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Synthesis and characterization of Copper (II) Phosphate nano particles

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ABSTRACT

Copper (II) Phosphate nano particles were synthesized via chemical co precipitation method from Copper Sulphate and Sodium Phosphate. The formed nano particle is characterized by powder X-ray diffraction, scanning electron microscopy, Ultra-violet spectroscopy and Fourier transform infrared spectroscopy, confirmed the preferential growth of Copper (II) Phosphate nano particles that width is 55.08 nm. The SEM image shows the synthesized Copper (II) Phosphate show well crystallized particles with cauli flower like morphology. The FTIR spectrum is used to study the stretching and bending frequencies of molecular functional groups in the sample. From UV spectrum, the band gap of Copper (II) Phosphate nano particles is found to be 2.5 eV. From AAS studies it is found that the absorbance is directly proportional to the concentration. The linear fit indicates that Copper (II) Phosphate nanoparticles have been distributed in proper proportion.

1.Introduction

A burst of research activity is witnessed in recent years in the area of synthesis and fabrication of different size and shape of metal nano particles. Nanometer sized particles display many interesting optical, electronic, magnetic and chemical properties yielding applications in biological nano sensors, optoelectronics, nano devices, nano electronics, information storage and catalysis [1, 2]. Amongst many metals like Au, Ag, Pd, Pt, towards which research is directed, copper and copper based compounds are the most important materials. The metallic Cu plays a significant role in modern electronics circuits due to its excellent electrical conductivity and low cost nano particles [1, 3]. So Cu will gain increasing importance as is expected to be an essential component in the future nano devices due to its excellent conductivity as well as good biocompatibility and its surface enhanced Raman scattering (SERS) activity [1, 4]. Metallic copper nano crystals homogeneously dispersed in silica layers have attracted great attention recently for the development of nonlinear optical devices [1, 5]. In this work, Copper (II) Phosphate nanoparticles were prepared and their structural and optical properties were studied.

Copper (II) Phosphate has been used as fungicide, fertilizer and corrosion inhibitor for oxidation and phosphoric acid, catalyst for organic reactions, emulsifier, and protectant for metal surfaces against oxidation.

2. Experimental Details

Nano particles of Copper (II) Phosphate were prepared by chemical co precipitation method by adding Copper Sulphate and Sodium Phosphate. Precise amounts of reagents taking into account their purity were weighed and dissolved separately in distilled water into 0.1M concentration. After obtaining a homogeneous solution, the reagents were mixed using magnetic stirring. The precipitate was separated from the reaction mixture and washed several times with distilled water and ethanol. The wet precipitate was dried and thoroughly ground using agate mortar to obtain the samples in the form of fine powder.

3. Tests conducted

X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the peaks. XRD line broadening method of particle size estimation was chosen in this investigation for determining the crystallite size of the powder sample. XRD study of the powder samples was carried out at Centre for Electro Chemical Research Institute, Karaikudi. The morphology of the powder samples was studied by the scanning electron microscope (SEM) analysis taken at STIC Cochin. The infra red spectroscopic (IR) studies of Copper phosphate nano particles were made by using 'SHIMADZU' FTIR 8400S model spectrometer through KBr method. The UV spectrum was taken in the absorbance mode in the wavelength range from 200 to 800 nm.

4. Results and discussion

4.1. XRD studies

The XRD patterns of the prepared samples of Copper (II) Phosphate are shown in fig.1. XRD studies reveal that the samples are nano sized and crystalline. The fine particle nature of the samples is reflected in the X-ray line broadening. The size of the synthesized Copper (II) Phosphate nano particles are calculated using Scherrer equation

$$D = 0.9\,\lambda / \beta \cos\theta \qquad (1)$$

where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle. The average grain size of the particles is found to be 55.08 nm. The peak list in the XRD pattern is given in table-1.

A good agreement between the Experimental diffraction angle [2θ] and Standard diffraction angle [2θ] of specimen is confirming standard of the specimen. Fifteen peaks at 2θ values of Copper (II) Phosphate is observed and tabulated in table-2 and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), Copper (II) Phosphate file No. 80-0992. The d-spacing values of experimental is also confirming to the standard values.

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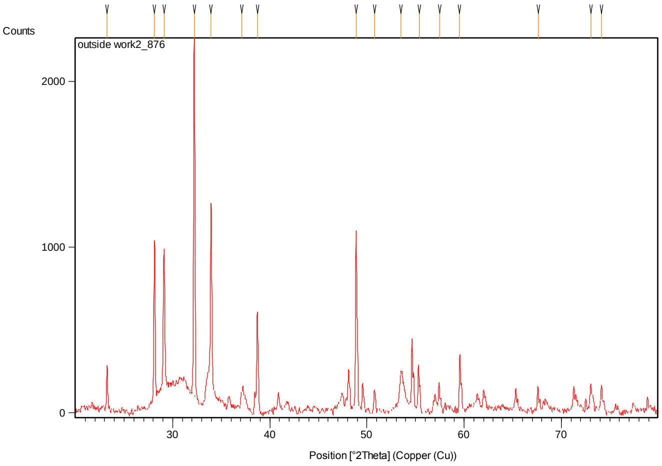

Figure.1 XRD pattern of Copper II Phosphate Nano particles

Table-1. Intensity of XRD peaks.

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
23.2523	265.95	0.1338	3.82552	12.44
28.1352	974.08	0.1506	3.17171	45.57
29.1038	870.37	0.1338	3.06833	40.72
32.2152	2137.69	0.1506	2.77873	100.00
33.9320	1188.42	0.1673	2.64196	55.59
37.1386	107.87	0.4015	2.42089	5.05
38.7142	599.14	0.2007	2.32592	28.03
48.8710	1027.76	0.1171	1.86366	48.08
50.7681	131.53	0.2007	1.79838	6.15
53.5124	239.67	0.4684	1.71245	11.21
55.3574	202.98	0.2007	1.65967	9.50
57.4730	122.82	0.2676	1.60350	5.75
59.5517	325.59	0.1338	1.55240	15.23
67.6085	122.75	0.2676	1.38569	5.74
73.0650	146.86	0.3346	1.29509	6.87
74.1089	129.67	0.4080	1.27835	6.07

2Theta = 32.2152

Theta = 32.2152/2 = 16.1076

D = (0.9 * 0.154) / (0.00251) * cos (16.1096) = 55.08 nm

Table.2. Experimental and standard diffraction angles of Copper (II) Phosphate specimen

Experimental		Standard – JCPDS 80-0992	
Diffraction angle (2θ in degrees)	D spacing (Å)	Diffraction angle (2θ in degrees)	D spacing (Å)
23.2523	3.82552	23.812	3.7336
28.1352	3.17171	27.737	3.2136
29.1038	3.06833	29.119	3.0641
32.2152	2.77873	32.214	2.7765
33.9320	2.64196	33.647	2.6615
37.1386	2.42089	37.405	2.4022
38.7142	2.32592	38.777	2.3203
48.8710	1.86366	48.739	1.8668
50.7681	1.79838	50.739	1.7978
55.3574	1.65967	55.409	1.6568
57.4730	1.60350	57.291	1.6068
59.5517	1.55240	59.632	1.5492
67.6085	1.38569	67.625	1.3842
73.0650	1.29509	73.096	1.2935
74.1089	1.27835	74.457	1.2732

4.1.2. XRD – Dislocation Density

The dislocation density is defined as the length of dislocation lines per unit volume of the crystal. In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The movement of a dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a larger hardness.

The X-ray line profile analysis has been used to determine the dislocation density. The dislocation density (δ) in the sample has been determined using expression.

$$\delta = \frac{15\,\beta\,cos\theta}{4aD} \qquad (2)$$

Where δ is dislocation density, β is broadening of diffraction line measured at half of its maximum intensity (in radian), θ is Bragg's diffraction angle (in degree), a is lattice constant (in nm) and D is particle size (in nm). The dislocation density can also be calculated from

$$\delta = \frac{1}{D^2} \qquad (3)$$

Where δ is dislocation density and D is the crystallite size. Results of the dislocation density calculated from both the formulas are given in table-3. The number of unit cell is calculated from

$$n = \pi\,(4/3) \times (D/2)^3 \times (1/V) \qquad (4)$$

Where D is the crystallite size and V is the cell volume of the sample [6].

Table-3. Dislocation Density and Number of Unit Cell from XRD

2θ (deg)	Particle Size D (nm)	Dislocation Density (m^2)		Number of Unit Cell
		δ = 15βcosθ /4aD	δ = 1 / D^2	
23.2523	60.82	$2.899x10^{14}$	$2.703x10^{14}$	$8.409\ x10^5$
28.1352	54.56	$3.601x10^{14}$	$3.359x10^{14}$	$6.071\ x10^5$
29.1038	61.55	$2.827\ x10^{14}$	$2.639x10^{14}$	$8.715\ x10^5$
32.2152	55.08	$3.525\ x10^{14}$	$3.296\ x10^{14}$	$6.246x10^5$
33.9320	49.81	$4.317\ x10^{14}$	$4.031x10^{14}$	$4.619\ x10^5$
37.1386	20.94	$2.445\ x10^{15}$	$2.281\ x10^{15}$	$0.343\ x10^5$
38.7142	42.09	$6.046\ x10^{14}$	$5.645\ X10^{14}$	$2.787\ x10^5$
48.8710	74.76	$1.914\ x10^{14}$	$1.789\ x10^{14}$	$15.61\ x10^5$
50.7681	43.96	$5.560\ x10^{14}$	$5.175\ x10^{14}$	$3.175\ x10^5$
55.3574	44.85	$5.329\ x10^{14}$	$4.971\ x10^{14}$	$3.372\ x10^5$
57.4730	33.97	$9.290\ x10^{14}$	$8.666x10^{14}$	$1.465\ x10^5$
59.5517	68.63	$2.276\ x10^{14}$	$2.123\ x10^{14}$	$12.08x10^5$
67.6085	35.85	$8.350\ x10^{14}$	$7.780\ x10^{14}$	$1.722x10^5$
73.0650	29.65	$1.220\ x10^{15}$	$1.137\ x10^{15}$	$0.974x10^5$
74.1089	24.48	$1.792\ x10^{15}$	$1.668\ x10^{15}$	$0.548x10^5$

It is observed from these tabulated details, and from figures.2, 3 & 4, dislocation density is indirectly proportional to particle size and number of unit cell. Dislocation density increases while both particle size and number of unit cell decreases.

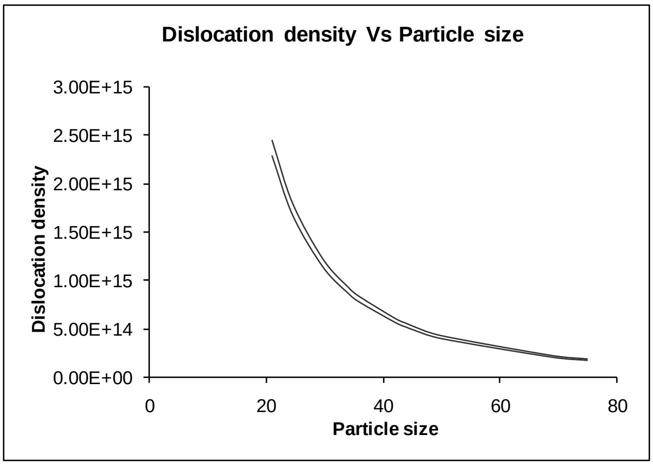

Figure.2 Dislocation density Vs Particle size

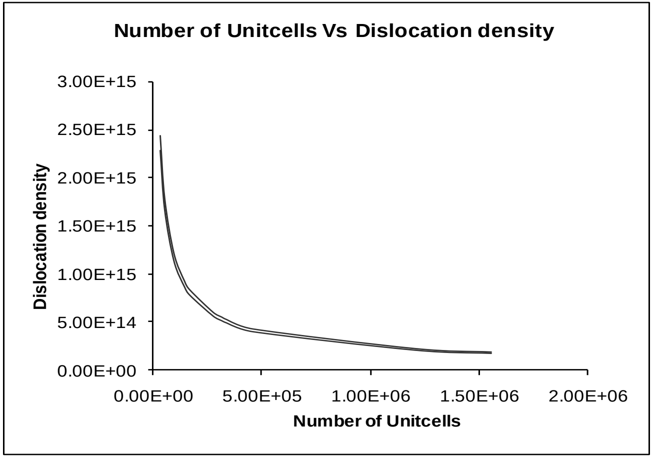

Figure.3 Dislocation density Vs number of Unit cells

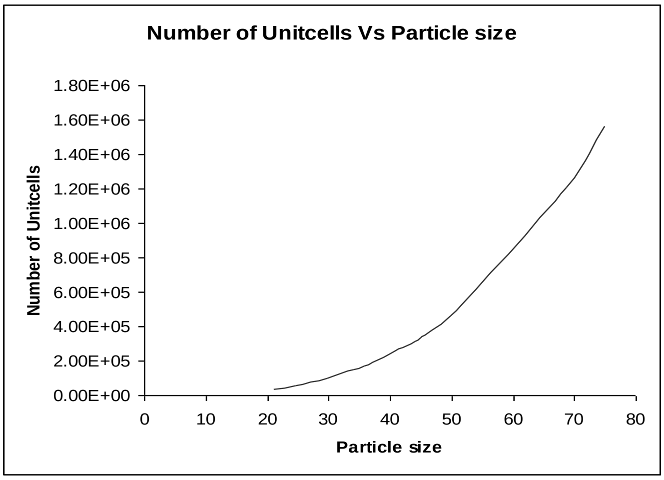

Figure.4 Number of unit cell Vs particle size.

4.1.3. XRD – Morphology Index

A XRD morphology index (MI) is calculated from FWHM of XRD data using the relation

$$M.I = \frac{FWHM_h}{FWHM_h + FWHM_p} \qquad (5)$$

Where M.I. is morphology index, $FWHM_h$ is highest FWHM value obtained from peaks and $FWHM_p$ is value of particular peak's FWHM for which M.I. is to be calculated. The relation between morphology index and particle size is shown in table-4.

Table-4. Relation between Morphology Index and Particle size

FWHM (β) radians	Particle Size(D) nm	Morphology Index (unitless)
0.00233	60.82	0.5292
0.00262	54.56	0.5
0.00233	61.55	0.5292
0.00262	55.08	0.5
0.00291	49.81	0.4737
0.00698	20.94	0.2729
0.00349	42.09	0.4288
0.00204	74.76	0.5622
0.00349	43.96	0.4288
0.00349	44.85	0.4288
0.00465	33.97	0.3604
0.00233	68.63	0.5292
0.00465	35.85	0.3604
0.00582	29.65	0.3104
0.00709	24.48	0.2698

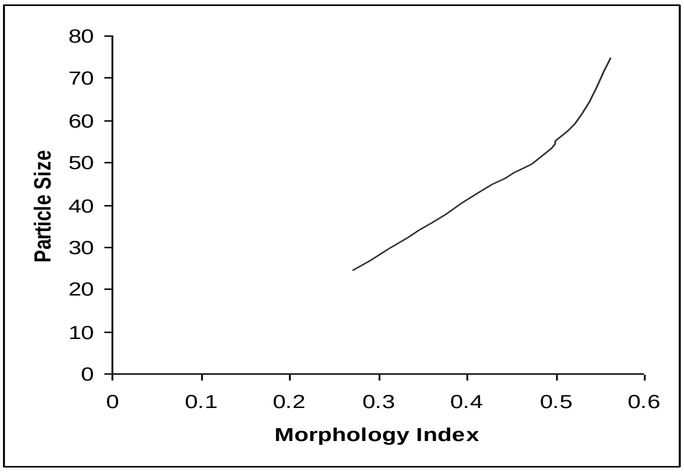

Figure.5 Morphology Index of Copper (II) Phosphate Nanoparticles

It is observed that MI has direct relationship with particle size and the results are shown in Figure.5.

4.1.4. XRD – Unit Cell Parameters

Unit cell parameters values calculated from XRD are enumerated in table-6.

Table-6. XRD parameters of Copper (II) Phosphate Nanoparticles

Parameters	Values
Structure	Primitive
Space group	P1(2)
Symmetry of lattice	Anorthic
Particle size	55.08 nm
Bond Angle	$\alpha = 72.3;\beta = 86.9;\gamma = 68.59$
Lattice parameters	a = 4.848;b = 5.28;c = 6.183
Vol.unit cell(V)	140.08
Density (ρ)	4.511
Dislocation Density	3.525×10^{14}
Mass	380.58amu

4.2. SEM studies

Scanning electron microscopy was used to analyze the morphology and size of the synthesized Copper (II) Phosphate nano particles. Fig.6, Fig.7 and Fig.8 show the SEM images of the Copper (II) Phosphate nano-particles at various magnifications. The SEM images of Copper (II) Phosphate nano particles show well crystallized particles with cauliflower like morphology. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with agglomeration.

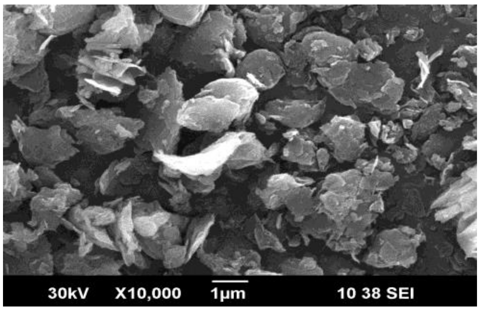

Figure.6 SEM image at 10000 magnifications

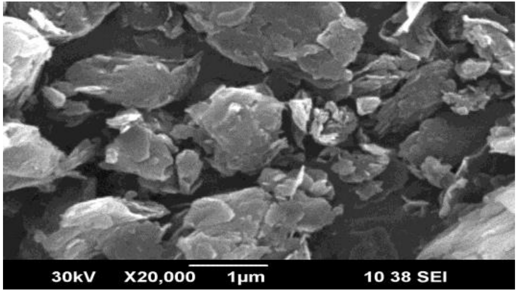

Figure.7 SEM image at 20000 magnifications

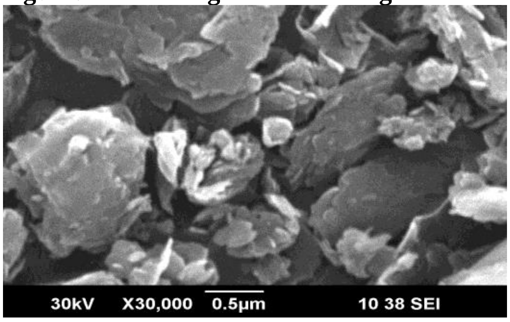

Figure.8 SEM image at 30000 magnifications

4.3. FTIR Studies

The FTIR spectrum of the Copper (II) Phosphate sample is shown in the fig.9.The FTIR spectrum for Copper (II) Phosphate shows a strong peak at 3421.48cm^{-1} corresponding to the free O-H group [1] and the peak at 1631.67cm^{-1} is bending mode of Hydroxyl group [1]. Another strong and sharp peak with a maximum of 1124.42cm-1 is due to the symmetric stretching mode of $[PO_4]^{3-}$ .The spectrum also shows peak at 1049.0cm-1 indicating P=O double stretching bond[7] and the peak at 752.19cm-1indicates P-O-P ring frequency[7] and the peak at 617.18cm-1 is due to the Cu-O stretching bond. The peaks at 565.10cm-1 represents the absorption peak of Cu nanoparticles and copper nanoparticles display a broad absorption from 550 to 700nm [8].

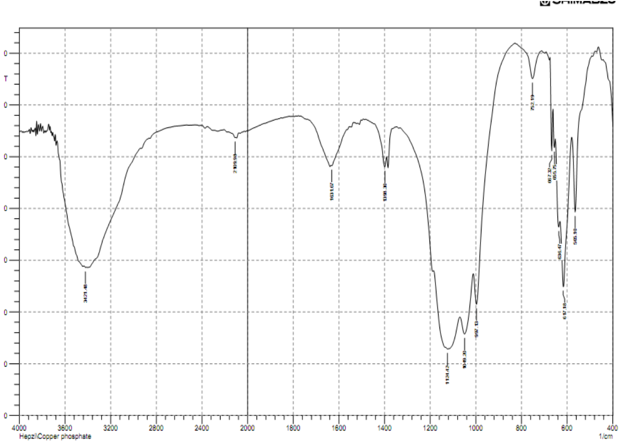

Figure.9 FTIR spectra of Copper II Phosphate Nano particles

4.4. UV Studies

The band gap of the prepared sample Copper (II) Phosphate was determined by using UV visible studies. From the UV spectrum the optical band gap of Copper (II) Phosphate is 2.5ev. Fig.10 shows the graph to find the band gap of Copper (II) Phosphate.

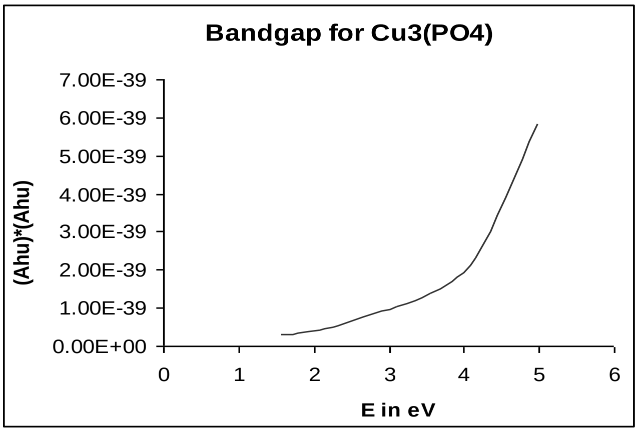

Figure.10 Graph to find the band gap of Copper (II) Phosphate Nano particles

4.5. AAS Studies

The synthesized Copper (II) Phosphate nanoparticles have been analyzed by AAS with optical parameter settings Cu wavelength 324.8nm and Air – C_2H_2 flame type. The results are given in table-7.A calibration curve diagram for Concentration of Copper (II) Phosphate nanoparticles in parts per million (ppm) Vs Absorbance has been drawn and a linear fit has been got. It is observed from the fig.11 that the absorbance is directly proportional to the concentration. The linear fit indicates that Copper (II) phosphate nanoparticles have been distributed in proper proportion [6].

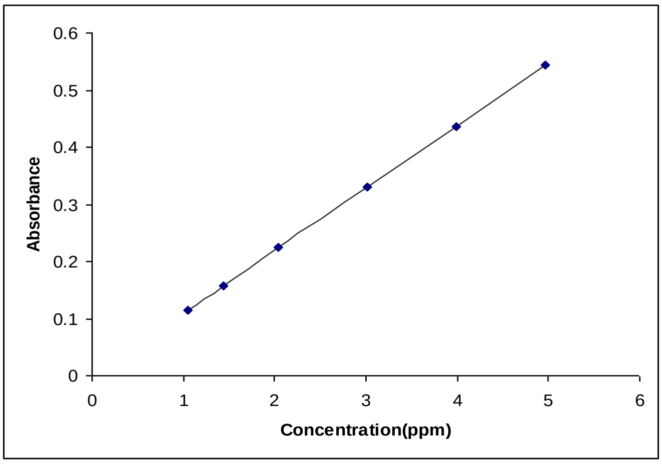

Figure. 11 Concentration Vs Absorbance

Table-7 AAS Analysis Result

True value	Standard	Sample	%R	Actual Concentration %	Concentration (ppm)	Absor bance
1.0000	1.0569	0.1156	106	12.7135	1.4382	0.1573
2.0000	2.0471	0.2239	102.5			
3.0000	3.0198	0.3303	100.7	Weight Factor = 1.000000		
4.0000	3.9872	0.4361	99.8	Volume Factor = 1.00		
5.0000	4.9682	0.5434	99.4	Dilution Factor = 1.00 Correction Factor = 1.000000		

5. Conclusions

The Copper (II) Phosphate nano particles have been prepared by chemical co-precipitation method. XRD analysis suggests that the average particle size is in the nano range

(55.08nm). The SEM picture reveals the well crystallized particles with cauliflower like morphology. From the FTIR spectrum, the stretching and bending frequencies of the molecular functional groups in the sample are studied. From the UV spectra, the band gap was found. From AAS studies it is found that the absorbance is directly proportional to the concentration. The linear fit indicates that Copper (II) Phosphate nanoparticles have been distributed in proper proportion.

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