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SYNTHESIS AND CHARACTERISATION OF CuO NANOPARTICLES BY SOLID-STATE THERMAL DECOMPOSITION OF SCHIFF BASE COPPER(II) COMPLEX

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ABSTRACT

Synthesis, spectral identification, and magnetic property of Schiff base Cu (II) complex is described. The general formula [M(L)(Phen)(H_2O)$_2$], where L is the Schiff base ligand derived from 4-chlorobenzaldehyde and amino acid. This complex was synthesized by one-pot synthesis method and characterized by elemental analysis, Fourier transform infrared spectroscopy, electronic spectra, room temperature magnetic moments and conductivity measurement. The resultant solid was subsequently annealed in the muffle furnace at 400 °C for 3 hours in air atmosphere. Nanoparticles of CuO were produced and characterized by X-ray powder diffraction (XRD) at 2ϑ degree 0-80°, FT-IR spectroscopy and scanning electron microscopy (SEM). The XRD and FT-IR results showed that the product is pure and has good crystallinity with cubic structure because no characteristic peaks of impurity were observed, while the SEM results showed that the obtained product is tiny, aggregated with spherical shape, narrow size distribution with an average size between 10-40 nm. Results show that the solid-state thermal decomposition method is simple, environmentally friendly, safe and suitable for preparation of CuO nanoparticles. This method can also be used to synthesize nanoparticles of other metal oxides.

KEY WORDS

Schiff base complex, Thermal decomposition, CuO nanoparticles, XRD, SEM.

INTRODCTION:

Metal complexes with Schiff base ligands have played an important role since the early days of coordination chemistry.[1] Indeed, a great deal of work has been carried out on the synthesis and characterization of transition metal complexes with these type ligands, mainly due to their applications in organic chemistry, as liquid crystals and in catalytic processes.[2] Schiff bases are regarded as privileged ligands.[3] Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions.[4] Schiff bases are an important class of compounds in medicinal and pharmaceutical field. Also, Schiff bases and their complexes have been used as biological models to understand the structures of biomolecules and biological processes. [5] Copper Schiff base complexes are amongst the most versatile catalysts known for oxygenation reactions. The role played by

copper ions in the active sites of a large number of metalloproteins has stimulated efforts to design and characterize copper complexes as models for a better understanding of biological systems. [6]

Macroscopic properties of materials strongly depend on both the size and the morphologies of the microscopic particles they are made up from. This is especially true for materials with morphological features smaller than a micron in at least one dimension which is commonly called nano-scale materials, or simply nanomaterials. In these materials the ratio of surface area to volume is vastly increased when compared to compounds with larger grain sizes and quantum mechanical effects such as the ''quantum size effect" begin to play a significant role. These effects only play a minor role when going from macro to micro dimensions, but become increasingly important when reaching the nanometer size range.[7] Thus synthesis and characterization of nano-structures with different particle sizes and morphologies are very important both from the viewpoint of basic science as well as for technological applications.[8] Nanoparticles have attracted great interest in recent years because of their unique chemical and physical properties, which are different from those of either the bulk materials or single atoms. Nano-materials have potential applications in optoelectronics, catalysis, and ceramics and so on. Among these materials metal oxide nanoparticles are of technological importance for solar cells, chemical sensors and liquid crystal displays. [9] CuO, as an important p-type semiconductor with a narrow band gap (1.4 eV), has received great attention owing to its important properties and widespread applications. Copper (II) oxide nanoparticles have been of considerable interest due to the role of CuO in antibacterial activity [10], electrocatalytic application [11] and interaction with amino acids. There are several methods to prepare CuO nanoparticles, such as electrochemical reduction, hydrothermal and alcothermal reaction, solid-state thermal decomposition, microwave irradiation and etc. Currently, the solid-state thermal decomposition of Schiff base complexes as new precursors is being used more and more, and as compared to conventional methods, it is much faster, economical and cleaner. Although CuO can be prepared using a number of methods, it still remains a major challenge to develop a facile, inexpensive and nontoxic route for the synthesis of CuO.[12] In this paper, we describe the synthesis and characterization of new copper(II) complex of Schiff base ligand derived from 4-chlorobenzaldehyde and an amino acid with [1,10] phenanthroline as a co-ligand. CuO nanoparticles were prepared via the decomposition of the corresponding copper Schiff base precursor complex at 400° C using a muffle furnace and the obtained CuO nanoparticles were characterized by FT-IR spectroscopy, XRD analysis and SEM.

MATERIALS AND METHODS:

Materials and Reagents

All chemicals were of analytical grade and purchased from Merck and Sigma Aldrich. Commercial solvents were distilled and then used for the preparation of Schiff base copper (II) complex

Instruments:

Elemental analysis was performed using a Perkin-Elmer elemental analyzer. Molar conductivity of the metal complex was determined by using DMF as a solvent in Equiptronics digital conductivity meter at room temperature. FT-IR spectra of Schiff base copper (II) complex and its copper oxide nanoparticles were obtained on a Schimadzu IR-Affinity-I spectrometer with samples prepared using KBr pellets. UV–Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200–800 nm with quartz cell. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα raiation ith nickel beta filter in the range 2Θ = 10º-80º. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM.

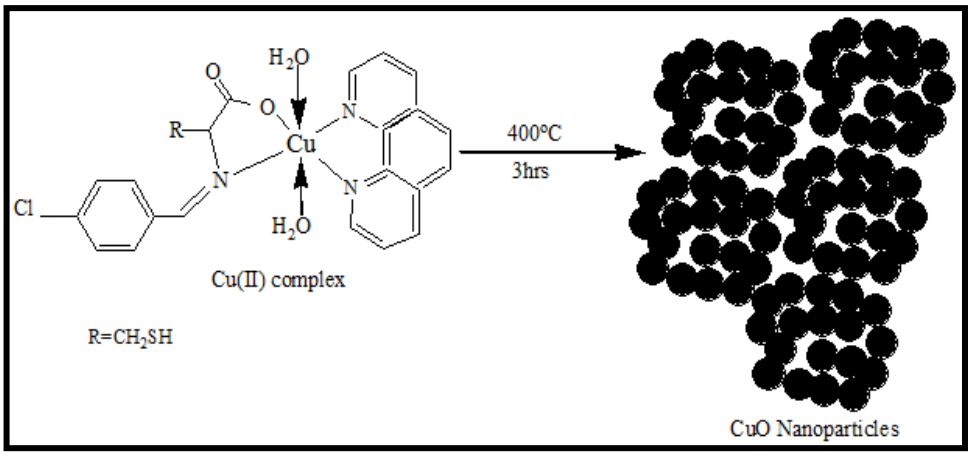
Synthesis of Schiff Base Copper (II) complex:

In a 250ml beaker, L-Cysteine (10mmol) and KOH (10mmol) in 25ml hot water was stirred and to that 4-chlorobenzaldehyde (10mmol) in 20ml of ethanol was added to the above solution and stirred for 2 hours at 60̊ C. Then an aqueous solution of copper (II) chloride was added to the reaction mixture and stirred for one hour. Finally, 1, 10-Phenanthroline (10mmol) in 15ml of ethanol was added to the above reaction mixture and again stirred for another 2 hours. Then the final product obtained was washed several times with alcohol, filtered and air dried.

Synthesis of copper oxide nanoparticles by thermal decomposition method:

Schiff Base Copper (II) complex precursor was taken in a silica crucible and heated to 400° C in a muffle furnace

at a ramping rate of 10°C min^{-1} for 3hours. The reaction heated to 400° C at a ramping rate of 10°C min^{-1}, the dark blue colored complex turned to black, which implied that Copper oxide nanoparticles had been produced. Nanoparticles were cooled down to room temperature.



RESULTS AND DISCUSSION:

The synthesized Schiff base copper (II) complex was characterized by Elemental analysis, UV-Visible, FT-IR and Molar conductance, Magnetic susceptibility measurement and the results are given below.

Elemental analysis:

The elemental analysis data of Schiff base copper (II) complex is given in Table 1. The calculated value was in good agreement with the theoretical value.

Table 1: Analytical and physical data of Schiff base copper (II) complex

Compound	Empirical Formula	μ_{eff} BM	Molar Conductance (mho cm^2 mol^{-1})	Elemental Analysis Found (Cal.) (%)		
				C	H	N
Complex-I	$C_{22}H_{20}O_4N_3SCu$	1.89	43	54.49 (54.43)	4.17 (4.12)	8.81 (8.66)

Molar conductivity and magnetic susceptibility measurement:

The molar conductance values measured in DMF solution ($1x10^{-3}$ mol dm^{-3}) and the value is 43 ohm^{-1} cm^2 mol^{-1} suggesting that the complex is non-electrolyte.[13] The room temperature magnetic moment (μ_{eff}) value of the copper(II) complex is observed in 1.89 B.M., which corresponds to a single unpaired electron and may be concluded that the copper(II) complex has octahedral geometry.

UV-Visible Spectra:

The electronic absorption spectra of Schiff base copper (II) complex (10^{-3} M) was recorded in DMF at room temperature and the data is represented in the Table 2. The band appeared around 287 nm and 376 nm corresponds to π→π* transition of aromatic chromophore as well as the imine moiety and the band at 441 nm is due to n→π* transition respectively.[14] The copper (II) complex exhibited a broad band at 677 nm due to d-d transition.

Table 2: UV-Visible spectral data of Schiff base copper (II) complex

Compound	π-π* (nm) (benzene)	π-π* (nm) (-HC=N)	n-π* (nm)	d-d (nm)
Complex-I	287	376	441	677

FT-IR Spectra:

The FT-IR spectrum provides valuable information regarding the nature of the functional group attached with the metal ion in the synthesized Schiff base copper (II) complex. The synthesized Schiff base copper (II) complex was characterized mainly using the C=N

(azomethine), M-O, M-N peaks. The assignments of important infrared spectral data are listed in Table 3. The peak observed in the range 1593 cm^{-1} was characteristic of azomethine (HC=N-) group. [15] The formation of M-N and M-O linkage was confirmed the appearance of peaks around 578 and 478 cm^{-1} respectively. The characteristic peak at 1593 cm^{-1} which is attributed to the (C=N) stretching is disappeared in FT-IR spectra of copper oxide nanoparticles whereas a new strong peak was appeared at 443 cm^{-1} in nanoparticles prepared from copper (II) complex indicating the spinel structure of Cu–O.

Table 3: FT-IR spectral data of Schiff base copper (II) complex

Compound	υ(-OH)	υ_{aro}(C-H)	υ(CH=N)	υ(Cu-N)	υ(Cu-O)
Complex-I	3406	3051	1593	578	478

XRD Analysis:

Fig. 1 shows the X-ray diffraction (XRD) pattern of the prepared CuO nano-structures. CuO nano-structures have shown the most crystallinity because of the existence of sharp peaks in the XRD pattern. The phase purity of the as prepared CuO nano-structures is completely obvious and all diffraction peaks are perfectly indexed to the monoclinic CuO phase with the lattice constants comparable to the reported data (JCPDS 01-1117). No characteristic peaks of impurities are detected in the XRD pattern. The broadening of the peaks indicated that the particles were of nanometer scale. [16-18] The crystalline size of the CuO nanoparticles based on X-ray peak broadening were determined using the Debye-Scherrer equation d (Å) = 0.9 λ / β cosθ. The calculated values are about 43 nm for CuO nanoparticles prepared from Schiff base copper (II) complex.

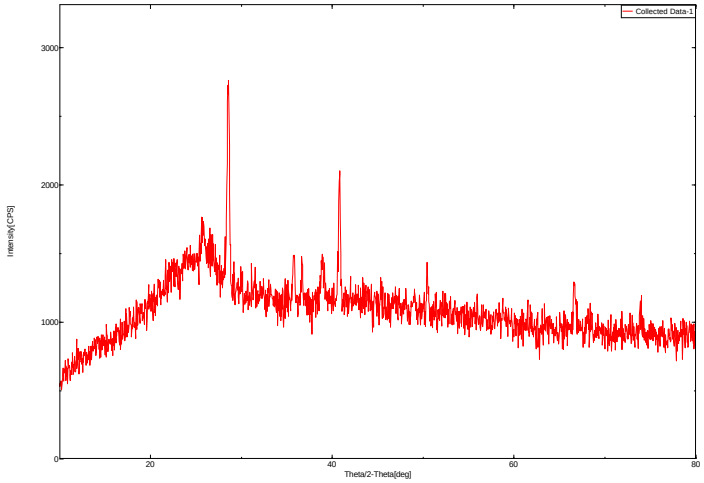


Figure 1: XRD Pattern of CuO nanoparticles

SEM image:

After characterization of the as-prepared CuO nanoparticles using FT-IR and XRD, for the determination of the morphology and structure of CuO, SEM measurements were carried out Fig. 2. The morphology evolution of the prepared CuO nanoparticles showed spherical shapes, aggregated with an average size of 56 nm. The differences between the results of the size of nanoparticles on SEM and XRD can be explained by agglomeration phenomena. [19] The agglomerated particles were related to many factors such as shape factor, surface area, porosity and density. Furthermore, in a colloidal system, consisting of a large number of small particles in a suspending fluid, particles will collide with one another in the course of their Brownian motion. [20] The aggregate may continue to grow, becoming less mobile, until it settles. Individual particles can only remain in such systems if there is some mechanism to prevent them from sticking together when they collide with one another.

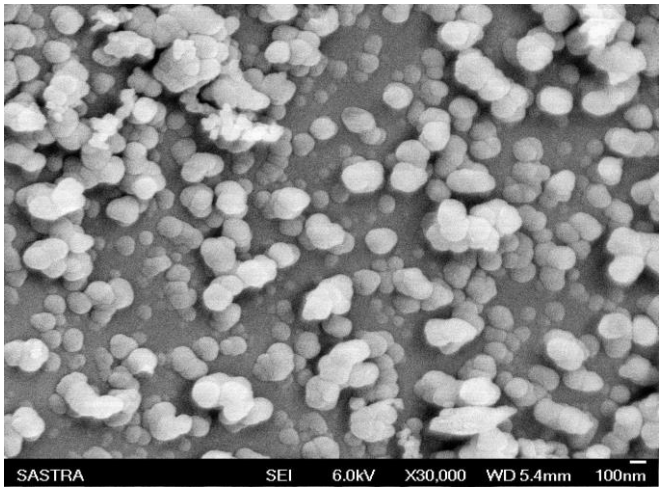


Figure 2: SEM image of CuO nanoparticles

CONCLUSION:

In the present work, a novel Schiff base copper (II) complex was prepared by using one pot synthesis method. Furthermore, this complex was used as a new precursor for the preparation of CuO nanoparticles with an average size of 56 nm. The obtained evidence of UV-Vis and magnetometry can support the octahedral geometry for the complex. In addition, this solid-state thermal decomposition method is simple, facile, inexpensive, nontoxic and safe to use, can be applied as a general method for the preparation of other transition metal oxide nanoparticles.

REFERECES:

[1] Bartyzel A. Synthesis, thermal study and some properties of N_2O_4-donor Schiff base and its Mn (III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. J. Therm. Anal. Calorim, 127: 2133-3147, (2017).

[2] Abbasi Z, Behzad M, Ghaffari A, Rudbari HA, Bruno G. Mononuclear and dinuclear salen type copper (II) Schiff base complexes: Synthesis, characterization, crystal structures and catalytic epoxidation of cyclooctene. Inorg. Chim. Acta, 414: 78-84, (2014).

[3] Mazurek W, Bond AM, Murray KS. Preparation and spectral, magnetic, and electrochemical characterization of a flexible phenoxo-bridged binuclear copper (II) complex. Inorg. Chem, 24(16): 2484-2490, (1985).

[4] Yunqi Tian, Jian Tong, Gerlinde Frenzen, Jin-Yu Sun. Proton-Template Synthesis, Structure, and Characterization of a Robson-Type Macrocycle with a totally ð-Conjugated System. J. Org. Chem, 64: 1442-1446, (1999).

[5] Geetha K, Nethaji M, Vasanthacharya NY, Chakravarty AR. Magneto-structural correlation in (μ-alkoxo/hydroxo)(μ-carboxylato)dicopper(II) systems: synthesis, X-ray structure and magnetic properties of aquo(μ-hydroxo) (μ-arylcarboxylato)bis (N,N,N',N'tetramethylethane1,2-diamine)dicopper(II) diperchlorate. J. Co-ord. Chem, 47: 77-89, (1999).

[6] Joy Chakraborty, Guillaume Pilet, M. Salah El. Fallah, Joan Ribas, Samiran Mitra. Synthesis, characterisation and cryomagnetic studies of a novel homonuclear Nd (III) Schiff base dimer. Inorganic Chemistry communications, 10(4): 489-493, (2007).

[7] Razavi RS, LoghmanEstarki MR. Synthesis and characterization of copper oxide nanoparticles within zeolite Y. J. Clust. Sci, 23: 1097-1106, (2012).

[8] Wang W, Varfhese OK, Ruan C, Paulose M, Grimes CA. Synthesis of CuO and Cu_2O crystalline nanowires using $Cu(OH)_2$ nanowire templates. J. Mater. Res, 18: 2756-2759, (2003).

[9] Jia W, Reitz E, Shimpi P, Rodriguez EG, Gao PX, Lei Y. Spherical CuO synthesized by a simple hydrothermal reaction: Concentration dependent size and its electrocatalytic application. Mat. Res. Bull, 44: 1681-1686, (2009).

[10] Wang HW, Xu JZ, Zhu JJ, Chen HY. Preparation of CuO nanoparticles by microwave irradiation. Journal of Crys. Growth, 224: 88-94, (2012).

[11] El-Trass A, Elshamy H, El-Mehasseb I, El-Kemary M. CuO nanoparticles: Synthesis, characterization, optical properties and interaction with amino acids. Appl. Sur. Sci, 258: 2997-3001, (2012).

[12] Khansari A, Enhessari M, Salavati-Niasari M. Synthesis and characterization of nickel oxide nanoparticles from Ni(salen) as precursor. J. Clust. Sci, 24: 289-297, (2013).

[13] Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord. Chem. Rev, 7: 81-122, (1971).

[14] Jiang X, Herricks T, Xia Y. CuO nanowires can be synthesized by heating copper substrates in air. Nano Lett, 2: 1333-1338, (2002).

[15] Suramwar NV, Thakare SR, Khaty NT. Synthesis and catalytic properties of nano CuO prepared by soft chemical method. Int. J. Nano Dimens, 3: 75-80, (2012).

[16] Safarifard V, Morsali A. Sonochemical syntheses of a nano-sized copper (II) supramolecule as a precursor for the synthesis of Copper(II) Oxide nanoparticles. Ultrason. Sonochem, 19: 823-829, (2012).

[17] Jadhav S, Gaikwad S, Nimse M, Rajbhoj A. Copper oxide nanoparticles: Synthesis, characterization and their antibacterial activity. J. Clust. Sci, 22: 121-129, (2011).

[18] Srivastava AK, Tiwari P, Kumar A, Nandedkar RV. Growth of copper oxide nanorods. Curr. Sci, 86: 22-23, (2004).

[19] Wu HQ, Wei XW, Shao MW, Gu JS, Qu MZ. Synthesis of copper oxide nanoparticles using carbon nanotubes as templates Chem. Phys. Lett, 364: 152-156, (2002).

[20] Sabbaghi S, Heydari O, Parvizi MR, Saboori R, Sahooli M. Effect of temperature and time on morphology of CuO nanoparticle during synthesis. Int. J. Nano Dimens, 3: 69-73, (2012).