Synthesis of Nano Copper Shell for Conductive Ink in Wearable Electronics

Akash Prabhu S, Geetha Kathiresan, Suganthy R

Abstract: Number of emerging synthesis techniques were revealed to synthesize the copper nanoparticles (CuNp) with reduced oxide states to improve the conductivity by various researchers. This research work highlights about the synthesis of surface oxide layer free copper nanoparticles (CuNp) using less expensive chemical reduction method by reducing the oxide states. Poly Vinyl Pyrolidone were used as a capping agent and Ascorbic acid as reducing agents for minimizing the oxide layer of CuNp. SEM, XRD, FTIR and Zeta Potential by particle size analyzer of synthesized powder were characterized. SEM images shows the particle size in the range of 100-300nm. XRD peaks expressed at 43.3482, 50.4653 and 74.1109 correspondence to the planes of (111), (200) and (220) confirms the presence of nanocopper in the sample. Particle size analyzer results exhibits the average particle size of CuNp as 141.2 nm. The peaks of FTIR spectrum at 3747 cm⁻¹, 1887 cm⁻¹, and 1690 cm⁻¹ confirm the presence of polyhydroxyl groups, which indicates the high dispersion rate of CuNp in the taken solvent. Further, the work reviewed to find the suitable binding agent to fabricate nanoconductive ink. The outcome of the study takes us closer towards to fabricate nanoconductive ink using CuNp for flexible electronics.

Index Terms: Conductive Binder, Copper Nanoparticle (CuNp), Flexible Electronics, Nano Conductive Ink.

I. INTRODUCTION

In recent years, printed and flexible electronics has attracted tremendous interests [1]. By manufacturing this printed electronics flexible substrates is most used for applications such as thin film transistors, LED, RFID tags, solar cells, transparent electrodes, flexible displays and sensor [2,3]. Flexible electronics are fabricate using conductive polymer or by conductive ink printed on different flexible substrate. Since, Conductive polymers usually have low conductivity then conductive inks, so that they can be used for RF applications. Due to instability of chemical and thermal nature, which have limits many applications [3,4,5,6]. The ability to produce various patterned structure on different flexible substrate of conductive ink to produce printed electronic circuits and flexible antennas [7,8]. This conductive ink can be fabricate in several types, such as metal based nanoparticles, polymer based, carbon nanotubes and etc. Recent years metallic nanoparticles specially silver nanoparticles (AgNp) are used to fabricate ink for its high conductivity. The oxidation of AgNp not affect its conductive because silver oxide nanoparticles itself conductive material. Major disadvantage of AgNp are too expensive to be employed for large scale production [9,10]. So, the scholars are focused on earth second abundant element with high thermal and electrical conductivity after silver is copper.

Cu are easily available, low cost methods are highly desirable. There many methods for synthesis of Cu-Nps such as thermal treatment, chemical reduction, atomic layered deposition (ALD), polyol method, chemical vapour deposition (CVD), photochemical method, sputtering, chemical dealloying, sonochemical treatment and mechanical milling [10-14]. Comparing above mention methods chemical reduction have advantages in terms of shape and size selectivity [15]. The major drawback of Cu NPs is forming the oxide layer, but this limitation could be overcome by using capping agent like PVA, PEG, PVP, Starch polymer or the synthesis under the inert gas like CO, H₂, N₃ gases [16,17,18]. This present works describes the chemical reduction method to synthesis copper nanoparticle by selecting the suitable reducing agent, capping agent and reviewed on suitable binding agent to fabricate ink without affecting conductivity. Conventional reducing agent like NaBH₄, polysyls, Glucose, N₂H₄ and hypophosphite and capping agent like ligands and oleylamine have toxic effects on the material and by products. Ammong this the ascorbic acid make nontoxic, process economical and environment friendly. Due to its antioxidant properties of ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules. Role of ascorbic acid while synthesis of copper nanoparticle. Accompanying the donation of electrons to give the semi-dehydroascorbate radical and dehydroascorbic acid as shown in fig 1.

Figure 1: Mechanism of Ascorbic Acid

Role of PVP as capping and stabilizing agent have advantage over others due to the non-toxic nature with C-N, C=O and CH₂ the functional group. PVP server as capping agent by repulsive force from hydrophobic carbon chains helps to prevent from the aggregates. Due to this PVP can be used as growth modifier, surface stabilizer, nanoparticle dispersant and reducing agent [19]. Yu et.al, they reported Cu NPs synthesised using polar solvent. The chemical used in this process are copper sulfate and ethylene glycol and water as a solvent with PVP as capping agent and ascorbic acid as reducing agent. 7 to 3 nm mean average of the Cu Nps [17]. Xiong et.al, using L-ascorbic acid they reported high stable mono dispersed nanosize copper particle. But here L-ascorbic acid used as both capping and reducing agent. NPs have less than 2 nm average size determine by TEM analysis [20]. Yang et.al, they reported Cu NPs yield upto 91.36% with 80 nm average size distribution and appearance as oblate shape. This as perform with ethanol

Revised Manuscript Received on August 05, 2019.
Akash Prabhu S, Nanotechnology Division, Periyar Maniammai Institute of science and Technology,Thanjavur, India.
Geetha Kathiresan*, Nanotechnology Division, Periyar Maniammai Institute of science and Technology,Thanjavur, India.
Suganthy R, Nanotechnology Division, Periyar Maniammai Institute of science and Technology,Thanjavur, India.

International Journal of Innovative Technology and Exploring Engineering (IJITTEE) ISSN: 2278-3075, Volume-8 Issue-10, August 2019
Synthesis of Sustainable Copper Nanoparticles with Reduced Oxide Layer and Reviewed on Suitable Binding Agent to Fabricate Nano Conductive Ink

as a solvent and used copper oxide, hydrazine hydrate and PVP. The exhibit absorption band at 580 to 600 nm due to its plasmonic resonance [21].

II. METHODS AND MATERIALS

A. Required Chemicals
In this process the following chemicals are used to synthesis Cu NPs. Copper sulphate, PVP, ascorbic acid and NaOH purchased for Sigma Aldrich with referring Khan et.al.,

B. Synthesis Procedure
In this experiment 0.1 M of CuSO₄ · 5H₂O is mixed with 120 ml of starch solution. The starch solution is made by 1.2% by weight with DI water. This mixture is vigorously stirred for 30 min and then 0.2 M ascorbic acid made with 50 ml is added. Subsequently 1 M of NaOH solution made with 30 ml of DI water is added and undergoes rapid stirring. This colloidal mixture is maintained at 80°C for 2 hrs. The solution is left overnight to allow the particle settle down. After that the supernatant was discard and the removing particle wash with ethanol and DI water three times and dried at room temperature. Further the particle was collected and stored for the characterization. The process have been done as shown in fig 2 as a flow chart.

0.1 M of CuSO₄ in 120 ml of PVP solution (1.2 %)
Vigorous Stirring 30 min
Add 50 ml of 0.2 M C₆H₈O₆
Subsequently add 30 ml of 1 M NaOH
2 Hrs 80°C
Remove the Supernatant after particle settle down
Wash with DI water and Ethanol three times
Dried at room temperature and store

Figure 2: Flow chart of synthesis process

The following picture are visualized the process and color change in solution during the process is observed and viewed in Fig 3.

Figure 3: a) After add C₆H₈O₆. b) After adding NaOH. c) After 2 Hrs at 800C. d) After settling over night

C. Characterization
Surface morphology of Cu NPs are studied using TESCAN VEGA 3LMU. The XRD spectra of the produced were record by XRD, DMAX2500, Rigaku spectrophotometer to determine the crystalline plane and to confirm the presence of copper nanoparticle comparing reference. The average size distributions of the synthesized Cu Nanoparticles were characterized by particle size analyzer (MALVERN 2000). FT-IR spectra were recorded with a Fourier transform infrared spectrophotometer (Brucker TENSOR 37 FT-IR spectrophotometer) between 4000 and 400 cm⁻¹, with a resolution of 0.09 cm⁻¹.

III. RESULTS AND DISCUSSION

SEM
The fig 4 shows the surface morphology of Cu NPs at different magnification with scale image of 10, 5 and 1 μm. From this fig the affect of ascorbic acid and PVP as observed, which prevent the Cu NPs to aggregate and reduce the oxide layer. Even though some of the particles are aggregate, but is dispersible in solvent.

Figure 4: SEM Image of CuNp magnification at a) 5 kx, b) 10 kx, c) 50 kx

XRD
The crystalline nature and size distribution can be determine by XRD spectrum. From fig 7 XRD spectrum the peaks observed at 20 values of 43.3482°, 50.4653° and 74.1109°, which is respected to Cu NPs and it confirms the presence Cu and with (111), (200) and (220) planes. Even through the Cu NPs are synthesis using capping agent some of the particle are get oxide this is confirmed, by several other diffraction peaks appeared at 25.5092°, 36.4601°, 43.3482°, 61.3811°, 74.1109° and 77.5259°, this indicate the formation of cubic copper (I) oxide nanocrystals with (110), (111), (200), (220), (311) and (222). This spectrum was compared with the Khan et al., (2016) and standard JCPDS Copper: 04-0836 [22].
The following tabulation exhibits the position 2Ө, height and FWHM are given. By applying FWHM on scherrer equation to determine the average size distribution of Cu NPs. The scherrer equation is:

\[
D = \frac{0.94 \lambda}{\beta \cos \theta}
\]

Whereas,

Peak width (β) or (FWHM) is inversely proportional to crystallite size (D), λ – X Ray Wavelength, K is scherrer constant (0.94).

Table 1: XRD Spectrum Data

| Pos. [°2Th.] | Height [cts] | FWHM Left [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|--------------|--------------|-------------------|---------------|--------------|
| 25.5092      | 38.65        | 0.4428            | 3.49195       | 5.18         |
| 36.4601      | 587.49       | 0.2952            | 2.46437       | 78.81        |
| 42.3118      | 196.78       | 0.2952            | 2.13611       | 26.40        |
| 43.3482      | 745.50       | 0.2460            | 2.08741       | 100.00       |
| 50.4653      | 245.16       | 0.2460            | 1.80846       | 32.89        |
| 61.3811      | 139.92       | 0.1968            | 1.51045       | 18.77        |
| 74.1109      | 143.69       | 0.1476            | 1.27938       | 19.27        |
| 77.5259      | 18.09        | 1.1808            | 1.23133       | 2.43         |

By substituting the above mentioned value the average crystalline size of Cu NPs as been calculated as 36.31 - 42.29 and 9.02 – 49.05 nm for CuO nanocrystals

FTIR Result

FT-IR spectroscopy was used to study the different groups and there chemical changes in presence of IR region. Fig. 8 shows the FT-IR spectrum for CuNp. The peaks at 1488 cm⁻¹ and 1319 cm⁻¹ are represent vibration of single bond between carbon atoms and organic hydroxyl group this are indicate the action of ascorbic acid. The peaks were observed at 3747 cm⁻¹, 1887 cm⁻¹, and 1690 cm⁻¹ respective to the carbonyl groups, and conjugated carbonyl groups this indicate the effect of PVP. These results confirm the surface of CuNp have polyhydroxyl structure, which give wonderful dispersion nature to CuNp in various solvent.
Synthesis of Sustainable Copper Nanoparticles with Reduced Oxide Layer and Reviewed on Suitable Binding Agent to Fabricate Nano Conductive Ink

Table 2: Review on Binding Agent

| Reference     | Binding Agent                      | Parameter Optimized                                                                 | Printed Technique | Resistivity |
|---------------|------------------------------------|-------------------------------------------------------------------------------------|------------------|-------------|
| Lee et.al.    | 2-(2-butoxythoxy)ethanol            | 30% weight (NPs to BA), dispersant for 15min and then micro fluidized, substrate maintained at 85 °C, sintered at 200 °C for 1h. | Inkjet Printing  | 1E-5 Ωm    |
| Yabuki et.al  | α-terpineol                        | 50% weight (NPs to BA), 70 °C for 15 min                                            | Screen Printing  | 1E-3 Ωm    |
| Kim et.al     | Non-polar Solvent                  | 40% weight, heated upto 85 °C                                                       | Piezoelectric    | 3E-6 Ωm    |
| Lee et.al     | DEG, Isopropyl Alcohol (IPA) and Ethanol | 6:2:2 % by volume sonicated for 1h, sintered at 350 °C for 4h                      | Piezoelectric Nozzle Inkjet Printer | 1.74 × 10-7 Ωm |

Table 5: Review on Polyaniline

| Reference     | Material                          | Form       | Application    | Outcome                                      |
|---------------|-----------------------------------|------------|----------------|----------------------------------------------|
| Wang et.al    | molybdenum disulfide (MoS2)/polyaniline (PANI) | Nanocomposite | Super capacitor | 390 F/g (specific capacitance) and 86% retained over 1000 cycles |
| Wu et.al      | CNT/Polyaniline                   | Membrane   | Transistor     | field-effect mobility of >5 Cm²V⁻¹s⁻¹       |
| Hong et.al    | PANI doped with camphorsulfonic acid | Fiber      | -              | ~0.15 to ~7.3 cm²/(V s) (~50 time improvement) |

V. CONCLUSION

In presence of Poly Vinyl Pyrrolidone and Ascorbic acid the CuNp have been synthesized with reduce surface oxide layer. SEM, XRD, FTIR and Zeta Potential by particle size analyzer of synthesized powder were characterized. SEM images shows the particle size in the range of 100-300nm. XRD peaks expressed at 43.3482, 50.465 and 74.1109 correspondence to the planes of (111), (200) and (220) confirms the presence of nanocopper in the sample. Particle size analyzer results exhibits the average particle size of CuNp as 141.2 nm. The peaks of FTIR spectrum at 3747 cm⁻¹, 1887 cm⁻³, and 1690 cm⁻¹ confirm the presence of polyhydroxyl groups, which indicates the high dispersion rate of CuNp in the taken solvent. From the review on binding agent the Polyaniline (PANI) is the suitable to use as a conductive binder for nano ink.

REFERENCES

1. S. Azoubel, S. Shemesh and S. Magdassi, 'Flexible electroluminescent device with inkjet-printed carbon nanotube electrodes', Nanotechnology, vol. 23, no. 34, p. 344003, 2012.
2. Kamshny and S. Magdassi, 'Conductive Nanomaterials for Printed Electronics', Small, vol. 10, no. 17, pp. 3515-3535, 2014.
3. Blayo and B. Pineaux, ‘Printing processes and their potential for RFID printing’, Proceedings of the 2005 joint conference on Smart objects and ambient intelligence innovative context-aware services: usages and technologies - 6th-EUSAI 05, 2005.
4. Y. Li, D. Lu and C. Wong, Electrical conductive adhesives with nanotechnology, New York: Springer, 2009.
5. R. Doering and Y. Nishi, Handbook of semiconductor manufacturing technology. Boca Raton: CRC/Taylor & Francis, 2007.

6. J. Song, L. Wang, A. Zibart and C. Koch, 'Corrosion Protection of Electrically Conductive Surfaces', Metals, vol. 2, no. 4, pp. 450-477, 2012.
7. D. Hecht, L. Hu and G. Irvin, 'Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures', Adv. Mater., vol. 23, no. 13, pp. 1482-1513, 2011.
8. S. Hellstrom, H. Lee and Z. Bao, 'Polymer-Assisted Direct Deposition of Uniform Carbon Nanotube Bundle Networks for High Performance Transparent Electrodes', ACS Nano, vol. 3, no. 6, pp. 1423-1430, 2009.
9. J. Chen, C. Jang, S. Xiao, M. Ishigami and M. Fuhrer, ‘Intrinsic and extrinsic performance limits of graphene devices on SiO2’, Nature Nanotech, vol. 3, no. 4, pp. 206-209, 2008.
10. G. Hanson, ‘Dryadic Green’s functions and guided surface waves for a surface conductivity model of graphene’, J. Appl. Phys., vol. 103, no. 6, p. 064302, 2008.
11. Ayesha Khan, Audil Rashid, Rafia Younas, Ren Chong, ‘A chemical reduction approach to the synthesis of copper nanoparticles’, Int Nano Lett (2016) 6:21–26.
12. Shikha Jain, Niharika Nagar and Vijay Devra, ‘Synthesis and characterization of highly efficient copper nanoparticles and their catalytic application in oxidative kinetic study’, Advances in Applied Science Research, 2015, 6(6): 171-180.
13. Dung Dang, Thi My, ‘Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method’, Adv. Nat. Sci: Nanosci. Nanotechnol. 2 015009, 2011.
14. Ihon L. Cuya Huaman, Kimtaka Sato, Satoshi Kurita, Takatoshi Matsumoto and Balachandran Jeyadevan, ‘Copper nanoparticles synthesized by hydroxyl ion assisted alcohol reduction for conducting ink’ J. Mater. Chem., 2011, 21, 7062.
15. Hyun-Jun Hwang1, Wan-Ho Chung1 and Hak-Sung Kim, ‘In situ monitoring of Flash-light sintering of copper nanoparticle ink for printed electronics’, Nanotechnology 23 (2012).
16. Felix Lewis Oscan, Davoodbasha MubarakAli, Chari Nithya, Rajendra Priyanka, Venkatraman Gopinath, Naiyf S. Alharbi and Nooruddin Thajuddin, ‘One pot synthesis and anti-biofilm potential of copper nanoparticles (CuNPs) against clinical strains of Pseudomonas aeruginosa’, Biofouling, 2015, Vol. 31, No. 4, 379–391.
17. Hongyan Liu, Tingting Wang and Heping Zeng, “CuNPs for Efficient Photocatalytic Hydrogen Evolution”, Part. Part. Syst. Charact. 2015, 32, 869–873.

18. Manoj B. Gawande, Anandarup Goswami, Francois-Xavier Felpin, Tewodros Asefa, Xiaoxi Huang, Rafael Silva, Xiaoxin Zou, Radek Zboril and Rajender S. Varma, “Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis”, Chem. Rev. 2016, 116, 3722-3811.

19. Supriya A. Patil, Chung-Hyeon Ryu, and Hak-Sung Kim, “Synthesis and Characterization of Copper Nanoparticles (Cu-Nps) using Rongalite as Reducing Agent and Photonic Sintering of Cu-Nps Ink for Printed Electronics”, International Journal Of Precision Engineering And Manufacturing-green Technology, vol. 5, no. 2, pp. 239-245, 2018.

20. Venkata Abhinav K, Venkata Krishna Rao. R, Karthik P.S, Surya Prakash Singh, “Copper Conductive Inks: Synthesis and its Utilization in Flexible Electronics”, RSC, 2015.

21. Swihart, M. T., “Vapor-Phase Synthesis of Nanoparticles,” Current Opinion in Colloid & Interface Science, Vol. 8, No. 1, pp. 127-133, 2003.

22. Song, X., Sun, S., Zhang, W., and Yin, Z., “A Method for the Synthesis of Spherical Copper Nanoparticles in the Organic Phase,” Journal of Colloid and Interface Science, Vol. 173, No. 2, pp. 463-469, 2004.

23. Huang, L., Jiang, H., Zhang, J., Zhang, Z., and Zhang, P., “Synthesis of Copper Nanoparticles Containing Diamond-Like Carbon Films by Electrochemical Method,” Electrochemistry Communications, Vol. 8, No. 2, pp. 262-266, 2006.

24. Johansson, A., Torndahl, T., Ottosson, L., Boman, M., and Carlsson, J. O., “Copper Nanoparticles Deposited Inside the Pores of Anodized Aluminium Oxide Using Atomic Layer Deposition,” Materials Science and Engineering: C, Vol. 23, No. 6, pp. 823-826, 2003.

25. Mott, D., Galkowski, J., Wang, L., Luo, J., and Zhong, C.-J., “Synthesis of Size-Controlled and Shaped Copper Nanoparticles,” Langmuir, Vol. 23, No. 10, pp. 5740-5745, 2007.

26. Hong, Z. S., Cao, Y., and Deng, J. F., “A Convenient Alcohothermal Approach for Low Temperature Synthesis of CuO Nanoparticles,” Materials Letters, Vol. 52, No. 1, pp. 34-38, 2002.

27. Lindberg, B. J., “Studies on Sulfinic Acids. VI. The IR-Spectra of Aromatic Sodium Sulfinates and Sulfonates,” Acta Chemica Scandinavica, Vol. 21, pp. 2215-2234, 1967.

28. Tang, R. Y., Zhong, P., and Lin, Q. L., “Sulfite-Promoted One-Pot Synthesis of Sulfides by Reaction of Aryl Disulfides with Alkyl Halides,” Synthesis, Vol. 1, pp. 85-91, 2007.

29. Kim, H. S., Dhage, S. R., Shim, D. E., and Hahn, H. T., “Intense Pulsed Light Sintering of Copper Nanoink for Printed Electronics,” Applied Physics A, Vol. 97, No. 4, pp. 791-798, 2009.

30. Ryu, J., Kim, H. S., and Hahn, H. T., “Reactive Sintering of Copper Nanoparticles Using Intense Pulsed Light for Printed Electronics,” Journal of Electronic Materials, Vol. 40, No. 1, pp. 42-50, 2011.

31. Hwang, H. J., Chung, W. H., and Kim, H. S., “In Situ Monitoring of Flash-Light Sintering of Copper Nanoparticle Ink for Printed Electronics,” Nanotechnology, Vol. 23, No. 48, Paper No. 485205, 2012.

32. Han, W.-S., Hong, J.-M., Kim, H.-S., and Song, Y.-W., “Multi-Pulsed white Light Sintering of Printed Cu Nanoinks,” Nanotechnology, Vol. 22, No. 39, Paper No. 395705, 2011.