International Journal of the Physical Sciences Vol. 6(18), pp. 4331-4336, 9 September, 2011
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS10.204
ISSN 1992 - 1950 ©2011 Academic Journals

Full Length Research Paper

Investigation on synthesis and size control of copper nanoparticle via electrochemical and chemical reduction method

Hassan Hashemipour[1,3]*, Maryam Ehtesham Zadeh[2,3], Rabee Pourakbari[2] and Payman Rahimi[1]

[1]Chemical Engineering Department, Shahid Bahonar University of Kerman, Iran.
[2]Material Engineering Department, Shahid Bahonar University of Kerman, Iran.
[3]Production and Separation Research Center, Mineral Industries Research Institute, Shahid Bahonar University of Kerman, Iran.

Accepted 20 June, 2011

Copper nanoparticles were synthesized and the effect of the operating conditions via both chemical and electrochemical synthesis methods was investigated in this paper. In the chemical reduction method, copper nanoparticles were prepared in a copper sulfate solution using $NaBH_4$ as reducing agent and then stabilized in the presence of polyvinylpyrrolidone under nitrogen atmosphere. Temperature and concentration ratio of reducing agent to precursor influenced the synthetic progress and size of the copper nanoparticles. Copper nanoparticles with average particle size 30 nm were formed when the concentration ratio is greater than 2 in the temperatures range from 60 to 75°C. In the electrochemical deposition method, copper nanoparticles were prepared using a bath containing homogeneously acidified copper sulfate solution. The nanoparticles were formed as spongy layers on the plating electrode which is easily separated. Average particle size 10 nm of copper nanoparticles is obtained with controlling of the electrolyte concentration and current density. The comparison shows that electrochemical deposition gives finer particle of copper but size controlling of the nanoparticles are more controllable than the chemical reduction method.

Key words: Copper nanoparticles, operating conditions, electrochemical deposition, chemical reduction.

INTRODUCTION

In recent years, much attention has been paid to metal nanoparticles which exhibit novel chemical and physical properties owning to their extremely small dimensions and special surface area. Specifically, these small particles are interesting materials for research on catalysts with specific activity and selectivity (Song et al., 2004). Melting point of nanoparticles decreases sharply as their size decreases. Among metal, copper nanoparticles have attracted much attention because of their catalytic and optical properties and high electrical and heat conductivity. Copper nanoparticles in comparison with bulk copper are potentially suitable materials for using in printed electronics and are good substitutes for conductive and expensive noble metals like gold and silver in the chemical and metallurgical processes (Song et al., 2004; Lee et al., 2008). Copper nanoparticles have been used to make conductive pastes for formation of thick film conductors such as electrodes or conductive patterns in multilayered electronic parts, printed circuit boards, hybrid integrated circuit and metallization of multilayer ceramic capacitor (MLCC) in the electronic industries (Yu et al., 2007).

Synthesis of nanostructure copper particles is studied base on different methods such as, chemical reduction in aqueous solutions (Kapoor et al., 2002; Zahmakiran et al., 2009; Khanna et al., 2007; Kobayashi et al., 2009; Kumar et al., 2001; Dhas et al., 1998; Park et al., 2007; Zhang et al., 2009), colloidal synthesis with reduction and extraction steps (Yang et al., 2007), evaporation and condensation of metal vapor on a cold surface (Vitulli et

---

*Corresponding author. E-mail: h-hashemipour@mail.uk.ac.ir.

Abbreviations: TEM, Transmission Electron Microscope; **MLCC,** multilayer ceramic capacitor; **PSD,** particle size distribution; **EDS,** energy dispersive X-ray spectroscopy; **XRD,** X-ray diffraction.

al., 2002; Liz-Marzán, 2004; Ponce and Klabunde, 2005), electrochemical methods (Molares et al., 2001; Sáez and Mason, 2009), hydrothermal process (Chu et al., 2007), gamma radiolysis method (Joshi et al., 1998) and laser ablation (Tilaki et al., 2007).

The synthesis of nanoparticles by reduction in aqueous solutions and precipitation of the nanoparticles is a laboratory method. In this method, there are many parameters such as temperature, reaction time, precursor and reducing agent type and concentration, additive type and even mixing affecting on nucleation, growth and agglomeration phenomena and consequently the particle size distribution. This method is used to synthesize several metal oxide nanoparticles with the same procedure (Eslami et al., 2008).

Electrodeposition of copper powder requires spongy deposition, that is encourages by rising current densities. Electrocrystallisation like chemical method has two main stages, nucleation and growth, Growth is enhanced over nucleation in smooth cathodes but the converse is true for powder production where each nucleus is a powder particle. Therefore, the key to change the particle size of the copper powder is changing the relative rates of nucleating and crystal growth (Xue et al., 2006). In high current densities, the nucleation rate increases with respect to the growth rate and then small crystals can be obtained.

In this paper, synthesis of copper nanoparticles in the copper sulfate solution was studied using a reduction chemical ($NaBH_4$) in the chemical method and current in the electrochemical deposition method. The aim of this work is to study the effect of the reaction parameters on the synthesis and size control of the copper nanoparticles.

MATERIALS AND METHODS

Copper sulfate pentahydrate ($CuSO_4.5H_2O$, Merck) as precursor, Sodium tetrahydridoborate ($NaBH_4$, Merck) as reducing agent, Sulfuric acid (H_2SO_4, >98%) as electrolite and poly vinylpyrrolidone (PVP, laboratory grade, Merck) as stabilizer were used in this study.

The nanosuspension solution containing copper nanoparticles was analyzed with a VinCary 50 UV-vis Spectrophotometer for detecting the synthesized copper nanoparticles. Particle size distribution (PSD) was analyzed by Zeta sizer Nano series of Malvern Instruments. Transmission Electron Microscope (TEM) images of the copper nanoparticles were prepared by CEM 902A (zice Germany) with accelerating voltage of 100 KV. X-ray diffraction (XRD) patterns of the powders were obtained using Philips analytical diffractometer with Cu Kα radiation (λ = 0.1542 nm) source performing scan range 2θ from 20 to 90°. A Scanning Electron Microscope (CAMSCAN, 2600 MV) is used to energy dispersive X-ray spectroscopy (EDS) analysis of the samples.

In the chemical reduction experiments, a solution of 0.001 molar $CuSO_4$ and 5 gr/lit of PVP were prepared by dissolving appropriate amount of the salt and the polymer in distilled water. The solution was purged by nitrogen to strip oxygen from the solution atmosphere. Then the solution was heated and stirred to the reaction temperature under the inert atmosphere. Thereafter 10 ml of $NaBH_4$ solution with predetermined concentration was added to the solution. Light blue color of the solution changed very quickly to different colors, which ranges from orange to dark red and black according to the reaction conditions. The concentration ratio of reducing agent ($NaBH_4$) to precursor ($CuSO_4$), which is named parameter R/P, and reaction temperature were considered as the most effective synthesis conditions.

In the electrochemical experiments, the electrolyte solution was prepared with 1 molar acidified copper sulfate. The experimental setup was designed as a typical glass electrolyte bath with pretreated and cleaned surface of copper and graphite plates as anode and cathode, respectively. A constant voltage 3 V was applied in the electrolyte which reduced into spongy deposition of copper nanoparticles for 20 min in constant current of 7 A.

RESULTS AND DISCUSSION

Formation of copper nanoparticles in the chemical reduction method

In the chemical reduction method, various nano-suspension of copper was prepared in different reaction conditions. Formation of the Cu nanoparticles based on the UV-vis spectroscopy is reported in Table 1.As shown in Table 1, the copper nanoparticles were not formed at temperatures below 60°C and whatever the parameter R/P is. The copper nanoparticles were formed at temperatures range of 60 to 75°C and the solution color became dark red when parameter R/P was higher than 2 (4 and 6). All copper nanoparticles formed in these conditions had a UV-vis spectrum as shown in the Figure 1. This figure shows the UV-vis spectra of sample No. 4 in Table 1 with an absorbance peak around 580 nm of UV-vis wavelength which proves the formation of the copper nanoparticles in the solution (Kapoor et al., 2002; Zhang et al., 2009). When the reducing agent was added to the precursor solution at temperatures higher than 85°C, the solution color became black and then a black precipitate was formed due to acceleration of the reduction rate. The precipitate might be CuO nano and microparticles formed during the process. Thus as a results, formation of copper nanoparticles took place in a narrow temperature range (60-75°C) with the parameter R/P range from 2 to 6.

The effect of reactants concentration ratio

Figures 2a and b show TEM images of the samples No. 4 and No. 5 in Table 1, which were synthesized at temperature 60°C in R/P ratio 4 and 6, respectively. These images were analyzed and the results showed that the synthesized nanoparticles had an average size about 30 nm for both samples. Figure 3 shows the size distribution of the nanoparticles given by zeta sizer for sample No. 5 in Table 1. This analysis clarifies the average size of nanoparticles about 26 nm that is in agreement with TEM image analysis.

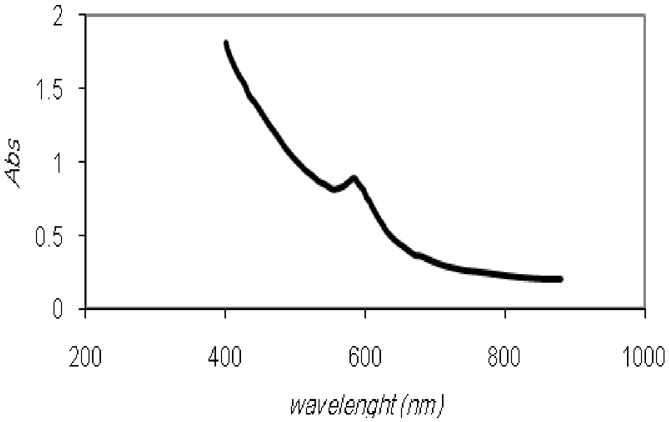

Figure 1. The UV-vis absorption spectra of synthesized copper nanoparticles.

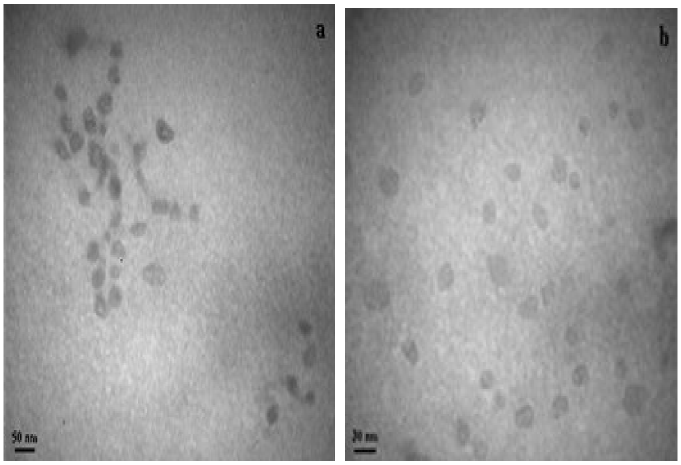

Figure 2. TEM images of copper nanoparticles synthesized at T=60℃ (a) R/P=4 and (b) R/P=6.

The reduction of copper nanoparticles did not occur at temperature 60℃ with R/P=2 and therefore nanoparticles were not synthesized (sample No. 3 in Table 1). In this value of parameter R/P, BH_4^- ions are stoichiometrically sufficient to reduce Cu^{2+} ions but BH_4^- may decompose directly to form H_2 (Stepanov et al., 2008). Therefore reduction of Cu^{2+} ions were not complete in R/P=2.

On the other hand, the reduction rate becomes independent of the reducing agent concentration at parameter R/P higher than 2 (4 and 6). This means that, in the high reducing agent concentration of the solution, the precursor concentration has no significant effect on reduction rate and size of the particles. Figure 3 shows the number percent particle size distribution given by zeta sizer for sample No. 5 of Table 1. This analysis verify the average size of nanoparticles about 25-30 nm.a.

Figure 4 shows the EDS of the synthesized copper nanoparticles of the sample No. 5 in Table 1. It is clear that synthesized nanoparticles are copper which are somewhat oxidized due to contact with air after placing the particles suspension on the grids. The copper nanoparticles were not oxidized during synthesis because the whole reaction was carried out in the N_2 atmosphere and the solutions were purged with N_2 before the reaction.

The effect of temperature

The nanoparticles did not form at temperature 50℃ in any reactant concentration. This shows that reaction constant at this temperature is too low to progress the reaction. Therefore, reaction temperature higher than 50℃ with appropriate parameter R/P should be inserted to the reaction environment to progress the reaction and synthesis the nanoparticles considerably.

In Figure 5, TEM image of the nanoparticles synthesized at T=75℃ and R/P=4 (sample No. 6 of Table 1) is shown. The image analysis of this TEM image showed an average size about 70 nm for the nanoparticles. Figure 6 presents the size distribution the sample with the average size 61.8 nm which is in agreement with the TEM result.

Comparison of figures 5 and 2a shows that the copper nanoparticles synthesized at 75℃ had a wide range of size distribution. In addition, the nanoparticles were agglomerated in these conditions while copper nanoparticles synthesized at 60℃ were well dispersed with an average size about 30 nm.

Basically, reduction rate of Cu^{+2} ions considerably increases with increasing the reaction temperature. Therefore the rate of synthesis is too high to control particle size at high temperature. When reducing agent was added to precursor solution at T = 85℃, rate of growth and agglomeration as well as nucleation of copper nanoparticles accelerate almost coincidently. These phenomena results in formation of nanoparticles with higher average size of the nanoparticles where precipitated (sample No. 7 in Table 1). Therefore in this method, moderate temperature (60<T<85℃) should be selected in the synthesis of the nanoparticle with appropriate controlling on the size.

Formation of copper nanoparticles in the electrochemical deposition method

Reduction of the metal copper on the cathode was started at lower potential and there was an increasing in the cathodic current due to the copper crystallization. The cathodic reduction potential indicated that the charge-transfer step was fast, and the rate of growth had been controlled by the rate of mass transfer of copper ions (Huang et al., 2005). These changes indicate the nucleation was existed during the copper electrochemical reduction process:

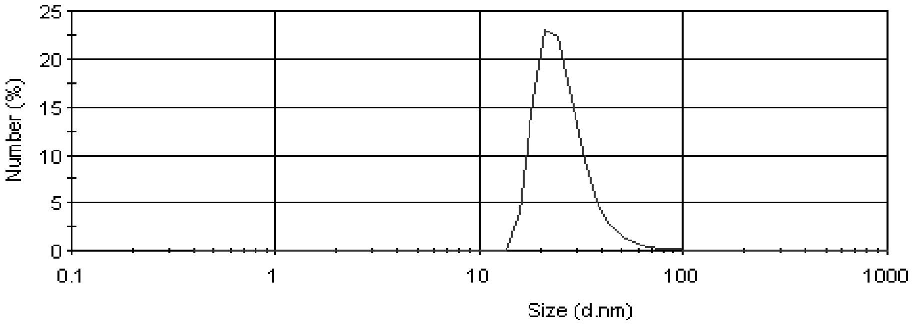

Figure 3. Size distribution of copper nanoparticle of sample No. 5 of Table 1.

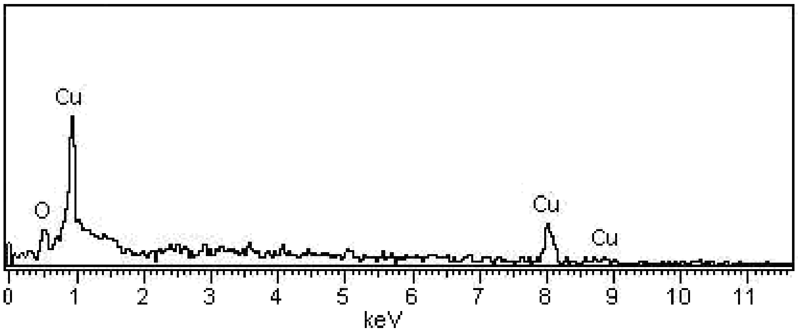

Figure 4. EDS spectra of copper nanoparticles of sample No 5 in Table 1.

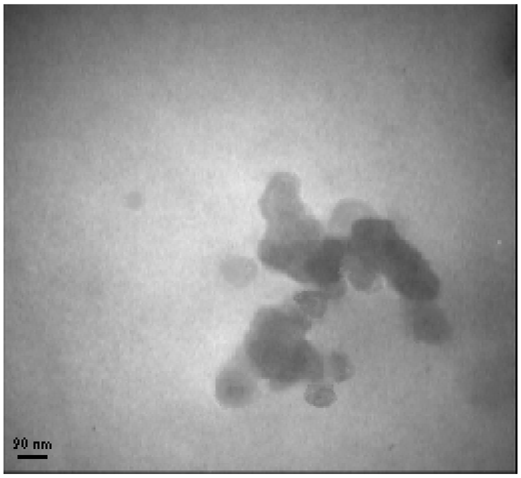

Figure 5. TEM image of samples copper nanoparticles synthesized with R/P=4 at T=75°C.

$$Cu^{+2} + 2e^{-} \rightarrow Cu_{(S)} \quad 1$$

Figure 6 shows a typical X-ray diffractogram of copper powder precipitated on the cathode and then separated, washed and dried. The 2θ values 43.4, 50.5, and 74.2 degree correspond to the (1 1 1), (2 0 0), and (2 2 0) peaks of copper.

From Scherrer's equation (Raja et al., 2008) and XRD spectrum of Figure 6, the particle size of the copper nanoparticles was found to be about 12 nm. The UV–vis absorption spectrum of copper nanoparticles displays an optical absorption band similar of Figure 1. It is well-known that the colloidal dispersion of metals exhibits an absorption band in the UV-vis regions due to collective excitations of the free electron (surface Plasmon band). A similar absorbance value for copper nanoparticles prepared by chemical methods was reported (Liu et al., 2003).

The particle size distribution of the nanopowders was analyzed with Zeta sizer instrument (Figure 7). This figure reports nanosize of the particles with average size 8 nm which confirm the XRD result.

The morphology of the nanopowder was found by dispersing the product on a copper grid coated with carbon and measuring its TEM. Figure 8 shows the TEM image of products obtained for 20 min of electrochemical deposition. It can be seen from the TEM images that spherical particles are obtained with agglomerated nanoparticles.

Conclusion

In this work, synthesis of copper nanoparticle is investigated by chemical reduction and electrochemical

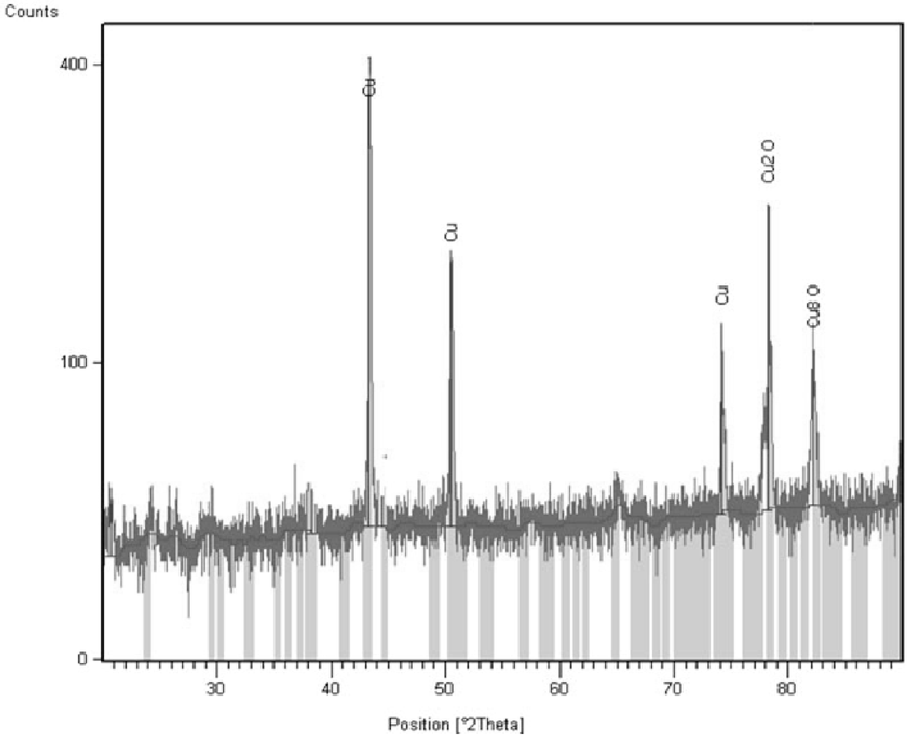

Figure 6. XRD pattern of copper nanoparticles.

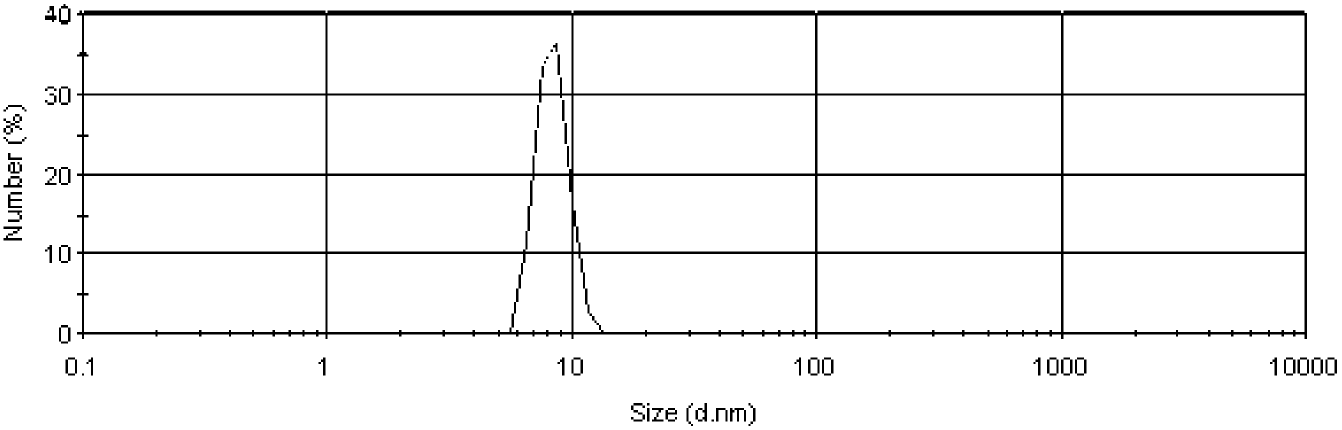

Figure 7. Size distribution of copper nanoparticle of sample synthesized in electrochemical deposition method.

deposition methods. Results of chemical reduction experiments showed that copper nanoparticles are formed in the temperature range of 60 to 75°C while the reducing agent to precursor ratio is higher than 2. Also, it was shown that when the R/P is greater than 4, the reduction rate becomes independent of the reducing agent concentration. In the optimum reaction conditions (R/P=4 at 60°C), well dispersed copper nanoparticles are formed. By increasing the reaction temperature from 60 to 75°C, agglomerated copper nanoparticles are produced with a wide range of size. Electrochemical deposition experiments were also described for synthesis of copper nanoparticle in presence of common commercial additive. The XRD and TEM results revealed that, the average particle size of prepared copper nanoparticles were between 20-100 nm. The UV–vis absorption spectrum of Cu nanoparticles displayed an optical absorption band which is attributed to the high purity of synthesized copper particle. Considering the low cost and easiness, relatively high purity and spherical shape copper nanoparticles were achieved through this method. This method can be extended to prepare other metals, bimetallic, core-shell nanoparticles by adopting suitable synthetic strategies. The comparison shows that,

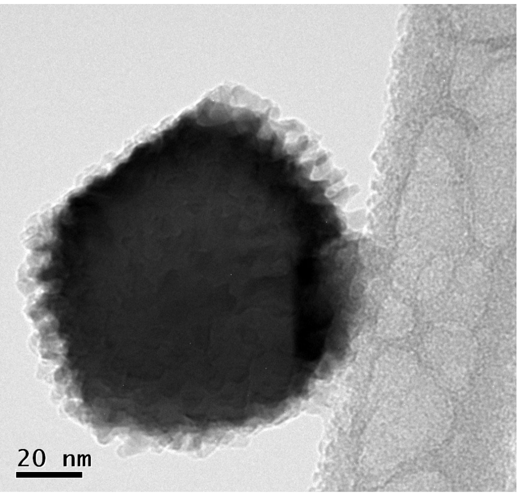

Figure 8. TEM image of the copper nanoparticles synthesized with electrochemical deposition method.

electrochemical deposition gives finer particle of copper but size controlling of the nanoparticles is more controllable than the chemical reduction method.

ACKNOWLEDGEMENTS

Authors would like to thank the Laboratory of Electron Microscopy of College of Science, University of Tehran for accomplishing the TEM analysis of the synthesized nanoparticles.

REFERENCES

Chu LY, Zhuo Y, Dong L, Li L, Li M (2007). Controlled synthesis of various hollow Cu nano/microstructures via a novel reduction route. Adv. Funct. Mater., 17: 933-938.

Dhas NA, Raj CP, Gedanken A (1998). Synthesis, characterization, and properties of metallic copper nanoparticles. Chem. Mater., 10(5): 1446-1452.

Eslami NH, Hashemipour H, Ranjbar M (2008). Effect of aging and calcinations on morphology and properties of synthesized nanocrystalline TiO_2. Inter. J. Modern. Phys., 22: 3210-3215.

Huang L, Lee ES, Kim KB (2005). Electrodeposition of monodisperse copper nanoparticles on highly oriented pyrolytic graphite electrode with modulation potential method. Colloids and Surfaces A: Physicochem. Eng. Aspects, 262(1): 125-131.

Joshi SS, Patil SF, Iyer V, Mahumuni S (1998). Radiation induced synthesis and characterization of copper nanoparticles. Nanostr. Mater., 10(7): 1135-1144.

Kapoor S, Joshi R, Mukhrejee T (2002). Influence of I^- anions on the formation and stabilization of copper nanoparticles. Chem. Phys. Lett., 354(5): 443-448.

Khanna PK, Gaikwad S, Adhyapak PV, Singh N, Marimuthu R, (2007). Synthesis and characterization of copper nanoparticles. Mater. Lett., 61(25): 4711–4714.

Kobayashi Y, Ishida S, Ihara K, Yasuda Y, Morita T, Yamada S (2009). Synthesis of copper nanoparticles coated with polypyrrole, Chem. Mater. Sci., 287(7): 877-880.

Kumar RV, Mastai Y, Diamant Y, Gedanken A (2001). Sonochemical synthesis of amorphous Cu and nanocrystalline Cu_2O embedded in a polyaniline matrix. J. Mater. Chem., 11: 1209-1213.

Lee Y, Choi J, Lee KJ, Stott NE, Kim D (2008). Large-scale synthesis of copper nanoparticles by chemically controlled reduction for application of inkjet-printed electronics. Nanotechnol. J., 19(41): 415604-415611.

Liu CM, Guo L, Xu HB, Wu ZYW (2003). Seed-mediated growth and properties of copper nanoparticles, nanoparticle 1D arrays and nanorods. J. Microelectron. Eng., 66(1): 107-114.

Liz-Marzán LM (2004). Nanometals: Formation and Color. Materials Today, 7(2): 26-31.

Molares MET, Buschmann V, Dobrev D, Neumann R, Scholz R, Schuchert IU, Vetter J (2001). Single-crystalline copper nanowires produced by electrochemical deposition in polymeric ion track membranes. Adv. Mater., 13(1): 62-65.

Park BK, Jeong S, Kim D, Moon J, Lim S, Kim JS (2007). Synthesis and size control of monodisperse copper nanoparticles by polyol method. J. Colloid. Interface. Sci., 311(2): 417-424.

Ponce AA, Klabunde KJ (2005). Chemical and catalytic activity of copper nanoparticles prepared via metal vapor synthesis. J. Mol. Catal. A-Chemical, 225(1): 1-6.

Raja M, Subha J, Binti Ali F, Ryu SH (2008). Synthesis of Copper Nanoparticles by Electroreduction Process. Materials and Manufacturing Processes. 23(8): 782-785.

Song X, Sun S, Zhang W, Yin Z (2004). A method for the synthesis of spherical copper nanoparticles in the organic phase. J. Colloid. Interface Sci., 273(2); 463-469.

Stepanov N, Uvarov V, Popov I, Sasson Y (2008). Study of by product of $NaBH_4$ hydrolysis and its behavior at a room temperature. Inter. J. Hydr. Ener., 33(24): 7378-7384.

Sáez V, Mason TJ (2009). Sonoelectrochemical Synthesis of Nanoparticles. Molecules, 14(10): 4284-4299.

Tilaki RM, Iraji Zad A, Mahdavi SM (2007). Size, composition and optical properties of copper nanoparticles prepared by laser ablation in liquids. Appl. Phys. A, Mater. Sci. Proc., 88(2): 415-419.

Vitulli G, Bernini M, Bertozzi S, Pitzalis E, Salvadori P, Coluccia S, Martra G (2002). Nanoscale copper particles derived from solvated Cu atoms in the activation of molecular oxygen. Chem. Mater., 14(3): 1183–1186.

Xue J, Wu Q, Wang Z, Yi S (2006). Function of additives in electrolytic preparation of copper powder. Hydrometallurgy, 82(3): 154-156.

Yang JG, Yang SH, Tang CB, He J, Tang MT (2007). Synthesis of ultrafine copper particles by complex-reduction-extraction method. Transactions of Nonferrous Metals Society of China, 17: 1182-1185.

Yu L, Sun H, He J, Dihua Wang D, Jin X, Hu X, George Z. Chen GZ (2007). Electro-reduction of cuprous chloride powder to copper nanoparticles in an ionic liquid. Electrochem. Comm., 9(6): 1374-1381.

Zahmakiran M, Ozkar S, Ketsuya T, Shiomi T (2009). A novel, simple, organic free preparation and characterization of water dispersible photoluminescent Cu_2O nanocubes. Mater Lett., 63(5): 400-402.

Zhang HX, Siegert U, Liu R, Cai WB (2009). Facile fabrication of ultrafine copper nanoparticles in organic solvent. Nanoscale Res. Lett., 4: 705-708.