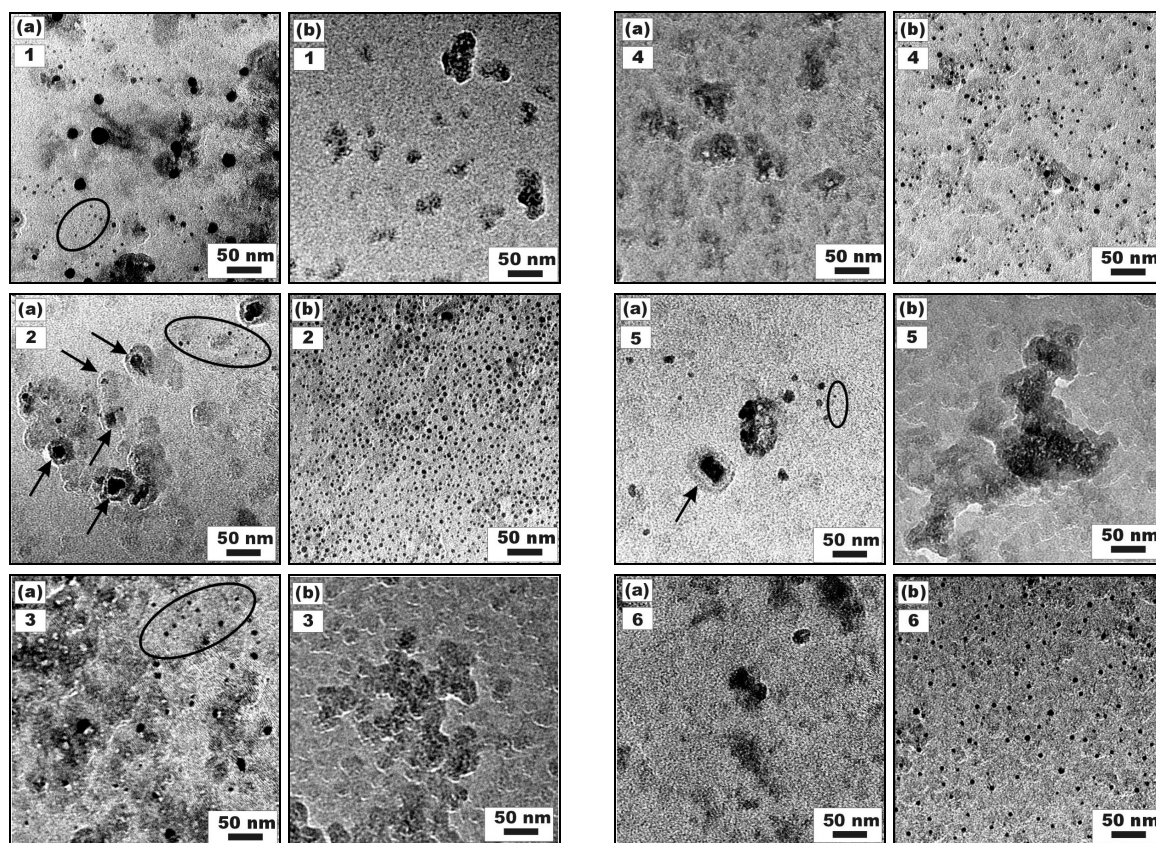


Fig. 3. TEM images of nanoparticles from as-prepared (a) and irradiated (b) suspensions produced by ac- (1, 2) and dc- pulsed discharges (3-6). The following electrode pairs were used: Cu and C for the ac-spark (1) and ac-arc (2) discharges; Cu as a cathode electrode and C as an anode electrode for the dc-spark (3) and dc-arc (5); Cu as an anode electrode and C as a cathode electrode for the dc-spark (4) and dc-arc (6).

It is clearly seen that many smaller particles with sizes around 2-7 nm were generated after the irradiation of samples 2, 4, and 6. The particles larger than 10 nm completely disappeared. The micrograph revealed that, after the irradiation, these suspensions consisted of particles with circular cross-sections, whereas, before the irradiation, the particle shape was not spherical. The nanoparticles were dispersed very well. No small nanoparticles were observed in suspensions 1, 3, and 5 after the irradiation. Though, as can be seen by comparing images of samples 1(a), 3(a), and 5(a) with images 1(b), 3(b), and 5(b), the shape of nanoparticles changed after the irradiation. The laser induced morphology change may occur through heating of the nanoparticles because of the absorption of the laser light [20]. According to the mechanism proposed by Takami et al. [20], the morphology of irradiated nanoparticles was

determined by the relationship between temperature of nanoparticles, their melting point and boiling point. The laser induced change in shape and size occurred, if the temperature of nanoparticles was at the boiling point. If the temperature was lower than the melting point, no changes took place. If the temperature was between melting point and boiling point, only the change in shape occurred. Thus, the difference in the morphology of the irradiated samples can be attributed to the difference in their composition. Even being irradiated with the same laser light intensity, the nanoparticles of different composition changed their morphology in different ways, as they have different melting and boiling points.

X-ray diffraction data were collected to identify synthesized samples. The XRD patterns of synthesized samples are shown in Fig. 4. The diffraction peaks at 43.2° and 50.3° correspond to the formation of face-centered-cubic Cu. There are three diffraction peaks with 2θ values of 36.5° , 42.3° , and 61.4° , which can be assigned to the primitive cubic Cu_2O . In addition, there are two peaks at 24.0° and 26.5° , which can be assigned to the hexagonal C. XRD revealed that discharge treatment of aqueous solution of CuCl_2 led to the formation of $\text{Cu}_2(\text{OH})_3\text{Cl}$ and Cu_2OCl_2 because of a strong affinity between chlorine and the metal (peaks with a value of 2θ around 16.5° , 19° , 31° , 32.3° , 32.7° , 33.0° , 38.7° , 39.8° , 40.1° , 50.3° , 50.5° , 53.8° , 17.8° , and 36.0° , respectively). For comparison, the XRD patterns of initial solution of CuCl_2 are also plotted at the top of Fig. 4. The non-treated aqueous solution of copper chloride was allowed to evaporate and then analyzed by XRD. The diffractogram of this sample showed peaks at 2θ around 16.2° , 22.0° , 24.0° , 26.7° , 28.9° , 32.8° , 34.0° , 34.8° , 35.2° , 40.9° , 43.0° , 44.8° , 45.3° , 49.0° , and 57.3° which are characteristic of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. As we can see in Fig. 4, the synthesized powder was a complex mixture comprising no CuCl_2 .

XRD data were used to semi-quantitatively determine the percentage of constituents. The semi-quantitative analysis of phase composition is shown in Table 2. The nanopowder composition was strongly dependent on the synthesis parameters. It should be noted that metallic copper was only formed by discharge treatment, when copper was acting as an anode electrode (samples 4 and 6). The synthesized material contained copper mostly in form of oxide (Cu_2O), copper hydroxychloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$), and copper oxychloride (Cu_2OCl_2). The difference in Cu_2O and C contents among all samples was significant. Samples 2 and 5 contained no copper oxide, while sample 6 had the largest percentage of copper oxide (about 80 vol %). On the other hand, sample 6 contained no carbon. The carbon content in sample

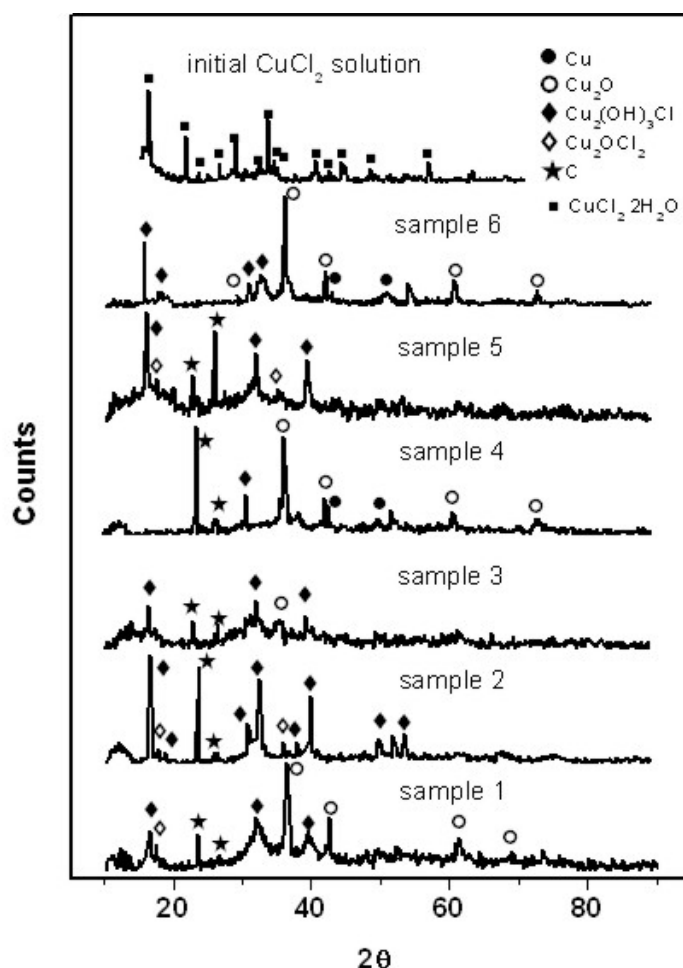


Fig. 4. XRD patterns of synthesized samples and initial CuCl_2 aqueous solution.

4 exceeded 80 vol %. The quantities of $\text{Cu}_2(\text{OH})_3\text{Cl}$ in samples ranged from less than 2 vol % to ~30 vol %. Only three samples contained Cu_2OCl_2 (samples 1, 2 and 5). The maximal amount of Cu_2OCl_2 detected by XRD corresponded to ~30 vol %. In spite of high copper electrode consumption rate, sample 4 contained unexpectedly small quantities of Cu and Cu-containing compound. It might be due to the formation of relatively large and heavy copper microparticles. They precipitated from colloid quickly after the synthesis. Therefore they were not collected and analyzed by XRD (see experimental section). A correlation was observed between the low copper electrode consumption rate and the absence of Cu and Cu_2O fractions in nanopowder composition (samples 2 and 5).

Table 2. Semi-quantitative analysis of synthesized powder by XRD.

№	Type of discharge; peak current, pulse duration	Electrodes material	XRD-analysis				
			Cu, vol %	Cu_2O , vol %	C, vol %	$\text{Cu}_2(\text{OH})_3\text{Cl}$, vol %	Cu_2OCl_2 , vol %
1	ac ¹⁾ spark; 60 A, 30 μs	Cu	-	13.5	40.3	16.5	29.7
		C					
2	ac arc; 10 A, 4 ms	Cu	-	-	64.6	30.0	5.4
		C					
3	dc ²⁾ spark; 60 A, 30 μs	Cu (cathode)	-	39.1	37.0	23.9	-
		C (anode)					
4	dc spark; 60 A, 30 μs	Cu (anode)	7.8	8.3	82.5	1.4	-
		C (cathode)					
5	dc arc; 10 A, 4 ms	Cu (cathode)	-	-	33.9	33.6	32.5
		C (anode)					
6	dc arc; 10 A, 4 ms	Cu (anode)	7.4	77.5	-	15.1	-
		C (cathode)					

¹⁾ Alternating current pulsed discharge.

²⁾ Direct current pulsed spark discharge.

It should be emphasized that the core-shell structures were observed only for samples 2 and 5. Taking into account, firstly, that samples 2, 5, and 6 were prepared by an arc treatment, secondly, that sample 6 contained no C and assuming that the shells consisted of carbon, we can suggest that arc discharge was more suitable for synthesis of core-shell nanoparticles. On the other hand, the chemical composition of the final product was governed by different competing reactions. As they have different equilibrium constants, they can form a network, where the ratios of the products are sensitive to concentrations of each of the many components. Therefore the slight difference in initial concentration might result in a significant difference in the composition and morphology of the synthesized material (compare samples 5 and 6).

Although the exact mechanism for formation of nanoparticles via discharge in solution process is not clear, the following possibility may be considered. During discharge treatment of the liquid, the copper and graphite electrodes were heated, melted, and vaporized in the region of the discharge generated. In the vicinity of electrodes, the liquid was also vaporized rapidly due to the extremely high temperature. Hence, the plasma region produced by the discharge adjacent to the electrodes was surrounded by a gas bubble. Following [3], the gas mixture may comprise CO and H_2 formed as follows:



This reaction might cause the discrepancy between the electrode consumption rate and the nanopowder synthesis rate, since some of carbon atoms formed gaseous CO. Sano et al. re-

ported that gas bubbles did not comprise water vapor since no condensation occurred [3]. However, we should consider that water vapour also existed in the discharge zone, as we did not obtain any evidence of its absence.

Copper chloride is an anionic compound that dissociates in an aqueous solution and can form different ionic species, such as Cu^{2+} and Cl^- or complex ions, such as CuCl_2^- , CuCl_3^{2-} , and CuCl_4^{2-} [21]. The reduction of copper ions into copper atoms likely took place in the plasma region during discharge treatment of the liquid as shown in Eq. 3



As the temperature in the vicinity of the electrodes was estimated to be around 4000 K [3], the thermal decomposition of complex ions to metallic copper possibly took place in the discharge zone (Eqs. (4)-(6))



The nanoparticles were then formed from a complex gas mixture through different transformation stages, namely nucleation, growth, condensation, and coalescence. Both evaporated copper from electrode and Cu produced by reduction of ions from solutions were supposed to be incorporated into the resulting nanoparticles. Since water vapor existed in gas bubbles, the copper nanoparticles were easily oxidized. The reduction of copper oxide by carbon monoxide and hydrogen was possible in the subsequent step (Eqs. (7) and (8)).



According to the XRD measurements (see Table 2), copper oxide was only partially reduced into copper in samples 4 and 6. The data of XRD analysis implied also a reaction of chlorine with copper and/or copper oxide to form $\text{Cu}_2\text{Cl}(\text{OH})_3$ and Cu_2OCl_2 . These reactions might involve hydrogen produced via reaction (2).

It should be noted that there was no direct evidence to support the above-mentioned formation sequence, and the true mechanism may be more complicated.

4. Conclusions

Powders of Cu-based nanoparticles with different contents of copper, copper oxide, copper hydroxychloride, copper oxychloride, and carbon were produced via submerged electrical discharge of bulk copper and graphite electrodes in a CuCl_2 aqueous solution. The synthesis rate varied in a range of 1.9–6.9 mg min^{-1} depending on peak current and pulse duration of discharge as well as the polarity of copper and graphite electrodes. The synthesis rate was found to be higher when copper was acting as an anode electrode. The synthesis rate increased with increasing discharge current and decreasing pulse duration. The composition and morphology of nanoparticles were also found to depend on discharge parameters. The copper nanoparticles were only formed by dc-discharge treatment, when copper was acting as an anode electrode. Three distinct structures were observed: dark small spherical particles, dark particles surrounded by gray shell, and gray flake-like structures with diffuse contours. The maximum diameter of nanoparticles did not exceed 50 nm, while the minimum diameter was around 2 nm. An arc pulsed discharge with a pulse duration of 4 ms and a peak current of 10 A was found to be suitable for the synthesis of core-shell nanoparticles. TEM study revealed that irradiation of nanoparticles in an aqueous solution by a pulsed Nd:YAG laser at 532 nm can serve a method for changing the shape and reducing the size of nanoparticles.

Acknowledgements

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