

**Republic of Iraq
Ministry of Higher Education
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**Synthesized , characterization of CuO and NiO nanoparticle
Via thermal decomposition for Schiff base metal ion
complexes**

A project

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Abstract

In this study, CuO and NiO NPs have been synthesized by facile thermal decomposition of Schiff base complexes and their physical properties have been examined. A tridentate Schiff base ligand was via the condensation reaction between 2-Chlorobenzylamine and 2-hydroxybenzaldehyde, and characterized by physical and analytical technique such as melting point, FTIR, UV-visibles and ^1H , ^{13}C -NMR spectroscopies. Cu(II) and Ni(II) complexes were synthesized from (E)-2-(((2-chlorobenzyl)imino)methyl)phenol Schiff base (CIMP) by reaction molar ratio 1:1 (Metal :Ligand). Also the metal ion complexes were characterized by melting point, FT-IR and UV-visible spectroscopies. FT-IR spectra of complexes indicate the deprotonated Schiff base ligand that coordinates with metal ions through azomethine nitrogen aryl chloride chlorine and phenolic oxygen. The crystalline structure of the product was studied by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). XRD indicated that the new products were copper oxide and Nickel oxide. A very uniform and narrow size distribution of nanoparticles with spherical morphology and an average diameter between 20 and 22 nm was obtained for all three nanoparticles.

Key word: Schiff base (Ligand), Metal ion complexes and Metal oxide nanoparticulate

Introduction :

In the last three decades, many research groups have paid attention to the synthesis of Schiff bases and prepared their metal complexes due to versatile properties and wide applications in catalytic industrial processes[1]. Nanotechnology is a field in science that deals with the production and manipulation of particles on a nanoscale. It is the ability to measure, see, manipulate, and manufacture things on an atomic or molecular scale, usually between 1 and 100 nanometres. Nanotechnology finds applications in computers, nanodiodes, nano transistors etc. This technology helps in the development of batteries, fuel cells and solar cells that are lighter, more durable, and stronger than those produced using other methods[2] to their extraordinary properties, metal oxide nanostructures are promising candidates for applications in various fields such as optoelectronics, optics, catalysts, sensors and electronics [3-6]. Among many metal oxides, CuO is a narrow band gap (1.2 eV) p-type semiconductor and thus it has received much attention for applications in optoelectronics, catalysis, semiconductors, batteries, gas sensors, biosensors and field transistors[7]. Also, NiO is a p-type semiconductor with relatively wide band gap (3.6 eV) and it has great potential applications such as electrode materials for supercapacitor devices, microbial fuel cells with lithium ion, gas sensing of hydrogen sulfide as well as photocatalytic reduction of methyl orange dye ethanol, and nitrogen dioxide. However, thermal decomposition techniques are considered as the most promising [8-10], because one can control the process conditions, particle size, particle crystal morphology, and purity. Moreover, it requires a short time, and has high yields, low costs and low power consumption. The ligand H₂L acts as tridentate through oxygen atoms, nitrogen atom and chlorine atom for Ni(II) and Cu(II) complexes. The Ni(II) and Cu(II) oxides nanostructures are collected through thermal decomposition process of (L) complexes which has many advantages like

controlling on the process conditions, particle size, particle crystal structure, decreasing the calcinations temperature, and purity.

Experimental

Materials:

The chemical compound used high purity without purification, Salicylaldehyde (Merck, Germany), 2-Chlorobenzylamine (Merck), Nickel acetate tetrahydrate $\text{Ni}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ and copper acetate hydrate $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ (BDH, England).

Instrumental

In Stuart melting point (digital) SMP30 apparatus was used to record the melting point. FTIR spectra were measured by a Shimadzu (FTIR) model Broker Spectrophotometer between the ranges (4000–400) cm^{-1} as KBr discs. UV-Vis ultraviolet Spectrophotometer model 1700 Shimadzu is used to measure the UV-visible spectra at R.T. °C using 1 cm quartz cell and examined between 200–1100 nm at 10⁻³ M in DMF. The ¹H- and ¹³C-NMR spectrum of ligand was recorded at a Bruker DMX-400 spectrophotometers (400 MHz) by using DMSO-d₆.

Procedures :

Synthesized of Schiff base Ligand

The Schiff base compound was prepared according to the method reported in the literature [11], 2-Chlorobenzylamine (5 ml., 0.035 mol) was added to a stirred ethanol solution of salicylaldehyde (5 ml. 0.035 mol). The reaction mixture was stirred at reflux for 4 h and then the mixture was allowed to stand at room temperature for give yellow crystals.

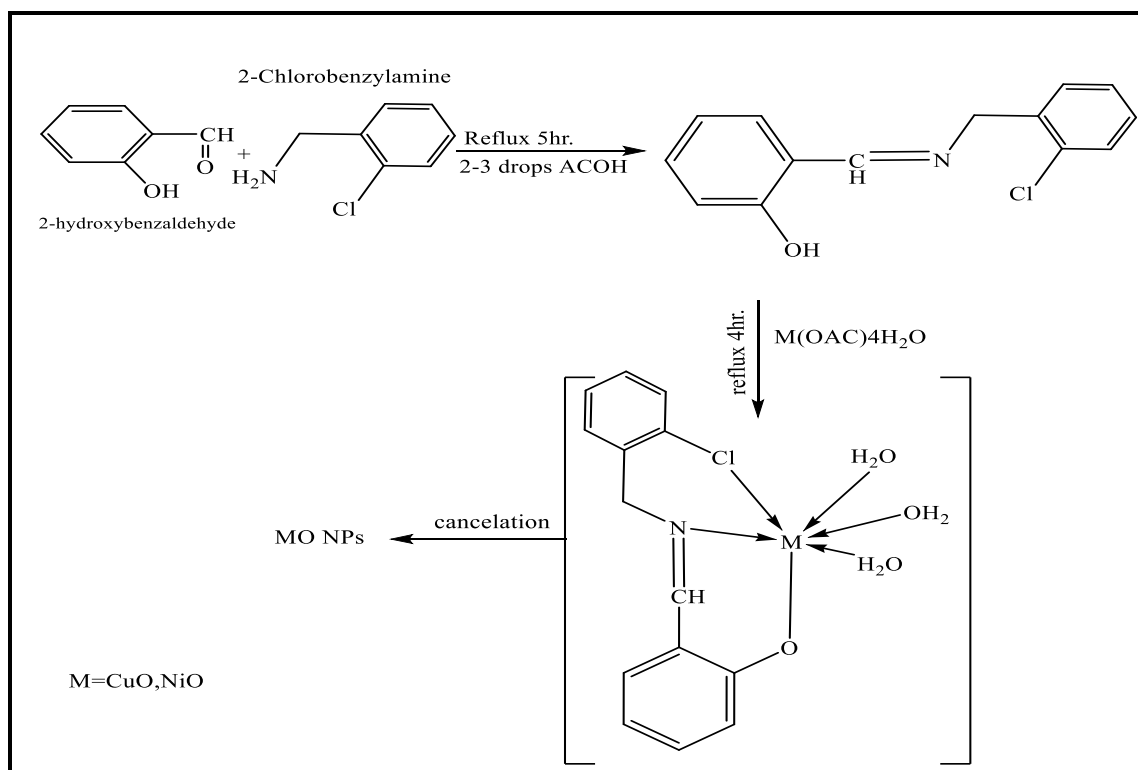
Synthesized of Metal ion complexes :

For the synthesis of transition metal complexes, Ni(L) and Cu(L) (1.06 g mol or 0.85 g, 0.004 Mol) of each, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ respectively was dissolved separately in 20 mL of distilled water. To this, a hot ethanolic

solution (20 mL) of L (1g,0.004 mol) was added dropwise with continuous stirring. The resultant mixture was refluxed for 5hours to obtain the precipitates of the metal complexes. These precipitates were then faltered, washed rigorously with methanol and then finally dried in an oven[12].

Synthesized of NiO and CuO nanoparticles:

The Schiff base complexes were loaded into crucible, placed in an oven and heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air. Nanoparticles of NiO and CuO were obtained at $500\text{ }^{\circ}\text{C}$, respectively, after 4 h. The final products were washed by ethanol to remove impurities, if any, and dried at room temperature for several days. The synthesized NiO and CuO nanoparticles were characterized by FT-IR, XRD, and SEM[13]



Scheme 1: synthesis Schiff base ,metal ion complexes and Metal oxide nanoparticular

Results and discussions

FT-IR spectra for Ligand ,metal ion complexes and Metal oxide nanoparticular

Some important infrared absorption frequencies of the ligands and their metal complexes are given in Table 1 with their probable assignments. All the free Schiff bases show their characteristic azomethine and OH frequencies at around 1650 and 3500 cm^{-1} , respectively. The former shifts towards the lower frequency region in the spectra of the complexes due to involvement of the N atom of the $\text{C}=\text{N}$ - group ,whereas the $\nu(\text{OH})$ bands almost disappear due to the deprotonation of the OH group. Strong bands around in Ligand and around 745 cm^{-1} in spectra of their metal complexes, suggesting the involvement of the halide group in coordination. The appearance of some new bands in the IR spectra of the metal complexes in the regions 450 and 360 are probably due to the formation of M-O and M-N bonds, respectively, developed through complexation. The foregoing results and discussion on Schiff base complexes denote that as a result of their chelation the $\text{C}=\text{N}$ bands are apparently shifted to lower wavenumbers. This is probably due to a change in the electrostatic field of the metal ions and in the vibrational dipoles of the ligand .Since all the metal ions under investigation have the same change, thus the distance between the metal ion and the coordinating centre would be the main factor affecting band shifts. The magnitude of the frequency shifts has been used and established elsewhere in determining the distance between the metal ion and the coordinating group, which is approximately equivalent to the length of the coordination bond. shifts in the IR spectra of organic ligands on coordination to metal ions are comparable to those shifts of the ligand bands when absorbed on a salt substrate. Thus, both cases can be treated more or less in the same manner[12, 14, 15]. The FT-IR techniques were used for the characterization of CuO nanoparticles. In the FT-IR spectra, the strong absorption

band at 480 cm^{-1} is related to the stretching vibrations of Cu-O , NiO nanoparticles generally give an absorption band at about 450 to 550 cm^{-1} . The peak at 420 cm^{-1} in the spectrum, undoubtedly assigned to Ni-O stretching, gave clear evidence about the presence of the crystalline NiO[12, 16]

Table 1: FT-IR spectra for Ligand ,metal ion complexes and metal oxide nanoparticles

Compound	$\nu\text{C}=\text{N}$ (cm^{-1})	$\nu(\text{O}-\text{H})$ (cm^{-1})	$\nu(\text{C}-\text{Cl})$ (cm^{-1})	$\nu(\text{M}-\text{O})$ (cm^{-1})
Schiff base (Ligand)	1633	3074	745	450
Ni(L) complex	1613	-----	756	458
Cu(L) complex	1621	-----	756	460
NiO Nps	-----	-----	----	461
CuO NPs	-----	-----	---	480

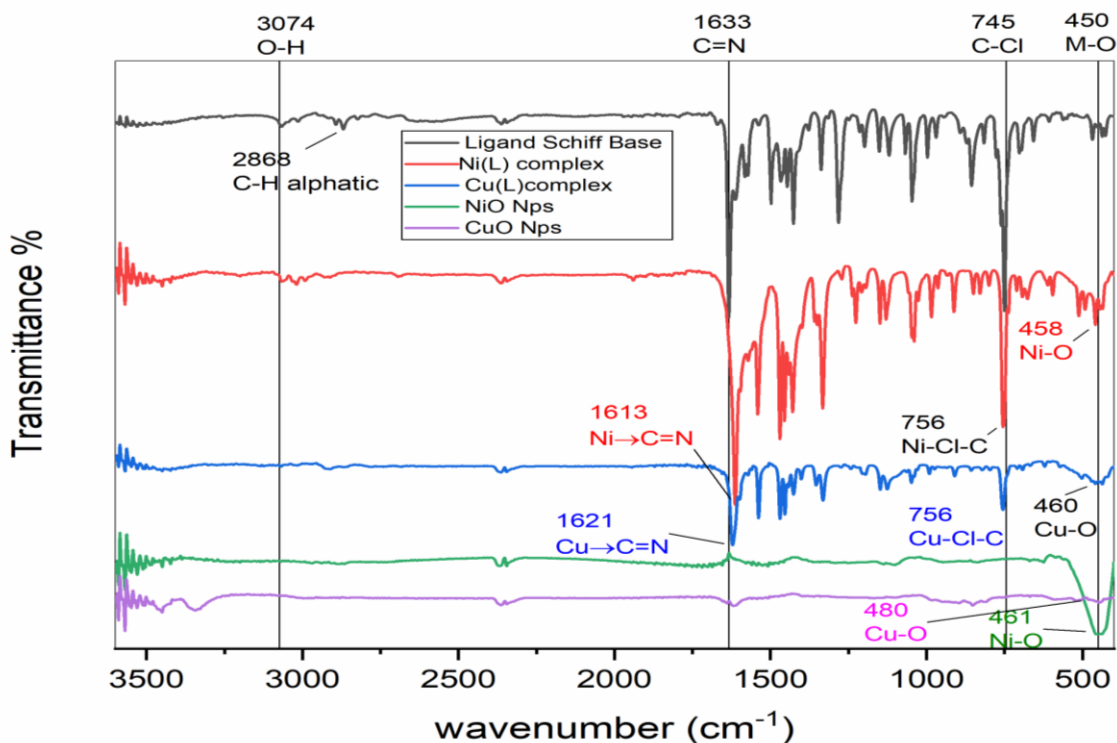


Figure1 :FT-IR spectra for Ligand ,metal ion complexes and Metal oxide nanoparticular

Electronic spectra of Ligand and its metal ion complexes :

The electronic spectrum of the ligand (L) was appeared a high intensity band appeared as a singlet due to intra-ligand transitions the band which was appeared at (268nm , 37313.43 cm^{-1}) was assigned to ($\pi \rightarrow \pi^*$) transition of the conjugated system. A lower intensity band appeared at (315nm, 31746.03 cm^{-1}) was assigned to ($n \rightarrow \pi^*$) [224]. Which are shown Figure(2). The electronic spectra of the Nickel ion complex Fig. 2 , exhibit four absorption bands in (15625 cm^{-1} , 640nm) , 24096.39 cm^{-1} , 415nm) and (, (29411.76 cm^{-1} , 340nm) ,(36764.71 cm^{-1} , 272nm) . An examination of these bands indicates that the complexes have an octahedral geometry and might possess D_{4h} symmetry. The ground state of Ni(II) in an octahedral coordination is $3A_{2g}$. Thus, these bands may be assigned to the three spin allowed transitions $3A_{2g}(F) \rightarrow 3T_{1g}(F) \text{---}(v_2)$, $3A_{2g}(F) \rightarrow 3T_{1g}(P) \text{---}(v_3)$, and MLCT respectively [17]. The electronic spectra of copper(II) complexes shows absorption bands (638nm, 15673.98 cm^{-1}) and (375nm, 26666.67 cm^{-1}), assignable respectively, to transitions $2B_{1g} \rightarrow 2B_{2g}$ and $2B_{1g} \rightarrow 2E_g$ of a square planar structure and 280nm, 35714.29 cm^{-1} due to MLCT. [18]

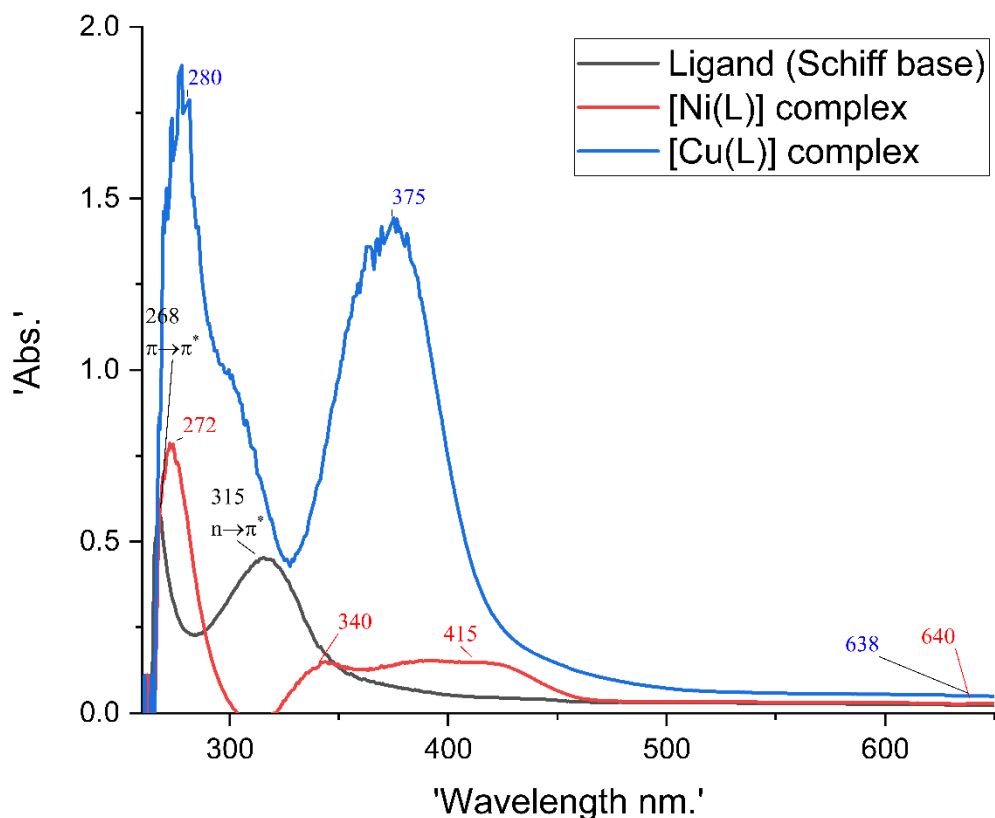


Figure 2: Electronic spectra of Ligand and its metal ion complexes

XRD for Metal oxide nanoparticles

Figure 3 displays the XRD pattern of NiO nanoparticles calcined at 500 C. All of the peaks match well with Bragg reflections of the standard facecentered cubic structure diffraction peaks at 37.28, 43.29 and 62.91, can be indexed as (111), (200), (220) crystal planes, respectively. The average crystallite size are found to be 26.72 nm is measured by X-ray diffraction line broadening using the Debye–Scherrer formula. Figure 3 represents the XRD pattern of the obtained CuO products calcined at 500°C. The entire diffraction peaks of copper oxide can be indexed to the monoclinic structure (JCPDS database No. 05-0661) [47]. The peaks at about 2θ values of 35.6°, 38.9°, 47.5° and 56.4° are assignable to (002), (111), (-202), and (202). The average size of CuO nanoparticles is also estimated

via Debye-Scherrer equation (D is the average size, λ is the X-ray source wavelength (1.54 Å), β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg's angle) to be approximately 26.7 nm.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{-----1}$$

In Eq. 1 D represents the average crystallite size, $K = 0.89$ is the Scherrer constant, $\lambda = 1.5406 \text{ \AA}$ is the wavelength of the X-ray (Cu K α 1 radiation), θ is the diffraction angle of the peak and β represents the full width at half maximum of the peaks. The average crystallite size of NiO products calcined at 500 C are found to be 22.7 nm.[19]

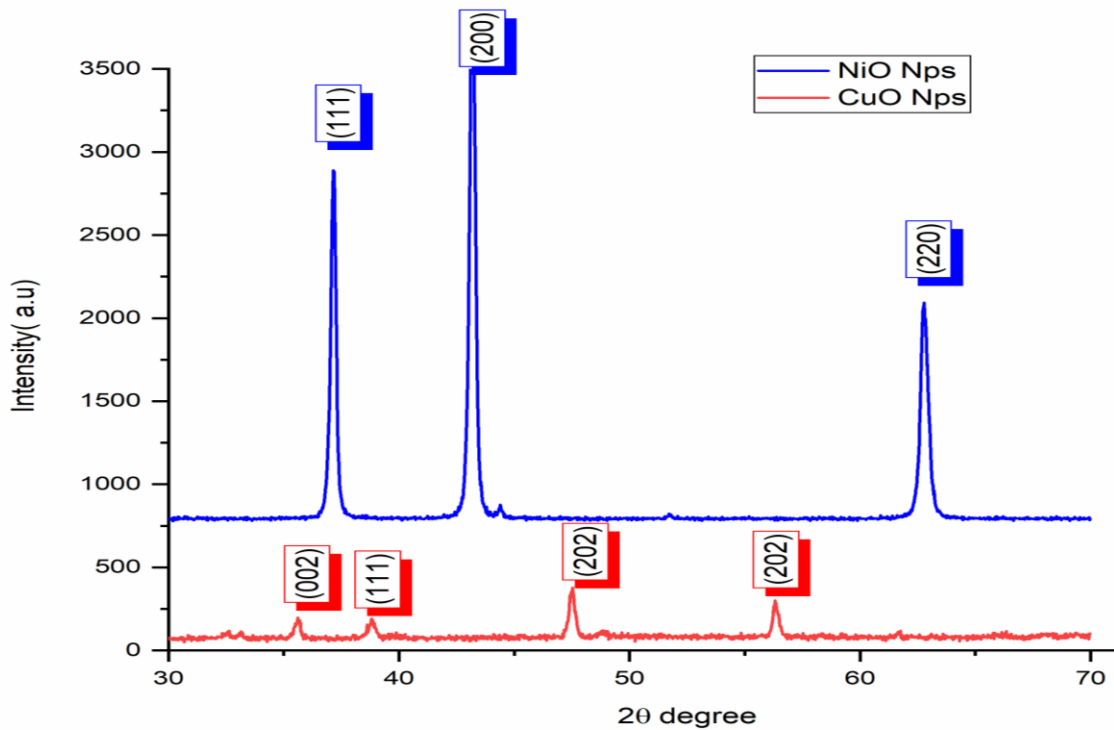


Figure: XRD paternt for NiO and CuO nanoparticles

Conclusions:

Salicylaldehyde, phenylmethanamine, and Metal acetate were used to create a binary Metal ion Schiff-base complex. FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and UV-Vis were utilized to determine the structure of the new M(II) complex produced and describe the formation of Schiff base ligand and metal with a molar ratio of 1:1. These observations led to the suggestion of deformed octahedral molecular for the Ni complex and square planar geometries. By thermal decomposition of Ni(II) and Cu(II) Schiff base complex, NiO and CuO nanoparticles that confirmed by XRD with average particle size about 26.7 and 22.7 nm are uniformly formed in polycrystalline monoclinic and cubic structures, respectively, without any observed impurity phases.

Referances:

1. Hossain, A.M.S., J.M. Méndez-Arriaga, C. Xia, J. Xie, and S.J.P. Gómez-Ruiz, *Metal complexes with ONS donor Schiff bases. A review.* 2022: p. 115692.
2. Parveen, K., V. Banse, and L. Ledwani. *Green synthesis of nanoparticles: Their advantages and disadvantages.* in *AIP conference proceedings.* 2016. AIP Publishing LLC.
3. Ali, M.A.E.A.A. and A.M.J.T. Abu-Dief, *CuFe₂O₄ nanoparticles: an efficient heterogeneous magnetically separable catalyst for synthesis of some novel propynyl-1H-imidazoles derivatives.* 2015. **71**(17): p. 2579-2584.
4. Abu-Dief, A.M., I.F. Nassar, and W.H.J.A.O.C. Elsayed, *Magnetic NiFe₂O₄ nanoparticles: efficient, heterogeneous and reusable catalyst for synthesis of acetylferrocene chalcones and their anti-tumour activity.* 2016. **30**(11): p. 917-923.
5. Abu-Dief, A.M. and W.J.M.R.E. Mohamed, *α -Bi₂O₃ nanorods: synthesis, characterization and UV-photocatalytic activity.* 2017. **4**(3): p. 035039.
6. Jia, W., E. Reitz, P. Shimpi, E.G. Rodriguez, P.-X. Gao, and Y.J.M.R.B. Lei, *Spherical CuO synthesized by a simple hydrothermal reaction: concentration-dependent size and its electrocatalytic application.* 2009. **44**(8): p. 1681-1686.
7. Bayansal, F., S. Kahraman, G. Çankaya, H. Çetinkara, H. Güder, H.J.J.o.A. Çakmak, and Compounds, *Growth of homogenous CuO nano-structured thin films by a simple solution method.* 2011. **509**(5): p. 2094-2098.
8. Salavati-Niasari, M., N. Mir, and F.J.P. Davar, *Synthesis and characterization of NiO nanoclusters via thermal decomposition.* 2009. **28**(6): p. 1111-1114.
9. Salavati-Niasari, M., F. Mohandes, F. Davar, M. Mazaheri, M. Monemzadeh, and N.J.I.c.a. Yavarinia, *Preparation of NiO nanoparticles from metal-organic frameworks via a solid-state decomposition route.* 2009. **362**(10): p. 3691-3697.
10. Farhadi, S. and Z.J.P. Roostaei-Zaniyani, *Simple and low-temperature synthesis of NiO nanoparticles through solid-state thermal decomposition of the hexa (ammine) Ni (II) nitrate, [Ni (NH₃)₆](NO₃)₂, complex.* 2011. **30**(7): p. 1244-1249.
11. Phurat, C., T. Teerawatananond, and N.J.A.C.S.E.S.R.O. Muangsin, *2-[(4-Chlorobenzyl) iminomethyl] phenol.* 2010. **66**(9): p. o2310-o2310.
12. Kargar, H., A. Adabi Ardakani, K.S. Munawar, M. Ashfaq, and M.N.J.J.o.t.I.C.S. Tahir, *Nickel (II), copper (II) and zinc (II) complexes containing symmetrical Tetradentate Schiff base ligand derived from 3, 5-*

- diiodosalicylaldehyde: Synthesis, characterization, crystal structure and antimicrobial activity*. 2021. **18**: p. 2493-2503.
13. Dehno Khalaji, A., M. Ghorbani, M. Dusek, V.J.I.J.o.C. Eigner, and C. Engineering, *Nickel (II) and Copper (II) Complexes of a New Tetradentate Schiff Base Ligand: Synthesis, Characterization, Thermal Studies and Use as Precursors for Preparation of NiO and CuO Nanoparticles*. 2018. **37**(6): p. 27-34.
 14. Parashar, R., R. Sharma, A. Kumar, and G.J.I.c.a. Mohan, *Stability studies in relation to IR data of some schiff base complexes of transition metals and their biological and pharmacological studies*. 1988. **151**(3): p. 201-208.
 15. Nakamoto, K., *Infrared and Raman spectra of inorganic and coordination compounds, part B: applications in coordination, organometallic, and bioinorganic chemistry*. 2009: John Wiley & Sons.
 16. Yang, C., X. Su, J. Wang, X. Cao, S. Wang, L.J.S. Zhang, and A.B. Chemical, *Facile microwave-assisted hydrothermal synthesis of varied-shaped CuO nanoparticles and their gas sensing properties*. 2013. **185**: p. 159-165.
 17. Chandra, S., L.K.J.S.A.P.A.M. Gupta, and B. Spectroscopy, *EPR and electronic spectral studies on Co (II), Ni (II) and Cu (II) complexes with a new tetradentate [N4] macrocyclic ligand and their biological activity*. 2004. **60**(7): p. 1563-1571.
 18. Singh, P.K., D.N.J.S.A.P.A.M. Kumar, and B. Spectroscopy, *Spectral studies on cobalt (II), nickel (II) and copper (II) complexes of naphthaldehyde substituted aroylhydrazones*. 2006. **64**(4): p. 853-858.
 19. Saadat, A., A. Banaei, P. Mcardle, and R.J.J.o.C. Jafari, *Spectral, structural, and antibacterial study of copper (II) complex with N2O2 donor schiff base ligand and its usage in preparation of CuO nanoparticles*. 2022. **2022**.