RESEARCH ARTICLE

Investigation of Parameters Effect on the Size and Morphology of Copper Nanoparticles using Various Reducing Agents

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ABSTRACT

Copper nanoparticles are widely used in various industries and products. Size and morphology are two important parameters to determine nanoparticle properties. In this study, copper nanoparticles were synthesized without an inert environment using two different reducing agents namely ascorbic acid and sodium hypophosphite. Various capping agents (PVP 10^5, PVP 4×10^4, PEG 6000, SDS, CTAB and glycerol) were used as stabilizers. The effect of several parameters including reducing agent concentration, type and amount of stabilizer and precursor concentration on the size and stability of the resulting nanoparticles have been investigated. The synthesis experiments have resulted in a 25-60 nm average size of nanoparticles based on the synthesis conditions, the stabilizer type and concentration. Also, this research provides a fast and simple way for the synthesis of stable pure colloidal copper nanoparticles in polyol, which is accomplished by decreasing $CuSO_4.5H_2O$ using sodium hypophosphite in glycerol, without inert and homogeneous medium and non-agglomeration, 25 nm copper nanoparticles were obtained. The as synthesized copper nanoparticles are characterized using scanning and transmission electron microscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and dynamic light scattering techniques.

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INTRODUCTION

Copper nanoparticles have attracted many research activities due to special properties such as thermal and electrical conductivity, catalytic, optical and antimicrobial properties. Also, copper nanoparticles are considered as an alternative for gold and silver in many applications due to lower price. Various synthesis techniques are used to prepare copper nanoparticles [1]. Physical methods such as laser ablation [2], vacuum vapor deposition [3] and mechanical milling [4] usually require either high vacuum or expensive equipment, which make them uneconomical. Various chemical methods have also been developed such as chemical reduction [5, 6], micro-emulsion [7], hydrothermal [8], microwave-assisted reduction [9], etc. [10]. The chemical reduction method is the simplest and the most commonly used technique for the synthesis of copper nanoparticles in which, a reducing agent such as hydrazine, etc. is used to reduce a copper salt. Thus, production of nano-sized copper particles with proper control over morphology and size is achieved by manipulating parameters such as temperature, concentration and rate of reactants addition [11-13].

Since nanoparticle properties such as catalytic activity, mechanical behaviour and magnetic properties depend on their size and morphology, it is very important to control the size, surface characteristics, internal structure and chemical composition [14]. The optimization

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of chemical reactions is performed through controlling temperature, surfactant and precursor concentration and solvent type in order to achieve a narrow particle size distribution [10].

Due to higher reactivity of copper in comparison with noble metals, the potential of oxidation into CuO (black) or Cu_2O (red or yellow) during or after precipitation is inevitable [15], facing synthesis procedure with serious challenges. Many studies have utilized inert environments for the synthesis of copper nanoparticles [16]. Another way is using of capping agents or surfactants. However, capping agents may cause surface deactivation or interference with the properties in special applications [17]. Also, some capping agents are toxic and uneconomical and making the production costly and risky [10].

In this synthesis, copper nanoparticles are synthesized with a nontoxic and green approach for the first time in glycerol as solvent and using ascorbic acid as a reducing agent. Two reducing agents of ascorbic acid and sodium hypophosphite were used to synthesize Cu nanoparticles using $CuSO_4.5H_2O$ in the atmosphere. Glycerol, SDS, CTAB, PVP (Mw =4×10^4 and 10^5) are used as stabilizers. Size and stability of the as-synthesized nanoparticles were investigated by various parameters such as precursor concentration, reducing agent to precursor molar ratio, type and concentration of the surfactant. Based on the results, the stabilizer type and its concentration and also reducing agent and precursor greatly influence the oxidation of copper nano-crystals.

MATERIALS AND METHODS

Materials

Ascorbic acid ($C_6H_8O_6$) and sodium hypophosphite monohydrate ($NaPO_2H_2.H_2O$) as reducing agents, Copper sulfate ($CuSO_4.5H_2O$) as copper precursor and PVP 10^5, PEG 6000, SDS, CTAB and glycerol were supplied by Merck Co and used without further purification. PVP 4×10^4 was supplied by Sigma-Aldrich Co. Deionized water is also used for the preparation of solutions in experiments.

Synthesis Procedure

Three main components of salt precursor, reducing and stabilizing agents are involved in the chemical reduction method. Synthesis conditions for all tests with both reducing agents are given in Tables 1 and 2. In case of ascorbic acid as the reducing agent, effect of stabilizer concentration and also the amount of precursor have been investigated. As an example, in synthesis 1 (Table.1), 50 ml of the aqueous solution of ascorbic acid containing PVP 10^5 was placed in a paraffin bath on heater stirrer at a constant temperature of 85°C.

The aqueous solution of copper sulfate (50 ml) was added to the reducing agent solution at a constant rate of 30 drops per min while vigorously stirring [14]. By adding the precursor, the color turns into light red showing the formation of copper nanoparticles (Fig.1.a).

In case of sodium hypophosphite as reducing agent, various experiments were done to evaluate the effect of reducing agent concentration and the amount and also type of surfactant. The temperature was fixed at 91°C. For example, in synthesis 14 (Table 2), 50 ml of a 0.8 molar aqueous solution of reducing agent containing 0.144 g SDS was stirred in a paraffin bath at constant temperature. Copper sulfate solution was previously heated with 0.2 molar concentrations (50 ml) and added rapidly. Fig. 2 shows color change of the reaction mixture.

Table 1. List of experiments performed with ascorbic acid as a reducing agent.

Test no.	Stabilizer	Reducing agent/precursor molar ratio	Stabilizer/precursor molar ratio	Temp. (°C)	$CuSO_4.5H_2O$ (g)
1	PVP 10^5	2.72	0.002	85	3.12
2	PVP 10^5	2.72	0.0048	85	3.12
3	PVP 10^5	2.72	0.0075	85	3.12
4	PEG6000	2.72	0.08	85	3.12
5	SDS	2.72	0.05	85	3.12
6	CTAB	2.72	0.05	85	3.12
7	Glycerol	2.72	---	85	3.12
8	PVP4×10^4	6	0.001	87	1
9	PVP4×10^4	6	0.001	87	2
10	PVP4×10^4	6	0.001	87	4

Table 2. List of experiments performed with sodium hypophosphite as reducing agent.

Test no.	Stabilizer	Reducer/precursor molar ratio	Stabilizer/precursor molar ratio	$CuSO_4.5H_2O$ (g)
11	PVP 10^5	4	0.0005	2.49
12	PVP 10^5	4	0.005	2.49
13	PVP4×10^4	4	0.005	2.49
14	SDS	4	0.05	2.49
15	PEG6000	4	0.08	2.49
16	CTAB	4	0.05	2.49
17	Glycerol	4	---	2.49
18	PEG6000	2	0.12	1
19	PEG6000	3	0.12	1
20	PEG6000	4	0.12	1
21	PEG6000	6	0.12	1
22	PVP 10^5	1.5	0.005	2.49
23	PVP 10^5	3	0.005	2.49
24	PVP 10^5	5	0.005	2.49

(a) (b)

Fig. 1.a) Schematic of the reaction mixture during synthesis with ascorbic acid, b) dried copper nanoparticles.

The color changes from blue to red brown during the reaction. In the polyol reduction synthesis 7 (Table.1) and 17 (Table.2), glycerol acts as a stabilizing agent and also solvent with no water in the synthesis process and so the stabilizer/precursor molar ratio is not specified in these tables.

Then the reaction solution was centrifuged (4000 rpm and 10 min) and copper nanoparticles were dried after washing with water and ethanol (Fig.1b).

Characterization

The synthesized nanoparticle was analyzed by XRD (D8 advance of Bruker Co.), Fourier transform infrared spectroscopy (FT-IR) (Spectrum of PerkinElmer Co.), Scanning electron microscope (SEM 3200 of KYKY Co.) and Transmission electron microscopy (Philips CM10 model).

RESULTS AND DISCUSSION

Ascorbic acid as the reducing agent

Generally, ascorbic acid has results in the stability of nanoparticles due to its anti-oxidant nature although reaction yield is not complete and this reducing agent cannot completely reduce the copper salt. The anti-oxidant characteristics of acid

(1) (2) (3) (4) (5 (6)

Fig. 2) The color change of reaction mixture in synthesis 14 (Table.2).

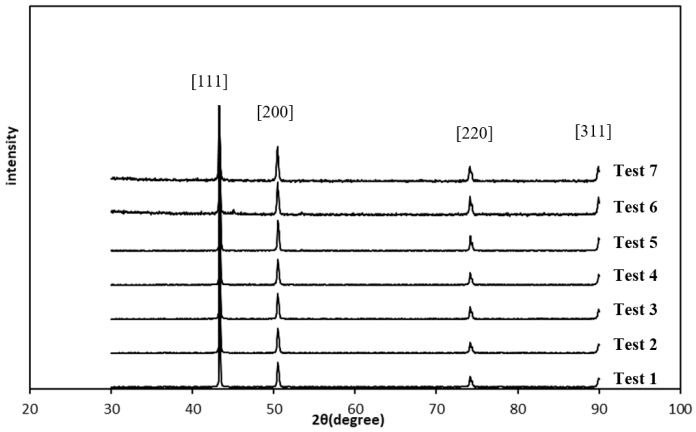


Fig. 3. XRD of Cu nanoparticles in case of ascorbic acid as reducing agent.

Table 3. The size of copper nano crystallite using various stabilizers from Scherrer equation.

Test No.	1	2	3	4	5	6	7
Stabilizer	$PVP10^5$	$PVP10^5$	$PVP10^5$	PEG6000	SDS	CTAB	Glycerol
Crystallite Size (nm)	61	48.8	57.4	50.6	51.1	40.4	36.8

ascorbic are attributed to capability to react with free radicals and active oxygen moieties [18].

The stabilizer type effect

To study the stabilizer effect on the stability and size of the produced nanoparticles, different experiments using [reducing agent: precursor] molar ratio = 2.72 and various stabilizers are conducted. XRD analysis of the as-produced nanoparticles are given in Fig. 3 which the peaks (2θ= 43.3 [111], 50.4 [200], 74.1 [220] and 89.9 [311]) show pure copper synthesized. Stable copper nanoparticles are obtained with no color changes even after 6 months**.** Table 3 shows the molar ratio for each stabilizer and the size of the resulting nanoparticles using Scherer equation.

Fig. 4 shows the SEM micrograph for sample 7 (table 1) which shows polyhedral particles without agglomeration. Agglomeration may be enhanced by surface oxidation of copper nanoparticles resulting in the enhancement of electrostatic attraction [19]. FT-IR analysis of this sample is also given in Fig. 5 with a wide peak in the 3300-3500 range showing OH functional group and good coverage of glycerol on the surface of nanoparticles. The stability of this sample can be attributed to the presence of both polyol and ascorbic acid.

Effect of precursor concentration

Controlling nucleation and growth steps for enhancement of nucleation rate and retardation of growth entails the engineering of initial concentrations [20]. Generally, burst nucleation results in smaller nanoparticles due to generation of smaller nuclei [19]. In this section, the effect of initial precursor concentration on the product is investigated by performing tests 8-10 (table and 4) under similar conditions. Ascorbic acid is

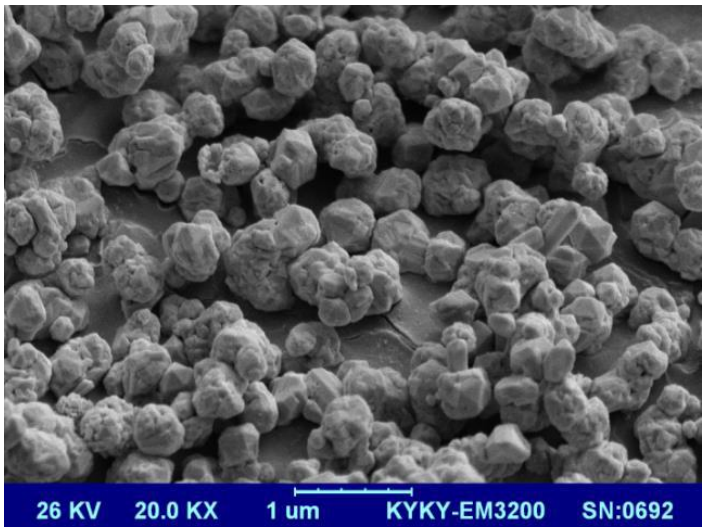


Fig. 4. FE-SEM result for sample 7 (Table 1).

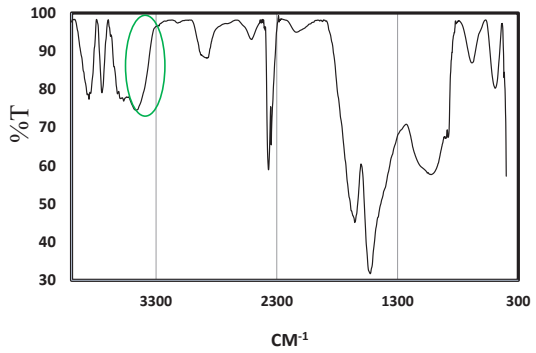


Fig. 5. FT-IR spectrum for sample 7 (Table 1).

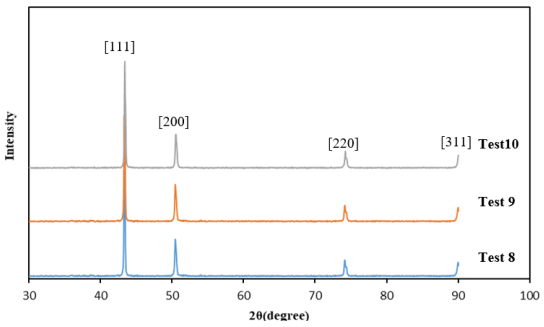


Fig. 6. XRD analysis of 8-10 samples (Tables 1 and 4).

used as the reducing agent and PVP (4×10^4) as the stabilizer. As mentioned in Table 1 the molar ratio of reducing agent and stabilizer is selected as 6 and 0.001, respectively, and experiments are performed at 87 ^{0}C.

Although various precursor concentrations are used, the rate of precursor introduction to the reaction media is tuned as 0.2 mmol/min in the three cases. XRD results (Fig. 6) confirm the purity of the product. The experimental conditions and size of nano-crystallites are summarized in Table 4. Based on Debye-Scherrer equation, the particle size of samples 8 and 9 is 42.8 nm. This shows that at high molar concentrations, particle size is independent of the initial precursor concentration [18].

Yield % is also given in Table 4 which shows yield enhancement by increasing the precursor concentration. The conversion percentage was calculated by weighing the nanoparticle powder obtained in each synthesis and comparison to the total amount of nanoparticles in the case of complete copper salt conversion.

TEM micrograph (Fig. 7) of synthesis 10 shows spherical copper nano-crystals and also some with a hexagonal structure almost at the same size of <40 nm which is close to XRD results. Also, this figure shows the nanoparticles are not agglomerated. These copper nano-crystals with ordered structure have hardly been synthesized from solution phase [21].

Effect of stabilizer concentration

Many surfactants are used to control the nanoparticles size and surface coating to prevent oxidation or agglomeration [22]. This is used to prevent the interconnection of nuclei created during synthesis through steric repulsion. Polymers such as PVP and PEG are considered for this purpose [23]. Size of nanoparticles, beside the surfactant

Table 4. The results obtained by changing precursor concentration.

Test No.	Precursor Concentration (mM)	Nanoparticle Size (nm)	Yield %
8	0.08	42.8	58.8
9	0.13	42.8	60.9
10	0.23	40.2	63.5

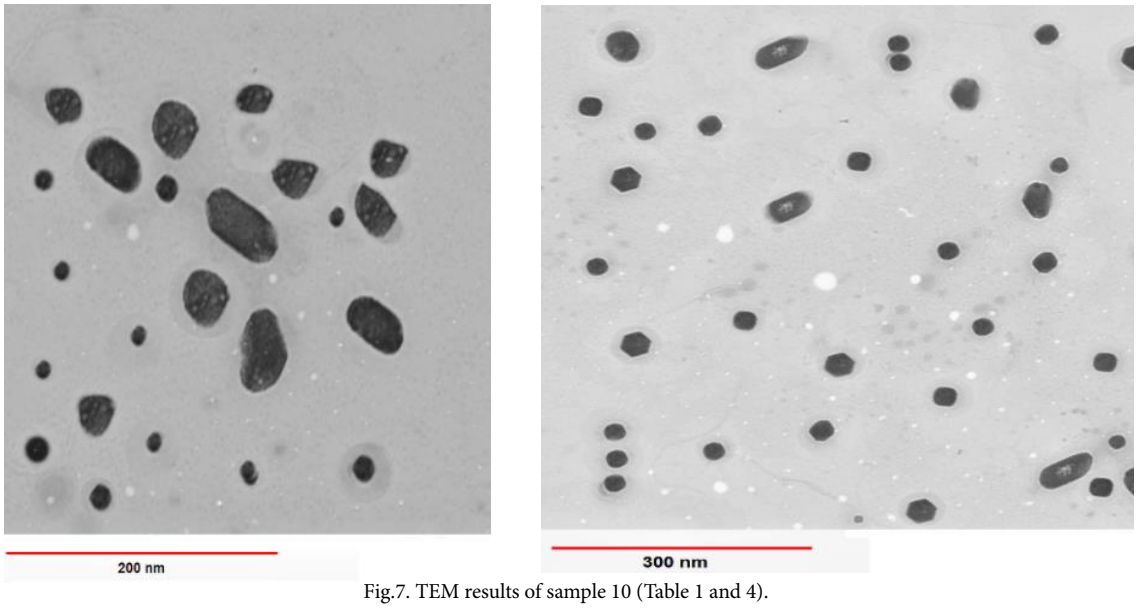


Fig.7. TEM results of sample 10 (Table 1 and 4).

type, depends largely on its concentration. On the other hand, considering the economic aspects of nanoparticle production, it seems that the amount of stabilizer is an important issue to be investigated.

To study the stabilizer content effect on the size and stability of the synthesized copper nanoparticles, experiments 1-3 (table 1) are performed by varying PVP ($Mw=10^5$) content keeping other parameters constant and the results are given in Fig. 8. Fig.. 8 (a) shows the size variation as a function of [PVP: precursor] molar ratio. The results show that increasing the surfactant content does not always result in the reduction of particle size but it is reduced up to an optimum amount (here 0.0048) and starts to re-increase ever after. It can be due to critical micelle concentration (CMC), after those surfaces of particles are coated by the polymeric chain, and increasing its concentration cause coagulation and also increasing the particle size. DLS analysis of sample 3 is given in Fig. 8. (b), which shows a good accordance with Debye-Scherer results. The average size is 62.4 nm with the maximum size as 54.5 nm.

Sodium Hypophosphite as the reducing agent

Effect of stabilizer type

Since the experiments are not carried out under inert medium, fast oxidation of copper surface makes oxygen diffusion rate be dependent on the type and concentration of the stabilizer [21]. Sodium hypophosphite is used as the reducing agent keeping constant other parameters varying the stabilizer type. XRD results are given in Fig. 9 showing copper peaks except for sample 14 (table 2 and 5) without any impurities and oxide formation. Table 5 shows the size and quality of the products. When SDS is used as a stabilizer, Cu_2O (Cuprite) peaks are observed at $2\theta= 36.5$, 42.4 and 61.5. So, SDS is not a good candidate in the case of sodium hypophosphite reducing agent and not able to produce pure copper nanoparticles. In samples 13 and 15, the product is not completely stable and shows colour change after some days indicating oxidation. In the experiments 11-16 (Tables 2 and 5), $PVP10^5$ at a 0.005 molar ratio (sample 12) gives the best stability which confirms total surface coverage of nanoparticles. The FE-SEM micrograph of this sample is given in Fig.10, showing agglomerated spherical copper nanoparticles.

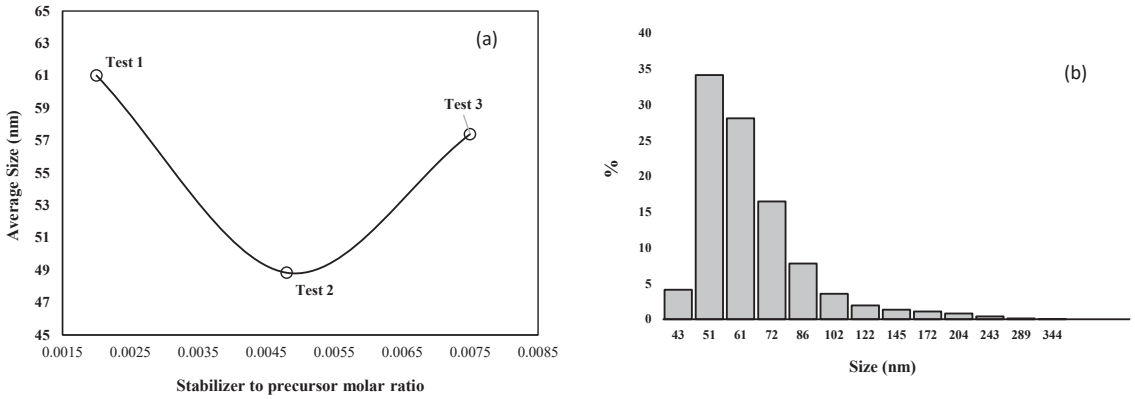


Fig. 8 a) Size variety of the synthesized nano-Cu particles by changing the stabilizer to precursor molar ratio. b) DLS analysis for sample 3.

Table 5. Results for sodium hypophosphite as the reducing agent.

Test No.	Stabilizer	Size (nm)	Stability
11	$PVP10^5$	--	Unstable – Oxidized completely after some days
12	$PVP10^5$	37.9	Pure copper - Stable
13	PVP 4×10^4	35.3	Pure copper – Unstable
14	SDS	42.4	Copper and copper oxide
15	PEG 6000	43.4	Pure copper – Unstable
16	CTAB	39.9	Pure copper – The color changed totally after some weeks
17	Glycerol	29	Pure copper – Stable (In case that no washing is performed)

Few studies on the synthesis of copper nanoparticles without stabilizing agents in polyols have been reported although high temperatures (135-185°C) or long stirring times were needed [24-25]. Ong et al. (2014) [26] synthesized copper nanoparticles by reducing copper chloride with hydrazine in glycerol. Within 8 h of stirring at room temperature, 2-10 nm copper nanoparticles were obtained with stability up to 4 days. In the present study, colloidal copper nanoparticles in glycerol are synthesized. The reaction progression is completed very fast in 5-10 min. Also, reaction temperature was 85 °C. The results of TEM and XRD of this synthesis are given in Figs.11 and 12, respectively.

TEM results show identical size spherical particles with no agglomeration. The average size shows ~25 nm which is in accordance with the size obtained from XRD results (29 nm).

The brown colloidal copper obtained (Fig. 13 a) was completely stable and its color did not change even in atmosphere for months. Fig. 13 b shows the solution after 4 months. The colloidal obtained can be directly used to prepare copper nanofluids in ethylene glycol and water without intermediate drying and dispersion stages.

Effect of reducing agent concentration

Experiments were performed using PEG6000 and $PVP10^5$ as a stabilizer. During experiments 18-21 (Table 2) with PEG6000, the reducing agent to precursor molar ratio is varied in the 2 to 6 range. According to the results, increasing this ratio, results in slower color variations since reaction progress is getting slower until the reaction is stopped at the [reducing agent: precursor molar ratio] = 6, which can be attributed to equilibration of mediating reactions.

Based on Fig. 14, increasing the reducing agent molar ratio from 2 to 4 results in the reduction of the nanoparticle average size from 40.2 nm to 32.8 nm. During experiments 22-24 (Table 2) with PVP 10^5 as stabilizer, the reducing agent molar ratio was increased from 1.5 to 5. The results showed the rate of reduction reaction is decreased and the nanoparticle size reduced from 44 nm to 33.9 nm. Obtaining nano-Cu is possible under special conditions of inert medium, a strong reducing agent and high [reducing agent: precursor] molar ratio [21]. It was also observed that the stability of as-synthesized powder was enhanced by increasing the reducing agent to precursor molar ratio.

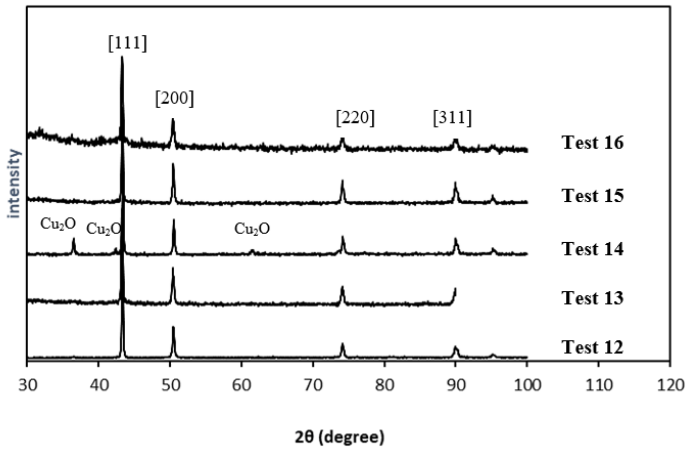


Fig. 9. XRD results for experiments with sodium hypophosphite as the reducing agent.

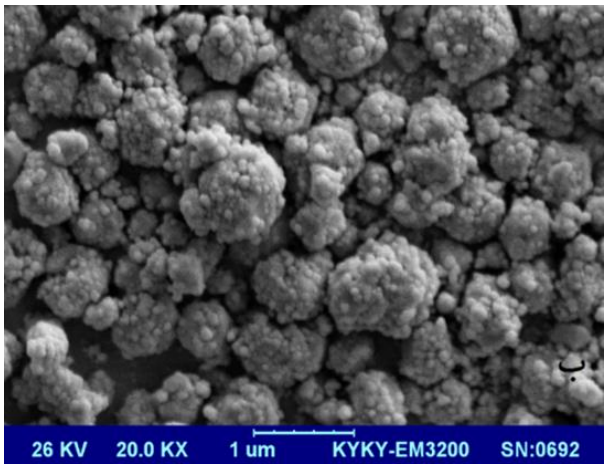


Fig. 10. FE-SEM micrograph of sample 12 (Tables 2 and 5).

Stabilizing agent concentration

According to experiments 11 and 12 (Tables 2 and 5), it is obvious that the stabilizer content greatly influenced the stability of Cu nanoparticles so that at low molar ratios of PVP 10^5, poor coverage is obtained and so the obtained nanoparticles are unstable and oxidized.

Effect of reducing agent type

Strong reducing agents result in smaller nanoparticles with good dispersion [27]. Reducing the capacity of sodium hypophosphite is higher than ascorbic acid [28] and as a result higher reaction rates are induced leading to smaller particles with narrower size distributions. On the other hand, using ascorbic acid to reduce copper salts is an environmental friendly technique since ascorbic acid has both reducing and antioxidant characteristics [10]. Generally, ascorbic acid results in stable nanoparticles although precursor yield is not complete and also because of its lower strength the synthesis process takes more time.

CONCLUSIONS

Stable copper nanoparticles from 25 to 60 nm were synthesized by chemical reduction in a non-inert environment. Ascorbic acid and sodium hypophosphite were used as reducing agents. The effect of various parameters on the synthesis was studied. The results show that ascorbic acid produces stable nanoparticles due to its antioxidant properties, but conversion of the reduction reaction is not 100%. Sodium hypophosphite is more potent compared to ascorbic acid, thus the reaction rate for the formation of nanoparticles is faster. According to the results, samples 17 and 24 were the most stable products in case of this reducing agent.

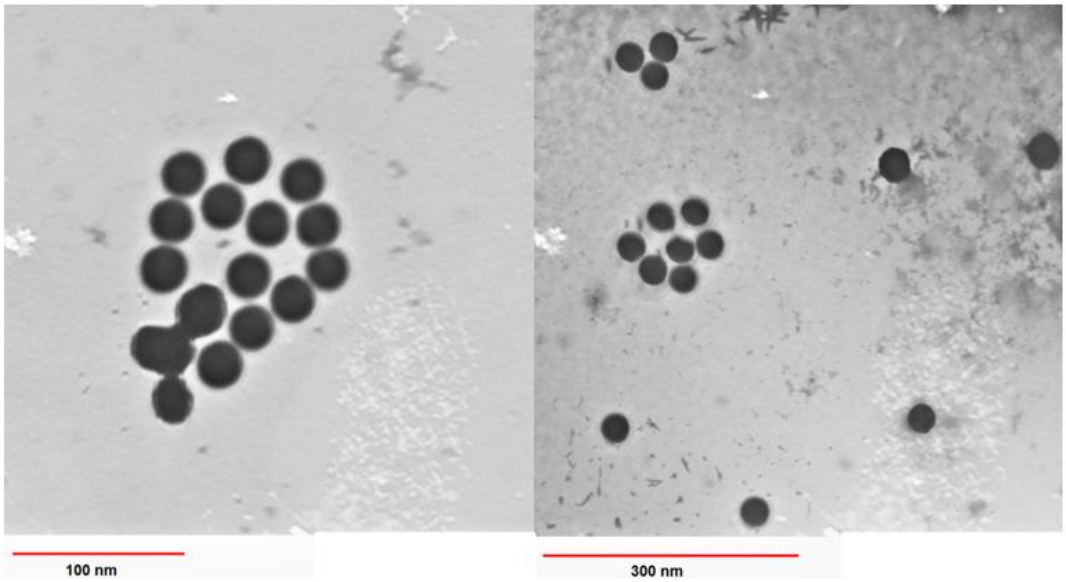


Fig. 11. TEM micrographs of experiment 17 (Tables 2 & 5).

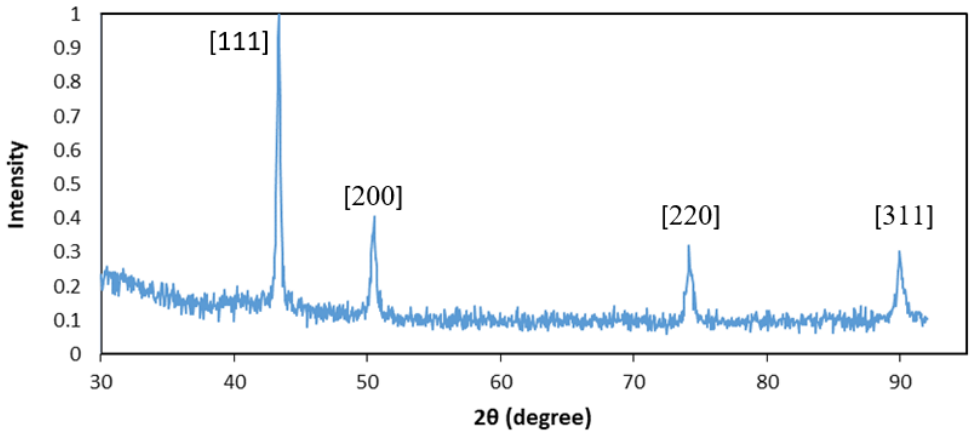
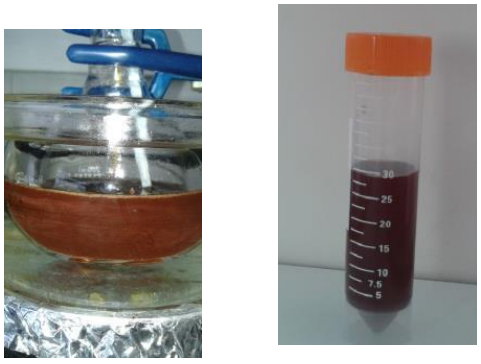


Fig. 12. XRD analysis of experiment 17 (table 2 and 5)



(a) (b)

Fig. 13. The polyol synthesis 17 a) after reaction completion, b) after 4 months.

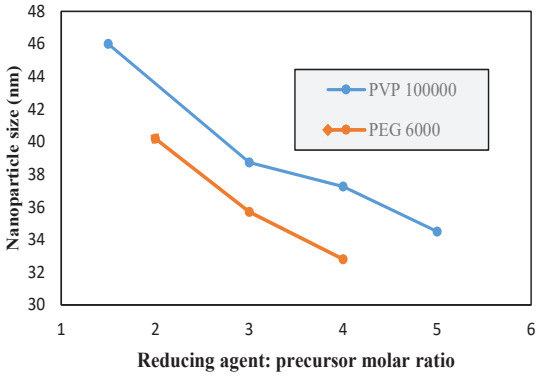


Fig. 14. Size of nanoparticles based on change in the reducing agent molar ratio using two types of stabilizers.

Stable and pure copper nanoparticle in glycerol was synthesized at low temperature without any surfactant. Copper nanoparticles were stable after several months with a homogeneous size of 25 nm and without agglomeration. Also due to simplicity, it seems that this method has the potential for nanofluid production in large scale.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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