IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
Vol. 3, Issue 5, May 2016

Synthesis, Characterization of Copper Nanoparticles - A Review

Rajesh Mittu

Assistant professor, Department of Chemistry, DAV College, Amritsar

Abstract: In this review paper it is to be discussed about the importance of copper nanoparticles, their different synthesis strategies and how these differ from one another in various aspects. Then also mentioned about the various characterization techniques employed for the identification of prepared copper nanoparticles on different parameters.

Keywords: XRD, SEM, TEM, FTIR, EDX, AFM.

INTRODUCTION

It is known that atoms and molecules possess totally different behaviour than those of bulk materials. It forms the basis of nanotechnology. The behaviour of a material changes between these two distinct domains and the nanometer range is considered as the threshold for the transition of a material's behaviour. Many metal nano particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase. Noble metal nanoparticles found many applications in different fields such as catalysis, photonics and electronics, because of their unique optical, electronic, mechanical, magnetic, and chemical properties. The most common method employed for the synthesis of metal nanoparticles is the reduction of metal ions in solution. Metals with free electrons possess plasmon resonances in the visible spectrum, which give rise to such intense colours. These properties are mainly observed in Au, Ag, and Cu because of the presence of free conduction electrons. As metal nanoparticles are widely used in the areas of human contact, the necessity to develop eco-friendly methods for nanoparticle synthesis that do not use toxic chemicals has been constantly growing. Development of green nanotechnology is generating interest of researchers toward ecofriendly biosynthesis of nanoparticles. Nanoparticles synthesized by physical and chemical methods are suffering from drawbacks like expensive reagent, hazardous reaction condition, longer time, tedious process to isolate nanoparticles. Hence, there is scope to develop new methods for the synthesis of nanoparticles which should be required inexpensive reagent, less drastic reaction condition and eco-friendly. Green Synthesis of copper nanoparticles is of great interest because of many advantages. Copper is highly conductive and also cheaper than silver and gold. However, aggregation and oxidation are the main problems concerned to the copper nanoparticles. But, we can overcome these problems by selecting suitable stabilizer for capping of copper nanoparticles. In recent years, Cu nano particles have attracted much attention of researchers due to its application in wound dressings and biocidal properties, potential industrial use such as gas sensors, catalytic process, high temperature superconductors and solar cells.

SYNTHESIS STRATEGIES

In literature, the Cu nanoparticles are synthesized from (a) vapor deposition , (b) electrochemical reduction, (c) radiolysis reduction , (d) thermal decomposition , (e) chemical reduction of copper metal salt and (f) room temperature synthesis using hydrazine hydrate and starch .In recent, green synthesis of Cu nanoparticles was achieved by using microorganisms, plant extract. Chemical reduction is the highly preferred method among all other methods as it is simple and economical. The chemical reduction methods using separate reducing and stabilizing agents are known to generate copper nanoparticles with controlled size and shape. The chemical reduction of metal salt in aqueous solution and precipitation of the nanoparticles is a novel approach. It was reported that the two stage chemical reduction process is necessary to avoid the formation of copper oxide. The synthesis of metal nanoparticles using natural extracts is greener from a chemical hazard standpoint and advantageous from an economical point of view (Huang et al., 2007).

Synthesis of Copper Nanoparticles using Hydrazine Hydrate as reducing agent:

All chemicals used were of analytical reagent grade. The copper chloride, copper sulphate, copper nitrate, L-Ascorbic acid, NaOH, Hydrazine Hydrate (HH) was used as received. All solutions were made with millipore water. In the present method, copper salts were used as basic precursors, papaya extract as stabilizer, Hydrazine Hydrate as reducing agent, L-Ascorbic acid as an anti-oxidant agent. NaOH was used as a catalyst and also to adjust the pH to 12. Copper chloride solution was prepared separately. L-Ascorbic acid was dissolved in Millipore water. Papaya extract and the solution of L-Ascorbic acid were added to copper chloride solution by heating to a temperature 50-60˚C under rapid stirring. Then the solutions of Hydrazine Hydrate and NaOH were added to the mixed copper salt solution under stirring. The initial blue color of the reaction mixture eventually turned to brown-black color. Stirring was continued for another 1 hr to complete the reaction. The precipitate was washed twice with methanol after filtration and then dried and then the powder was obtained. Following same procedure, copper

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
Vol. 3, Issue 5, May 2016

nanoparticles were also prepared using the other copper salts, copper sulphate and copper nitrate.

Synthesis of Copper Nanoparticles using sodium borohydride as reducing agent:
In this work, Copper sulphate $CuSO_4$, sodium borohydride $NaBH_4$ and tri-sodium citrate $C_6H_5O_7Na_3$ of analytical grade purity were used without further purification as starting materials. The copper colloid was prepared using chemical reduction method. The solutions of all the reacting materials were prepared in distilled water. 100 ml of $1x10^{-3}$ M $CuSO_4$ solution kept in a specially designed reaction chamber was reduced by drop wise addition of highly dilute and chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction, the solution was stirred vigorously. As the colour of the solution turned to light yellow 5 ml of 1 % trisodium citrate was added drop by drop as stabilizer.

Synthesis of Copper Nanoparticles Using Ocimum sanctum leaf extracts:
All the chemical reagents used in this experiment were of analytical grade purchased from Loba chemicals. The Ocimum sanctum leaves were collected from in and around Rajgurunagar, Pune Maharashtra, India. Thoroughly washed leaves (100 g) were cut and boiled with 100 ml of deionized water for 15 min in heating mental at temperature 80^{o}C. The resulting product was filtered and stored in refrigerator for further experiments. For the Cu nanoparticles synthesis, 1 ml of Ocimum sanctum leaf extract was added to 100ml of 1mM aqueous $CuSO_4.5H_2O$ solution in a 250 ml Erlenmeyer flask. The flask was then kept overnight at room temperature. The Cu nanoparticles solution thus obtained was purified by repeated centrifugation at 12,000 RPM for 15 min followed by re-dispersion of the pellet in deionized water. Then the Cu nanoparticles were dried in oven at 80^{o}C.

Synthesis of Copper Nanoparticles Using Bacterial strains:
Bacterial strains were enumerated from soil around the sewage outfall of the small scale electroplating industry from Dhakran, Agra by Serial dilution-agar plating method (Nigam 1965). 1 x $10^{-3}dm^3$ inoculum was transferred into 50 x $10^{-3}dm^3$ medium containing *(gil)* Peptone, Beef extract, Sodium chloride, Agar, pH 7.2 in Erlenmeyer flasks. Cells were grown at 37°C for 24 h and then harvested by centrifugation (8,000 rpmmin.$^{-1}$, 10 min. at room temperature). The cell pellet was resuspended and centrifuged three times in deionized water. Copper sulfate was purchased from Hi-media, and was used as received. In a typical synthesis for nanoparticles using *Pseudomonas stutzeri*, the carefully weighted 0.1 g biomass was added to 100 ml of 1mM aqueous $CuS0_4$ solution in conical flasks of 250 ml content. The flasks were thereafter incubated in incubator shaker at 150 rpm at room temperature.

Synthesis of Copper Nanoparticles Using Electrolysis:
We synthesize copper Nanoparticles (T.Theivasanthi and M.Alagar, 2010) by dissolving copper sulphate salt in distilled water and electrolyzed. The copper Nanoparticles are formed at the cathode and they are removed carefully.

CHARACTERIZATION TECHNIQUES

UV-Vis Spectra Analysis:
The absorbance of colloidal solution was recorded at different stages of synthesis using UV-visible spectrophotometer (Shimadzu UV-2450, Japan) in the wavelength range: 300 nm to 700 nm. UV-Vis absorption spectra of the copper nanoparticles shows the copper nanoparticles prepared using different copper salts and papaya extract stabilizer display an absorption peak at around 560 nm. This peak can be assigned to the absorption of copper nanoparticles. The broadness of the absorption peak probably stems from the wide size distribution of nanoparticles.

XRD:
XRD patterns of copper nanoparticles were recorded using Philips X-ray diffractometer coupled with graphite monochrometer. Crystallite size was calculated using Scherrer's formula given by equation (1).

$$D = 0.89\ \lambda / \beta \cos\theta$$

where λ is wavelength of X-rays, β is the full width at half maximum of X-ray profile and θ is the Bragg angle.

XRD patterns of copper nanoparticles synthesized using different copper salts and papaya extract shows three main characteristic diffraction peaks for Cu were observed at around $2\theta = 43°, 50°, 74°$ which correspond to the (111), (200), (220) crystallographic planes of face-centered cubic (fcc) Cu phase (JCPDS No.04-0784). A small peak is also observed at around 29° indicates that a small amount of copper is oxidized and converted into copper oxide. The lattice parameter 'a' has been calculated by using these profiles and the average value of lattice parameter is found to be in the range 3.61 A° - 3.63 A°. These values not only agree with each other but also in agreement with reported value 3.615 A° in literature. In general, the width of XRD peaks is related to crystallite size. Crystallite size of copper nanoparticles was calculated using the Scherer's equation (1), and found to be around 10 nm.

XRD pattern of synthesized Copper nanoparticles using a leaf extract of Ocimum sanctum shows a high crystallinity of Cu sample level with diffraction angles of 22.3°, 25.9°, 28.3° and 44.8°, which correspond to the characteristic face centered cubic (FCC) of copper lines indexed at (111), (200), (210) and (222), respectively. The diffraction angle observed at 21.1° is related to the tulsi leaf extract medium. The size of the nanoparticles obtained were estimated to be 77 nm using Debye-Scherrer Equation, which may indicate a high surface area, and surface area to volume ratio of the nano-crystals.

SEM:
SEM images of copper nanoparticles stabilized by papaya extract prepared using copper chloride, copper sulphate and copper nitrate shows copper nanoparticles nearly monodispersed distribution of particle sizes. The average particle size of the Cu nanoparticles is around 20 nm.

Copper nanoparticles deposited on carbon coated aluminium sheet and on glass plate were examined using scanning electron microscope (SEM).

TEM

Transmission electron microscopy (TEM) has been employed to characterize the size, shape and morphology of synthesized copper nanoparticles. Copper sulphate is found to be the best precursor that gives better result among other salts used for the synthesis of copper nanoparticle i.e., good particles size control along with papaya extract as capping agent. The TEM image of copper nanoparticles synthesized using copper sulphate stabilized by papaya extract is shows the average size of copper nanoparticles is around 20 nm.

FTIR:

The FTIR spectra were recorded using FTIR spectrometer. A known amount of sample was ground with KBr and the pellet form of the samples was analyzed with FTIR instrument. FTIR measurement was carried out to identify the possible molecules responsible for capping and reducing agent for the copper nanoparticles synthesized using papaya extract stabilizer. FTIR spectra of copper nanoparticles synthesized using different copper salts stabilized by papaya extract are shown in Fig. 2.

The broad bands observed at around 3480 cm-1 and 617 cm-1 illustrates the stretching frequency of hydroxyl group (OH group) present in the surface of the copper nanoparticle. The FTIR spectrum of Cu nanoparticles in ocimum extract shows band at 3373 cm^{-1}, 1635 cm^{-1}, 1516 cm^{-1}, 1376 cm^{-1} , 1198 cm^{-1} corresponds to O-H Stretching H-bonded alcohols and phenols, carbonyl stretching, N-H bend primary amines, corresponds to C-N stretching of the aromatic amino group and C-O stretching alcohols, ethers respectively. FTIR spectrum of Cu nanoparticles suggested that Cu nanoparticles were surrounded by different organic molecules such as terpenoids, alcohols, ketones, aldehydes and carboxylic acid.

EDX:

The composition of copper nanoparticles was probed by energy-dispersive X-ray analysis. EDX pattern of copper nanoparticles prepared using copper sulphate indicates the presence of Cu and small amount of oxygen.

AFM:

Morphology of Copper nanoparicles deposited on glass plate was examined with an Atomic Force Microscope (easy Scan 2, Nanosurf AG, Switzerland) operating in a contact mode (cantilever force constant 3 N/m). Copper nanoparticles deposited on carbon coated aluminium sheet and on glass plate were examined by atomic force microscope (AFM) respectively.

Particle size analyzer

Particle size and size distribution of the Copper colloid were analyzed using particle size analyzer (Malvern instrument, DTS version 4.20. U.K.).

HRTEM:

In the HRTEM images, the dark spots and light features corresponds to Copper nanoparticles and carbon matrix, respectively. HRTEM study shows that particles produced were almost spherical and 8-15 nm in size range. A thin coating can be observed on all particles and the thickness is a few nanometers. This indicates that the bacterial surface acts both as reducing as well as capping agent. The micrograph also demonstrates that as-synthesized Cu nanoparticles are well-dispersed with no conspicuous agglomeration and stable even up to one month; since the x-ray diffraction studies confirmed.

CONCLUSION

Nano Copper colloids were successfully prepared, by reducing various Cu^{+2} salts. The stability of the particles was improved by the introduction of stabilizer in the colloidal system. Addition of stabilizer resists major agglomeration of particles. Eco-friendly synthesis of Cu nanoparticles can be carried out using leaf broth extract of Ocimum sanctum. This method has merits over other reported methods are easily available starting materials, inexpensive and procedure is easy to carry out any laboratory, use of toxic reagent is avoided and pollution. Spherical nanoparticles of copper are synthesized by using a non pathogenic bacterial strain is a simple, rapid, cost efficient and green method which is free from using any toxic reducing chemicals. The characterization of copper nanoparticles prepared by different methods involves same basic techniques i.e. presence of characteristic absorption peak, diffraction peaks, particle size distribution and morphology etc.

REFERENCES

[1]. Aruldhas N., Raj C. P., Gedanken A., Synthesis, Characterization, and Properties of Metallic Copper Nanoparticles Chem. Mater., (1998) 10(5), 1446–1452.
[2]. Joshi S. S., Patil S. F., Iyer V., Mahumuni S., Radiation induced synthesis and characterization of copper nanoparticles Nanostru. Mater., (1998) 10(7), 1135–1144
[3]. N.R. Jana, Z.L. Wang, T.K. Sau and T. Pal, Seed-mediated growth method to prepare cubic copper nano particles, Current Science, 79 (2000), 1367-1370.
[4]. Hyungsoo C., Sung-Ho P., Seedless Growth of Free- Standing Copper Nanowires by Chemical Vapor Deposition J. Am. Chem. Soc. (2004) 126(20), 6248–6249.Guo Z., Liang X., Pereira T., Scaffaro R., Hahn H. T., CuO nanoparticle filled vinyl-ester resin nanocomposites: Fabrication, characterization and property analysis Compos. Sci. Tech. (2007) 67(10), 2036-2044.
[5]. N. Prakash, S. Jayapradeep and P. N. Sudha, "Investigation of Antimicrobial Properties of Silver and Copper Nanoparticles Encspsulated in Chitosan", First International Conference on Nanostructured Materials and Nanocomposites, Kottayam, India, April 6-8, 2009, pp. 311-317.
[6]. D.P. Chattopadhyay and B.H. Patel, Effect of nano sized colloidal copper on cotton fabric,
[7]. Journal of Engineered Fiber Fabrics, 5 (2010), 1-6.
[8]. T. Theivasanthi and M. Alagar, "X-Ray Diffraction Studies of Copper Nanopowder", Archives of Physics Research, Vol.1, No.2, 2010, pp.112-117.Lanje A. S., Sharma S. J., Pode R. B., Ningthoujam R. S., Synthesis and optical characterization of copper oxide nanoparticles Advances in Applied Science Research (2010) 1 (2), 36-40.
[9]. Borkow G., Molecular mechanisms of enhanced wound healing by copper oxide –impregnated

[10]. dressings Wound Repair Regen (2010) 18(2), 266- 275.
[11]. Hashemipour H., Rahimi M. E. Z., Pourakbari R., Rahimi P., Investigation on synthesis and size control of copper nanoparticle via electrochemical and chemical reduction method Int. J. Phys. Sci., (2011) 6(18), 4331-4336.
[12]. Surmawar N. V., Thakare S. R., Khaty N. T., One-Pot, Single Step Green Synthesis of Copper Nanoparticles: SPR Nanoparticles International Journal of Green Nanotechnology, (2011) 3(4), 302–308Yang G., Chai S., Xiong X., S. Zhang, YU L., Zhang P. Preparation and tribological properties of surface modified Cu nanoparticles Trans. Nonferrous Met. Soc. China (2012) 22(2), 366-372.
[13]. D P Chattopadhyay and B H Patel Preparation, Characterization and Stabilization of Nanosized Copper Particles Int. J. Pure Appl. Sci. Technol., 9(1) (2012), pp. 1-8
[14]. Honary S., Barabadi H., Gharaeifathabad E., Naghibi F., Green synthesis of copper oxide nanoparticles using penicillium aurantiogriseum, penicillium citrinum and penicillium waksmanii Digest Journal of Nanomaterials and Biostructures (2012) 7(3), 999 – 1005.
[15]. Gunalan S., Sivaraj R., Venckatesh R., Aloe barbadensis Miller mediated green synthesis of monodisperse copper oxide nanoparticles: Optical properties Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2012) 97, 1140–1144.
[16]. Vasudev D. Kulkarni, Pramod S. Kulkarni Green Synthesis of Copper Nanoparticles Using Ocimum Sanctum Leaf Extract Vol. 1 No. 2 2013