International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.3, pp 1544-1547, 2014-2015

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Optical band gap analysis of chemically synthesized Copper nanoparticles

Blessy Babukutty[1]*, Fasalurahman Parakkal[1], Swapna.S.Nair[1]

[1] Department of Physics, Central University of Kerala, 671314, India

Abstract: Copper nanoparticles are synthesized with trioctylphosphine oxide (TOPO) as the surfactant using sulphates as precursors. Surface morphology is analyzed by using Scanning Electron Microscopy (SEM).The SEM image shows that the average grain sizes of the particles, lies in the range 20-30nm. Optical absorption characteristics are studied by UV Visible spectrophotometer (PG-T80+UV VIS spectrophotometer). Absorption spectra while plotted as Tauc curves show different band edges, keeping band to band transition of the bulk metallic nanoparticles. Bigger particles above 10 nm show bulk like behavior contributing to the band gap of 0.8 eV while confined particles contribute to the second and most dominant band edge corresponding to a band gap of 3 eV. The particles, because of their smaller size, have much higher band gap than that of bulk material.

Introduction

Nanomaterials exhibit fascinating properties with modification in physical and chemical properties by varying the different sizes of the particle [1]. As the particle size decreases, surface to volume ratio increases such that large proportion of atoms will be present on the surface of the particle. In recent years, colloidal metal particles had been prepared with a wide range of particle sizes ranging from nm-μm range by different methods. Metal nanoparticles have diverse technological applications such as field induced sensors, field induced optical limiters, storage devices etc. They also possess application in quantum computing, drug targeting and magnetic hyperthermia [2].

Copper nanoparticles have found remarkable applications in electronic optical devices and catalysis[3,4], reducing the cost compared with the usage of gold and silver nanoparticles. Several synthetic techniques of CuNPs based on the chemical reduction of copper salt using reducing agents like ascorbic acid, hydrazine or sodium borohydride[5-8], in the presence of stabilizers such as surfactants forming micelles, polyvinyl pyrrolidone(PVP),or capping agents [9,10] were investigated.

Synthesis of monodisperse nanoparticles is the ability to separate nucleation from growth. For a well known shape, size and growth of copper nanoparticles certain conditions are required such as high concentrations of stabilizers also by increasing the temperature[11-15].

In this paper, CuNP's were synthesized by chemical reduction method using sodium borohydride as reducing agent and Lewis base, trioctylphophine oxide(TOPO) used as a solvent and passivating ligand.

Experimental Details

Synthesis of Cu nanoparticles

CuNP's are prepared in which $NaBH_4$ (1M) and $CuSO_4$ solution (0.5M) are mixed for 30 minutes at room temperature so as to get a homogeneous solution. A precipitate is formed, dissolved in the surfactant using TOPO (3mL) inorder to obtain fully dispersed and stabilized Cu nanoparticles. The precursors used are of analytical grade with purity greater than 96%. The synthesized particles are then sonicated for homogenization.

UV-VIS spectra analysis

The optical spectra of CuNP's were measured after diluting a small aliquot of the sample into distilled water. UV-VIS spectra were taken using PG T-80 UV-VIS spectrophotometer. The wavelength is tuned in such a way that starts from 900 to 190nm.

SEM analysis

Scanning Electron Microscopy measurement of the sample was taken on Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM). The obtained micrograph is then examined for the particle size and shape and surface morphology.

Results and Discussion

Chemical reduction of aqueous solution of copper sulphate for the formation of copper nanoparticles was investigated. In order to examine size and shape controlled CuNP's in aqueous suspensions, the reaction mixtures were characterized by UV-visible spectroscopy (Fig.1). The increase in intensity of light over the time indicates the completion of the reaction in the sample.

Absorption spectra of Copper nanoparticles formed in the reaction media have absorbance peaks at about 300 ,370 and 510nm might be assigned to the step like characteristics of copper nanoparticles above 650nm due to quantum confinement at nanoregime [16,17,18].

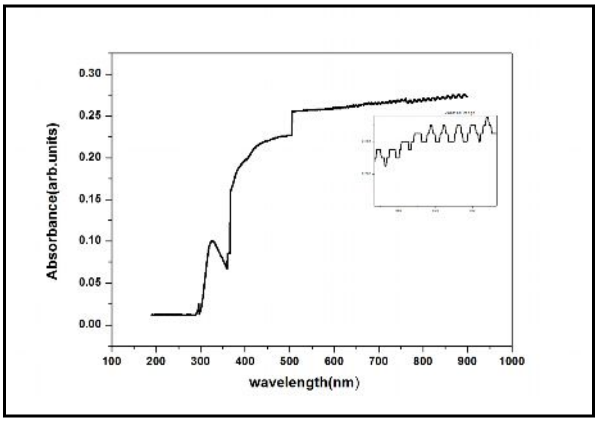

Fig. 1: Absorption Spectra of Copper nanoparticles

The spectra were plotted as Tauc curves in which different band edges were depicted shown in figure 2. The absorption edges corresponds to1.14eV and 2.44 eV. These are due to the narrow size distribution of the particles in which confined particles below 10nm contribute to band edge corresponding to a band gap of 3eV.

NP's with narrow size distribution show narrow absorbance and that of broad size distribution shows broad absorbance [19,20,21]. As the particle size decreases, the band gap of the material decreases leading to blue shift region.

Band gap in semiconductor in which absorption coefficient can be measured by using the equation(1),

$$\alpha = \frac{A(h\nu - Eg)^{\frac{1}{2}}}{h\nu}$$

Where A is a constant, Eg is band[1] gap energy and α is absorption coefficient.

When αhν=0, Eg=hν .ie, by plotting a graph between hν and αhν, a straight line is obtained. It is clear that energy of emitting radiation is equal to the band gap energy. Thus band gap of the material can be measured.

In bottom up chemical approach particle size vary from ultrafine to large particles. So the nanoparticles system contains particles of different band gaps. Due to the variation of band gaps in the sample, there arises absorption of varying wavelengths.

The inset of Fig .1 shows that the optical absorption spectra possess step like absorption showing quantum confinement. The confinement energy can be calculated from the equation(2),

$$Eg_{confinement} = \frac{\hbar^2\pi^2}{2mR^2} \qquad (2)$$

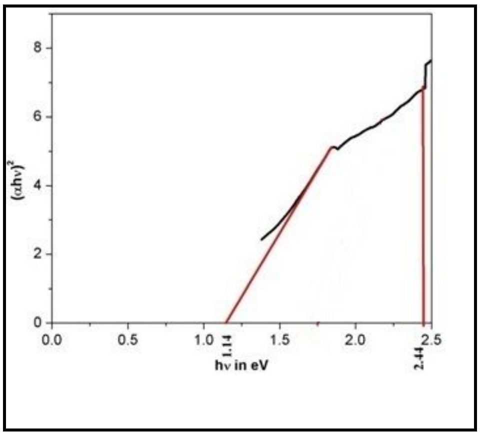

Fig. 2: Band edges of Copper Nanoparticles

Owing to the wide spectrum of particle sizes, confinement energy will change and hence there are multiple steps in the absorption. SEM images showed microstructure of the sintered specimen with different sizes ranging from 20-30nm (Fig.3).

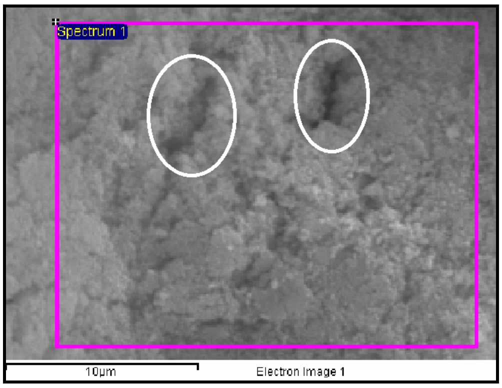

Fig 3: SEM image of Copper nanoparticles

Conclusions

Copper nanoparticles have been synthesized by chemical reduction route using trioctylphosphine oxide (TOPO) as surfactant. Formation of nanoparticles is analyzed by UV-VIS spectroscopy and SEM. The UV-VIS spectra of nanoparticles showed distinct absorption peaks at 300,370 and 510nm. Band gap analysis based on the sample has been done. Different band edges were obtained at 1.14eV and 2.44 eV leading to quantum confinement regime. The surface morphology of the nanoparticles was obtained, determining the average size of the particle. The chemical route addressed here is eco-friendly and can be used for further applications.

References

1. Misra, P., Blackman, J.A., Metallic Nanoparticles, Elsevier, Oxford, UK, 2009, 8.
2. Wu, N., Fu, L., Su, M., Aslam, M., Wong, K.C., and Dravid, V.P., Interaction of fatty acid monolayers with cobalt na0noparticles, Nanoletters, 2004, 4; 383-386.
3. Liu, X., Cai, W., and Bi, H., Optical absorption of copper nanoparticles dispersed within pores of monolithic mesoporous silica, J.Mater.Res. 2002, 17, 1125-1128.
4. Singh, P., Katyal, A., Kalra, R., and Chandra, R., Copper nanoparticles in ionic liquid: An easy and efficient catalyst for the coupling of thiazolidine-2,4-dione,aromatic aldehyde and ammonium acetate, Catal. Commun., 2008, 9, 1618-1623.
5. Lisiecki, I., Billoudet and Pileni, M.P., Control of the Shape and the Size of Copper Metallic Particles, J. Phys. Chem., 1996, 100, 4160–4166.
6. Qi, L., Ma, J., and Shen, J., Synthesis of Copper Nanoparticles in Nonionic Water-in-Oil Microemulsions, J. Colloid Interface Sci., 1997,186, 498–500.
7. Kanninen, P., Johans, C., Merta, J., and Kontturi, K., Influence of ligand structure on the stability and oxidation of copper nanoparticles, J. Colloid Interface Sci., 2008, 318, 88–95.
8. Wu, C., Mosher, B., and Zeng, T., One-step green route to narrowly dispersed copper nanocrystals, J. Nanopart. Res., 2006, 8, 965–969.
9. Lisiecki, I., and Pileni, M.P., Synthesis of Copper Metallic Clusters Using Reverse Micelles as Microreactors, J. Am. Chem. Soc., 1993,115, 3887–3896.
10. Mott, D., Galkowski, J., L., Wang, J., Luo and Zhong, C., Synthesis of Size-Controlled and Shaped Copper Nanoparticles, Langmuir, 2007,23, 5740–5745.
11. Kapoor, S., and Mukherjee, T., Photochemical formation of copper nanoparticles in poly(N-vinylpyrrolidone), Chem. Phys. Lett., 2003, 370, 83–87.
12. Condorelli, G. G., Costanzo, L. L., Fragala, S., Giuffrida, S., and Ventimiglia, G., A single photochemical route for the formation of both copper nanoparticles and patterned nanostructured films, J. Mater.Chem., 2003, 13, 2409–2411.
13. Yin, Y. and Alivisatos, A., Colloidal nanocrystal synthesis and the organic–inorganic interface, Nature, 2005, 437, 664–670.
14. Filankembo, A., Giorgio, S., Lisiecki, I., and Pileni, M.P., Is the Anion the Major Parameter in the Shape Control of Nanocrystals?, J. Phys.Chem. B, 2003, 107, 7492–7500.
15. Nakamura, T., Yasunori, T., Sakata, T., Mori, H., Kanbe, Y., Bessho, H., and Wada, Y., Preparation of Monodispersed Cu nanoparticles by Microwave-Assisted Alcohol Reduction, Bull. Chem. Soc. Jpn., 2007, 80, 224–232.
16. Petranovskiia, V., Stoyanov, E., Gurin, V., Katadad, N., Hernandez ,M.A., Avalos, M., Pestryakov, M., Ch´avez Rivas, F., Zamorano Ulloa, R., and Portillo, R., Formation of copper nanoparticles in mordenites with variable SiO2/Al2O3 molar ratios under redox treatments, Rev. Mex. Fis., 2013, 59, 170–185.
17. Lisiecki, I., and Pileni, M.P., Copper Metallic Particles Synthesized "in Situ" in Reverse Micelles: Influence of Various Parameters on the Size of the Particles, J. Phys. Chem.1995, 99, 5077-5082.
18. Pestryakov, M.P., Petranovskii, V.P., Kryazhov, A., Ozhereliev, O., Fänder, N.P., Knop Gericke., A, Study of Copper nanoparticles formation on supports of different nature by UV-visible diffuse reflectance spectroscopy, Chemical Physics Letters, 2004, 385,173-176
19. Liz-Marzan, L.M., Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles, Langmuir, 2006, 22, 32-41.
20. Schultz, D.A., Plasmon resonant particles for biological detection, Current Opinion in Biotechnology 2003,14, 13-22.
21. Eustis, S., El-Sayed, M.A., Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes, Chemical Society Reviews, 2006, 35, 209-217.

*****