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FACILE SYNTHESES OF COPPER SULFIDE NANOPARTICLES: ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY STUDY

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ABSTRACT

Three varieties of copper sulphide nanoparticles, namely CuS-I, CuS-II and CuS-III have been synthesized from three different precursors $Cu(Im)_2(SCN)_2$ (**1**), $Cu(Mim)_2(SCN)_2$ (**2**) and $Cu(Bim)_2(SCN)_2$ (**3**), [Im: imidazole; Bim: Benzimidazole and Mim: 1-methyl imidazole respectively] using pyrolytic technique and have been characterized by routine physicochemical techniques where **1** has further been characterized by X-ray single crystal structure analysis. The synthesized nano particles were characterized by powder X-ray diffraction study and the surface morphology have been assigned by FE-SEM analysis. CuS-I, CuS-II and CuS-III have granular, spherical and agglomerate shape respectively. The size distribution of the nanoparticles has been determined by dynamic light scattering. The nanoparticles have size of ~100 nm. The CuS-I and CuS-II nanoparticles show an effective anti-bactarial and anti-fungal activity against five bacterial and five fungal species whereas CuS-III remains inactive.

Keywords. Coordination compound, Pyrolytic technique, CuS nanoparticles; FE-SEM; Power XRD; Photoluminescence; Antibacterial and antifungal study.

INTRODUCTION

In recent years, semiconductor nanomaterials have gathered much interest due to their novel physical and chemical properties which often determined by their size, shape, and composition.[1] Copper sulphide (CuS) is one of the most important p-type semiconductors amongst the transition-metal chalcogenides and is gaining intense attention in material science because of its exceptional optical, electronic and other physical and chemical properties[2].However, CuS nano particles may have a number of stable, metastable and intermediate compositions and structures in between the two common sulfide end members, Cu_2S (chalcocite) and CuS (covellite).[3] Hence the synthesis of CuS nanoparticles by a simple method is still a challenge. Many methods have been developed to synthesize copper sulphide nanoparticles, including microwave, electrosynthesis, thermolysis [4-6] and so on. However, most of these synthetic methods involve template or complex equipments. Recently, we have developed an indigenous pyrolytic technique to synthesize metal sulfide nano particles employing coordination compounds as sole precursors[7]. In the present study we have utilized the same methodology to get copper sulphide nano particles. Here, we have employed three coordination compounds, $Cu(Im)_2(SCN)_2$ (**1**), $Cu(Mim)_2(SCN)_2$ (**2**) and $Cu(Bim)_2(SCN)_2$ (**3**) [Im: imidazole; Bim: Benzimidazole and Mim: 1-methyl imidazole respectively], to get three varieties of CuS nano particles namely **CuS-I**, **CuS-II** and **CuS-III**, respectively. Complexes **1**, **2** and **3** have been characterized by routine physicochemical techniques and **1** has further been characterized by X-ray single crystal structure analysis. The size, shape and morphology of **CuS-I**, **CuS-II** and **CuS-III** nanoparticles have been determined by X-ray powder diffraction, FE-SEM and DLS studies. It is noteworthy that in recent days much effort has been directed in the search for new antibacterial agents to fight against the gradual developing resistivity of the bacteria toward the potent antibiotics.[8] It is now well recognized that inorganic materials can destroy bacteria, without toxicating the surrounding tissue.[9] Copper and its complexes have been used for centuries as disinfectants due to their

antibacterial as well as antiviral properties.[10] However, the possible antimicrobial activity of copper sulphide nanoparticles is not yet explored, although it can act as an efficient radiotracer for pharmacokinetics, biodistribution, and positron emission tomography.[11] In the present manuscript, we have thoroughly investigated the antibacterial activity of three varieties of synthesized copper sulphide nano particles using Staphylococcus aureus and Escherichia coli as model microbial species.

EXPERIMENTAL

Materials and Methods

Imidazole, Benzimidazole and 1-methyl imidazole were purchased from sigma-Aldrich chemical company. Sodium thiocyanate and copper perchlorate were purchased from LOBA and Merck chemical company respectively. Solvents were dried according to standard procedure and distilled prior to use. All other chemicals used were of AR grade. Water used in all experiments was Milli-Q grade. Electronic spectra (200-1200nm) were obtained at 25°C using a UV-2450 HITACHI spectrophotometer. Thermal analysis (DT-TGA) was carried out using Mettler Toledo (TGA/SDTA 851) thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 40 cm^3 min^{-1}). All the samples were heated in a platinum crucible at a rate of 10 degree per minute with inert alumina as a reference from 30 to 700 °C. The powder XRD measurements were carried out using Bruker D8 Advance X-ray Diffractometer. The morphology and size of CuS particles have been characterized by Hitachi S-3400N scanning electron microscopy (SEM). Fluorescence spectra were recorded in solid state with a Perkin-Elmer model LS 5583 Luminescence spectrometer.

General procedure

Complexes **1**, **2** and **3** were prepared according to slightly modified reported method.[12] The general synthetic procedure are described here. A methanol solution (5 mL) of the respective ligand (0.068 g, imidazole, 1.0 mmol; 0.082 g, 1-methylimidazole 1.0 mmol; 0.118g, benzimidazole, 1.0 mmol) was added to a methanolic solution (5 mL) of copper perchlorate (0.365 g; 1.0 mmol) with constant stirring. The resulting solution was allowed to stir for 30 min. After that a water-methanolic solution (5 mL) of sodium thiocyanate (0.246 g; 3 mmol) was added to it and stirring was continued for an additional 30 min. The reaction mixture was now filtered and the filtrate was kept in a $CaCl_2$ desiccator.

$Cu(Im)_2(SCN)_2$ (1)

Yield: 328 mg 90%; IR / cm^{-1}: = 3292 vs, 3230 m, 2921 m, 2876 m, 2084 s, 1617 w, 1488 s, 1407 m, (vs, very strong; s, strong; m, medium; w, weak). TGA: 10.3 mg weight loss (30 % of 34.31 mg complex: expected weight loss: 10.4 mg) at 650 °C. Elemental analysis: Calculated for $C_8H_8CuN_6S_2$; C, 30.42; H, 2.55; N, 26.61; Found: C, 30.35; H, 2.48; N, 25.87%.

Cu $(Mim)_2(SCN)_2$ (2)

Yield: 310 mg 85%; IR / cm^{-1}: = 3291 vs, 3232m, 2923 m, 2875 m, 2083 s, 1619 w, 1487 s, 1402 m, (vs, very strong; s, strong; m, medium; w, weak). TGA: 6.4 mg weight loss (28% of 22.85 mg complex: expected weight loss: 6.25 mg) at 650 °C. Elemental analysis: Calculated for $C_{10}H_{12}CuN_6S_2$; C, 38.5; H, 3.85; N, 26.96; Found: C, 38.35; H, 3.55; N, 25.98%.

Cu $(Bim)_2(SCN)_2$ (3)

Yield: 321 mg 88%; IR / cm^{-1}: 3288 vs, 3228 m, 2924 m, 2875 m, 2083 s, 1615 w, 1487 s, 1408 m, (vs, very strong; s, strong; m, medium; w, weak). TGA: 5.5 mg weight loss (23.5% of 23.4 mg complex: expected weight loss: 5.23 mg) at 650 °C. Elemental analysis: Calculated for $C_{16}H_{12}CuN_6S_2$; C, 46.21; H, 2.88; N, 20.22; Found: C, 45.98; H, 2.48; N, 19.87%.

Caution! Transition metal perchlorate salts should be handled with precautions.

The three varieties CuS nano particles were prepared by heating the corresponding precursors, i.e., complexes **1**-**3**, respectively at 620 °C for 5 h.

CuS-I

Yield: 283.5 mg 90 %; IR / cm^{-1} :1110 vs, 617 cm^{-1} s, UV-visible / λ_{max} (solid) nm: 812 sh, 660, 302.

CuS-II
Yield: 302.3 mg 88 %; IR / cm^{-1} :1103 vs, 610 cm^{-1} s, UV-visible / λ_{max} (solid) nm: 810 sh, 665, 303.

CuS-III
Yield: 352.75 mg 85 %; IR / cm^{-1} :1107 vs, 617 cm^{-1} s, UV-visible / λ_{max} (solid) nm: 811 sh, 667, 301.

Antimicrobial Activity
Antimicrobial activity of CuS nanoparticles were tested against five bacterial species (viz., *Bacillus subtilis, Listeria monocytogens, E. coli, Pseudomonas fluorescens* and *Salmonella typhimurium*) and five fungal species (viz., *Mucor, Rhizopus, Fusarium oxysporum, Alternaria* and *Helminthosporium*). The test samples were prepared by dissolving CuS nanoparticles in DMF medium using DMF solvent as control.

In Vitro Antimicrobial Activity
Antibacterial activity of the CuS nanoparticles was tested against the five bacterial species namely *Bacillus subtilis, Listeria monocytogens, E. coli, Pseudomonas fluorescens* and *Salmonella typhimurium* following Kirby Bauer Disc diffusion method.[13] Antifungal activity of the nanoparticles were also examined by the disc diffusion method against five fungi species namely *Mucor, Rhizopus, Fusarium oxysporum, Alternaria* and *Helminthosporium* respectively. Before proceeding into detail study the species were cultured on malt extract agar medium. The test organisms were grown on nutrient agar medium in petri plates. The disks were soaked with test samples, drained and then placed on the nutrient agar plate using sterilized forceps. After that they were again placed on the previously seeded plates and incubated at 37 ºC (for bacteria) and 28 ºC (for fungi) and the diameter of inhibition zone (Ferrari *et al*., 1999) around each disc was measured after 24 h for bacteria and 72 h for fungi. At the end of the incubation period, the zones of inhibition around the disc were measured in cm. 100 µL of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Isolated colonies of each organism which plays a pathogenic role were selected from primary agar plates and their susceptibility was examined by disc diffusion method.
The linear growth of the fungus was obtained by measuring the diameter of the colony on a Petri plate after 72 h and the percentage of inhibition was calculated from the following relationship:

$$\% \text{ inhibition} = [(C-T)/C] \times 100$$

Where C = diameter (in mm)^2 of the fungus colony in the control plates after 72 h and T = diameter of the fungus colony in the treated plates.

RESULTS AND DISCUSSION

Characterization of CuS Nanoparticles
In order to determine the appropriate calcinations temperature, the thermal behavior of the synthesized **1-3** was investigated by TGA. From thermogram it is evident that the calcination temperatures for complexes [Cu $(SCN)_2(Im)_2$], [$Cu(SCN)_2(Mim)_2$] and [$Cu(SCN)_2(Bim)_2$] are more than 650°C respectively as there is no change in sample weight after those temperatures. The FTIR spectrum of synthesized CuS particles exhibits sharp and very intensive bands at 1107 and 617 cm^{-1} as characteristic feature of CuS nanoparticles reported by other group.[14] Fig.-1 represents the XRD pattern of the synthesized CuS nanoparticles which corresponds to hexagonal structure. The diffraction pattern of the synthesized nanoparticles corroborates well with the standard diffraction pattern of hexagonal-phase CuS as found in literature.[15]
The morphology of the particles was studied by FE-SEM analysis. From the morphogram it is evident that morphology of the nanoparticles strongly depends on the precursor used (fig.-2). CuS-I nanoparticles obtained from complex **1** have granular shape. Complexes **2** and **3** produce spherical CuS-II and agglomerates CuS-III nanoparticles respectively. Interestingly, all the prepared CuS nanoparticles have size ~ 100 nm.

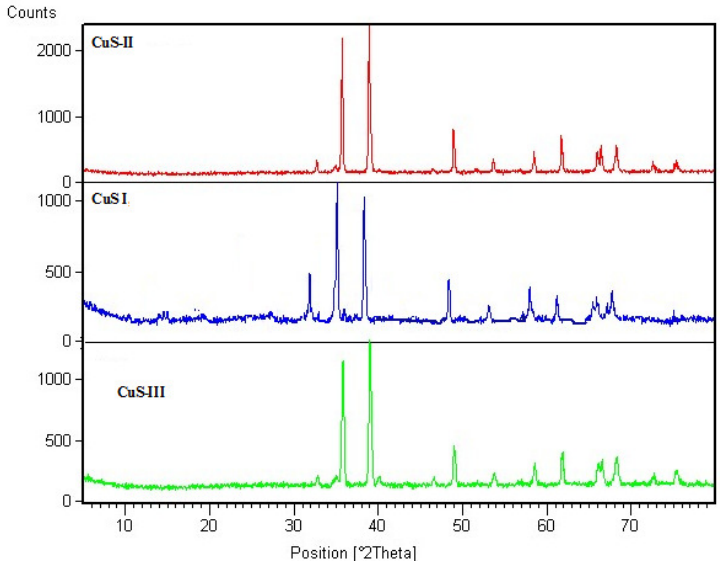
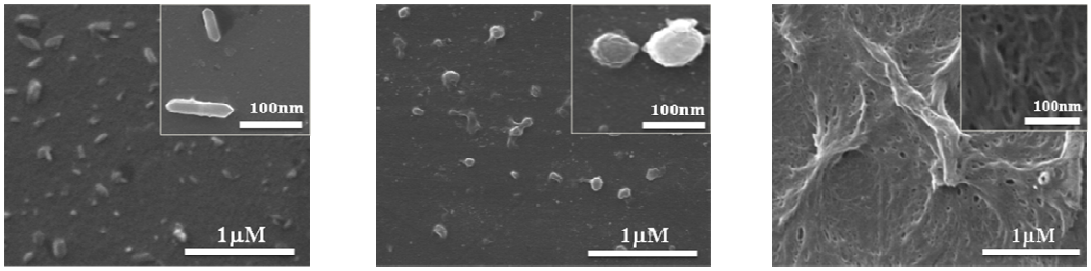


Fig.-1: Powder- XRD pattern of CuS-I , CuS-II and CuS-III nanoparticles.



(a) (b) (c)

Fig.-2: SEM images of (a) CuS-I, (b) CuS-II and (c) CuS-III nanoparticles.

The hydrodynamic diameter of synthesized nanoparticles was determined by dynamic light scattering method. The representative DLS data of copper sulphide is shown in fig.-3.

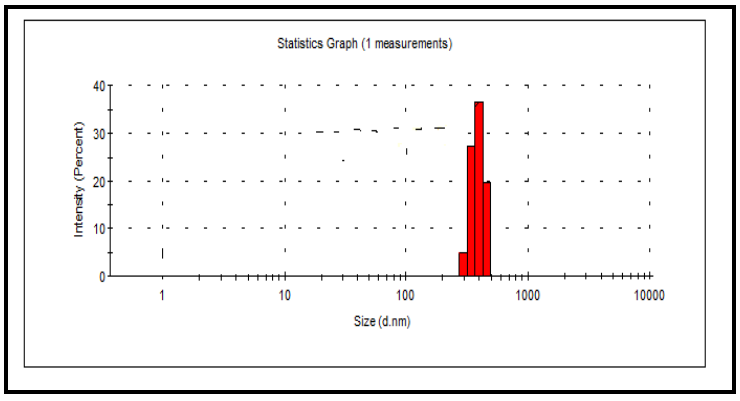


Fig.-3: Dynamic light scattering of CuS-I nanoparticles.

UV–Vis spectrophotometer was used to find out the absorption property of the synthesized nanoparticles. The spectrum (fig.-4) shows that all of them absorb in the region of 350-650 nm and exhibit a shoulder at about 480 nm. The similar result is also reported by Roy et al.[16] Additionally, all

the samples show a broadband in the near-IR region, which is the characteristic band for covellite CuS.[17,18]

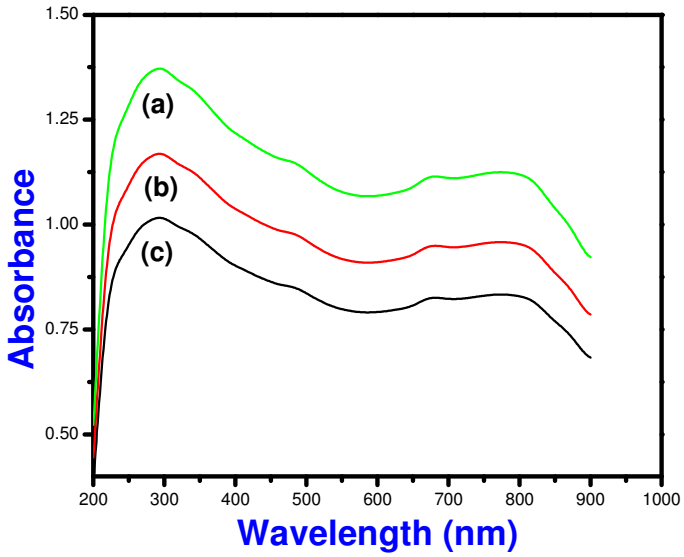


Fig.-4: Solid state UV spectra of Absorption spectra of (a) CuS-I, (b) CuS-II and (c) CuS-III nanoparticles at room temperature respectively.

Photoluminescence spectra of three varieties of CuS at room temperature are shown in fig.-5, which is obtained by exciting the samples at 290 nm in each case. Although Jiang et al.[19] reported no emission peak for CuS nanoparticles in the range of 400–800 nm, a broad peak at 620 nm is observed in our case. Similar luminescent peaks have ever seen by Roy and Srivastava[15, 20] for copper sulfide nanowires and nanorods at 450 and 515 nm respectively. Rao and co-workers [21] also found a peak at 560 nm with a shoulder at 480 nm for CuS nanorods. Different morphologies of copper sulfides may be responsible for such different PL spectra observed in our case, though the detailed reasons are unclear at present.

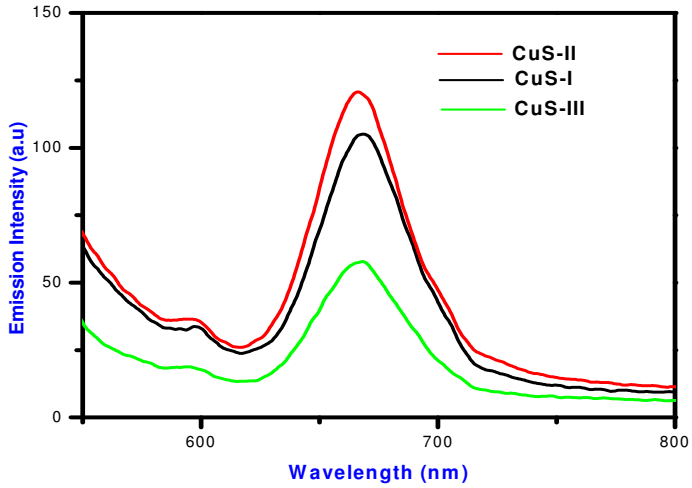
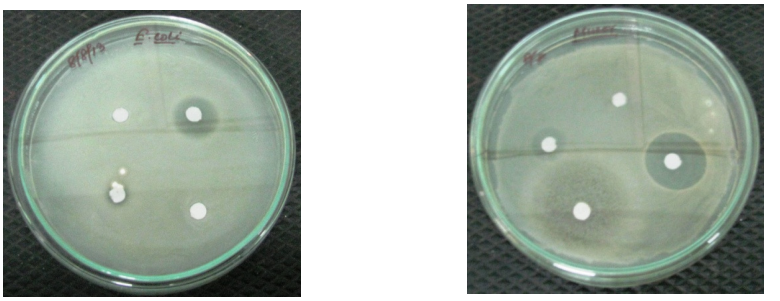


Fig.-5: Solid state fluorescence spectra of three different CuS nanoparticles.

Bio-Assay Investigations of CuS-I, CuS-II and CuS-III

In the cell of microorganism, lipid and polysaccharides are some important constituents of cell walls and membranes, which are responsible for metal ion interaction. In addition to this, the cell wall also contains amino phosphates, carbonyl and cysteinyl ligands, which maintain the integrity of the membrane acting as a diffusion barrier and also provides suitable site for bonding. Our synthesized nanoparticles (CuS-I and CuS-II) possibly adsorbed on the surface of the cell wall of microorganisms and disturb the respiration process of the cell. This may lead to breakdown of the permeability barrier of the cell, resulting in interference with the normal cell process and thus blocks the synthesis of the proteins that restricts further growth of the organisms. The representative of antibacterial and antifungal activity of copper sulphide nanoparticles is shown below (Fig.-6).



(a) **(b)**

Fig.-6: Antibacterial and antifungal activity of CuS-I nanoparticles against (a) *E. Coli* and (b) *Mucor* sp.

Interestingly the adsorptions of the nanoparticles on the surface of the cell wall depend on their shape and size. The granular shape CuS-I nanoparticles and the spherical shape CuS-II nanoparticles show antibacterial activities whereas the agglomerates CuS-III nanoparticles did not. The diameters of inhibition zone against bacterial and fungal species are demonstrated in table-1 and table-2.

Table-1: Diameter of inhibition zone (cm.) against bacterial species

Samples	*B. subtilis*	*L. monocytogens*	*E. coli*	*P. fluorescence*	*S. typhimurium*
Control (DMF)	-	-	-	-	-
CuS-I	1.0	2.5	1.7	1.5	0.7
CuS-II	1.9	2.2	-	1.2	-
CuS-III	-	-	-	-	-

Table-2: Diameter of inhibition zone (cm.) against fungal species

Samples	*F. oxysporum*	*Mucor*	*Rhizopus*	*Alternaria*	*Helminthosporium*
Control (DMF)	-	-	-	-	-
CuS-I	2.0	2.2	2.0	-	1.9
CuS-II	1.7	1.2	1.2	-	0.7
CuS-III	-	-	-	-	-

CONCLUSIONS

In the present work, we have reported the synthesis of three different varieties of CuS nanoparticles by pyrolytic technique using three easily synthesizable single source precursors namely **1**-**3**. The XRD pattern indicates the formation of a covellite nature of copper sulphide nanoparticles. The morphology of the product was studied by FESEM analysis which reveals that the source precursor had notable effects in determining the morphology of the products. Antimicrobial and antifungal activities of CuS

nanoparticles have been investigated which suggest that the activity depend largely on the morphology of the nanoparticles.

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