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Experimental Investigation Of Copper Oxide Nanoparticles Synthesized Via Chemical Route And Study The Catalytic Activity In Reduction Of P-Nitrophenol

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Abstract
In this paper copper oxide nanoparticles are prepared by Chemical Approach and different characterization techniques like UV spectroscopy, XRD, RAMAN, TEM are used to investigate various microscopic properties of CuO nanoparticles. The initial formation of CuO nanoparticle was confirmed by UV-visible spectrophotometer. Purity, morphology and size of the Nano sized powder were studied. The XRD studies also reported. The copper powder has a high purity with mean size of particles about 16-18nm nanometer. XRD analysis confirms that the crystals, sizes are in Nano sized range. For the comparison transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements were made through JCPDS. The EDX analysis was performed to investigate the elemental analysis of synthesized materials there is good agreement between data produced by spectroscopy and the microscopic measurements. The CuO Nano powders show excellent catalytic reduction on the p-nitrophenol.
Keyword*: - NP's, XRD, TEM, EDX, UV-vis, TLC.*

1- INTRODUCTION

Nano science and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. Nanoparticles are defined as particles with size in the range of 1 to 100 nm at least in one of the three dimensions. Because of this very small size scale, they possess an immense surface area per unit volume, a high proportion of atoms in the surface and near surface layers, and the ability to exhibit quantum effects [1, 2]. Nanoparticles exist with great chemical diversity in the form of metals, metal oxides, semiconductors, polymers, carbon materials, organics or biological [3]. Copper oxide is a compound from two elements copper and oxygen, which are block d and block p elements in periodic table respectively [4]. In a crystal copper ion is coordinated by four oxygen ions. Copper (Cu) and cupric oxide (CuO) nanoparticles have attracted considerable attention because copper is one of the most important in modern technologies and is readily available. There is increasing interest on copper nanoparticles due to their optical, catalytic, mechanical and electrical properties. Copper oxide is widely used in the field of catalysis, superconductors, and ceramics as a kind of important inorganic materials. Compared with the ordinary copper oxide, nano CuO has peculiar physical and chemical properties such as: surface effect, superiority of the quantum size effect, volume effect and macroscopic quantum tunnelling effect in magnetic, optical absorption, chemical activity and thermal resistance, catalysis, and the melting point. Different characterisation techniques are used to study the various properties of this metal oxide nanoparticles. CuO particles are

characterized by means of transmission electron microscope (TEM), and X-ray diffraction (XRD) which will give much valuable information about these materials [5].Raman spectroscopy is a powerful non-destructive technique that has been successfully used to study a wide range of materials. Raman spectroscopy is of particular relevance to investigate structural properties of nanosized materials because slight variations are easily detected [6].

2- EXPERIMENTAL PROCEDURE

2.1- Materials & Method

For present work we used analytical grade chemicals such as Copper chloride dehydrate, ($CuCl_2.2H_2O$),Ethanol, sodium borohydride($NaBH_4$), & Sodium hydroxide pellets (NaOH) were purchased from Merck India Pvt Ltd. All chemical were used as received without any purification.

2.2- Synthesis of Copper Oxide Nanoparticle:

The procedure for getting nanoparticle is different with different precursors. In this paper the copper chloride dehydrate used as a precursor salt. Ethanol is used to dissolve copper (II) chloride dehydrate (9 gm) and sodium hydroxide (5.4 gm) separately. Amount of ethanol should be as minimum as possible. NaOH solution is added drop wise into $CuCl_2.2H_2O$ with constant stirring at room temperature until pH reaches to 10.

The color of the solution turned from green to bluish green and finally to black as the reaction proceed. The black precipitate was copper hydroxide.

Overall reaction is

$$\mathbf{CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl}$$

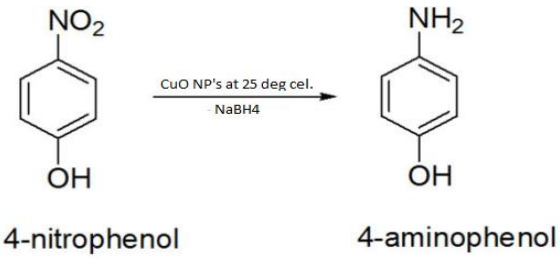
After this, washed the precipitate by ethanol and deionized water to remove the sodium chloride salt solution. Then the cooper Nano powder was dried at 60°C in oven.

Fig1: Dried CuO Nano powder

2.3- Reduction of P-Nitrophenol to P-Aminophenol using CuO NPs

For this catalytic activity test we simply did hydrolysis of p-Nitrophenol under the catalyst as copper oxide nanoparticles with strong base $NaBH_4$. In this reaction a nitro (NO_2) group changes to amino (NH_2) after hydrolysis [7, 8]. The procedure follow for this reaction is given as:

- Dissolve the p-Nitrophenol(.043gm) in ethanol. The amount of ethanol is as minimum as possible.
- Overall reaction:



- Dissolve sodium borohydride (2.29gm) in deionised water.
- Add the nanoparticles (.01gm) after adding the $NaBH_4$.
- Stirr them for 15 minutes on magnetic stirrer with the help of condenser. Be careful to maintain the temperature of reaction at almost equal to 25^0celcius.
- Let the reaction to be settling down and then take its thin layer chromatography (TLC).

3- RESULT AND DISCUSSION

3.1- UV-visible Spectroscopy

UV-vis absorption spectroscopy is one of the most convenient methods to reveal the energy structures and an optical property of semiconducting materials. Figure shows the UV–Vis absorption spectrum of the synthesized CuO nanoparticles. The spectrum shows a absorption peak whose center is at about 362 nm. Light absorption leads to transmission of an electron into

the conduction band and formation of a positive hole in the valence band. In small particles, they are confined to potential wells of small lateral dimension and the energy difference between the position of the conduction band and a free electron which leads to a quantization of their energy levels. The UV visible spectra displayed excitonic absorption peak at 280 nm. It shows that the absorption edge at 389 nm. Fig shows the uv graph of the sample in which result is broad peak in the range 358(nm) to 365(nm) and centre of the peak is 362(nm).

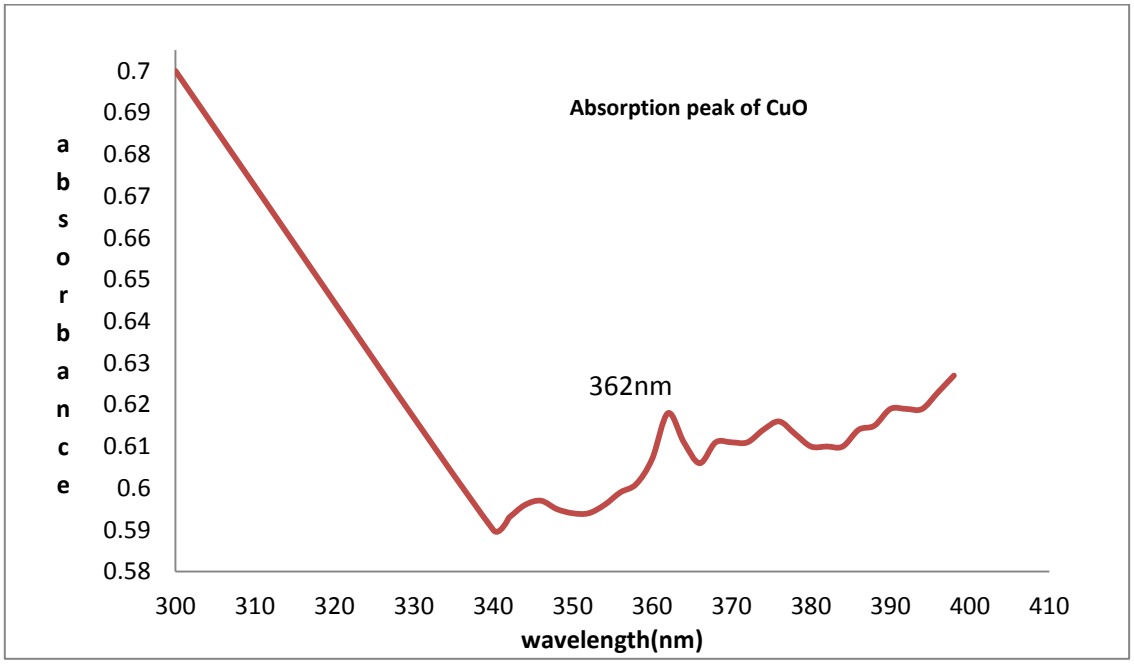


Fig 2: U-V spectra of Copper Oxide nanoparticle

3.2- Raman spectroscopy

Raman Spectroscopy is a vibrational spectroscopy technique used to collect a unique chemical fingerprint of molecules .CuO nanoparticles belong to the C^6_{2h} space group with two molecules per primitive cell. There are nine zone-centre optical phonon modes with symmetries $4A_u + 5B_u + A_g + 2B_g$ among which only three $A_g + 2B_g$ modes are Raman active. The Raman shift indicated in the graph given below at 282 cm^{-1} can be ascribed to be originating from the A_g mode while other peaks at 330 (shoulder to the main peak at 282 cm^{-1}) and 616 cm^{-1} represent B_g mode. [9, 10, 11]

The Raman spectum corresponding to CuO nanoparticles is fit as per the given three peak and is shown in the figure given below which exhibit a good fit (on the basis of residue to the fit).

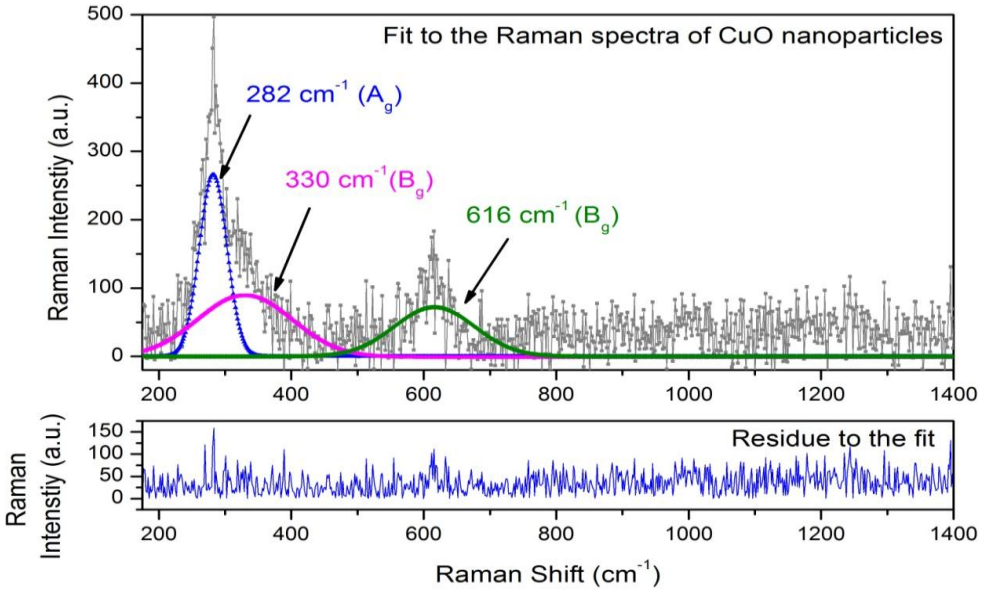


Fig: 3 Raman spectra of synthesized copper oxide nanoparticles

3.3- X-ray diffraction pattern(XRD)

X-ray powder diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline materials and can provide information on unit cell dimensions. In X-ray diffraction method, the incident monochromatic radiation strikes the finely powdered contained in capillary tube. The photographic film is wrapped around the inside of cylindrical chamber concentric with the s1ample. The rays are diffracted from individual crystal which happened to be oriented with plane making Bragg angle with the beam. The x-ray diffraction is used to analyze the phase and estimate the crystallite size of the samples using X-ray Diffractometer with a source in 2theta range from 20 to 80 degree. X-ray diffraction spectra is carried using a Bruker D8- Advance diffractometer equipped with a source delivering a monochromatic Cu Kα1 radiation (λ = 1.54056 Å). XRD analysis of prepared nanoparticles was performed on a PANalytical X'PertPRo Software.

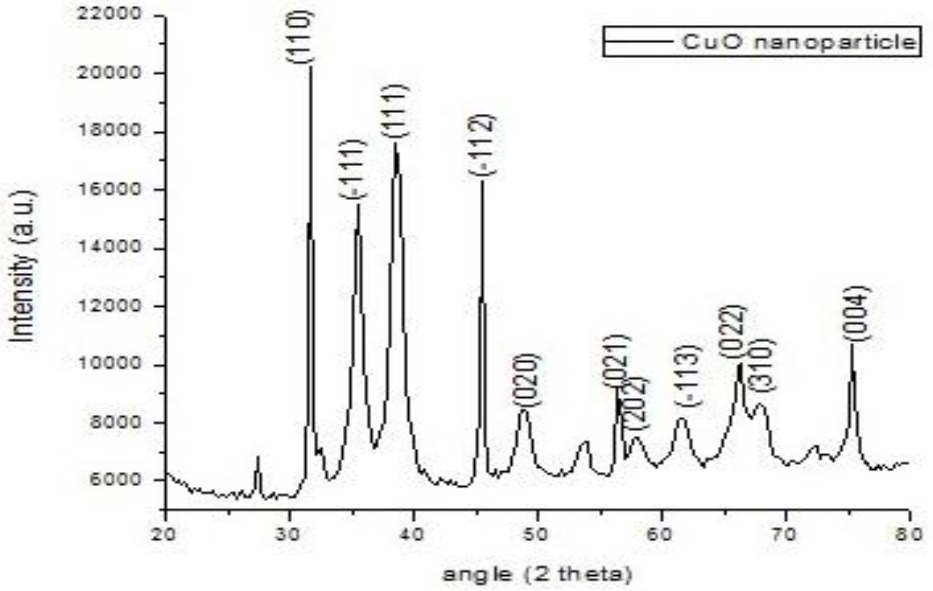


Fig 4: XRD curve of Synthesized Copper oxide nanoparticle

Lattice parameter of a cell of CuO a (Å) = 4.6833, b (Å) = 3.4208, c (Å) = 5.1294

In the XRD patterns of copper oxide nanoparticles different peaks were observed at 2Θ corresponds to different planes of monoclinic phase of CuO and lattice constant(JCPDS 01-074-1021). It is clear that major peaks located at $2\Theta=32.36^0$ and 38.39^0 are the monoclinic phase of copper oxide nanoparticles. The sharp peaks are shows that materials have no impurities. The average crystalline size of the CuO nanoparticles was calculated by using Debye-Scherrer[12] formula as about 16.7nm.

3.4- TEM and EDX (energy dispersive X-ray)

From TEM images given below the size of particles can be find out and further it would be well agreed with XRD result. Copper chloride dehydrate is found to be the best precursor that gives better result among other salts used for the synthesis of copper oxide nanoparticle. As we measure or examine several regions of pic which is taken at 50nm.The estimated average size observed from histogram is equal to **18.41nm** Which is slightly greater than result studied by XRD.Dots in diffraction pattern indicates the presence of nanoparticles through which reflection takes place. The histogram corresponding to that figure is shown below:

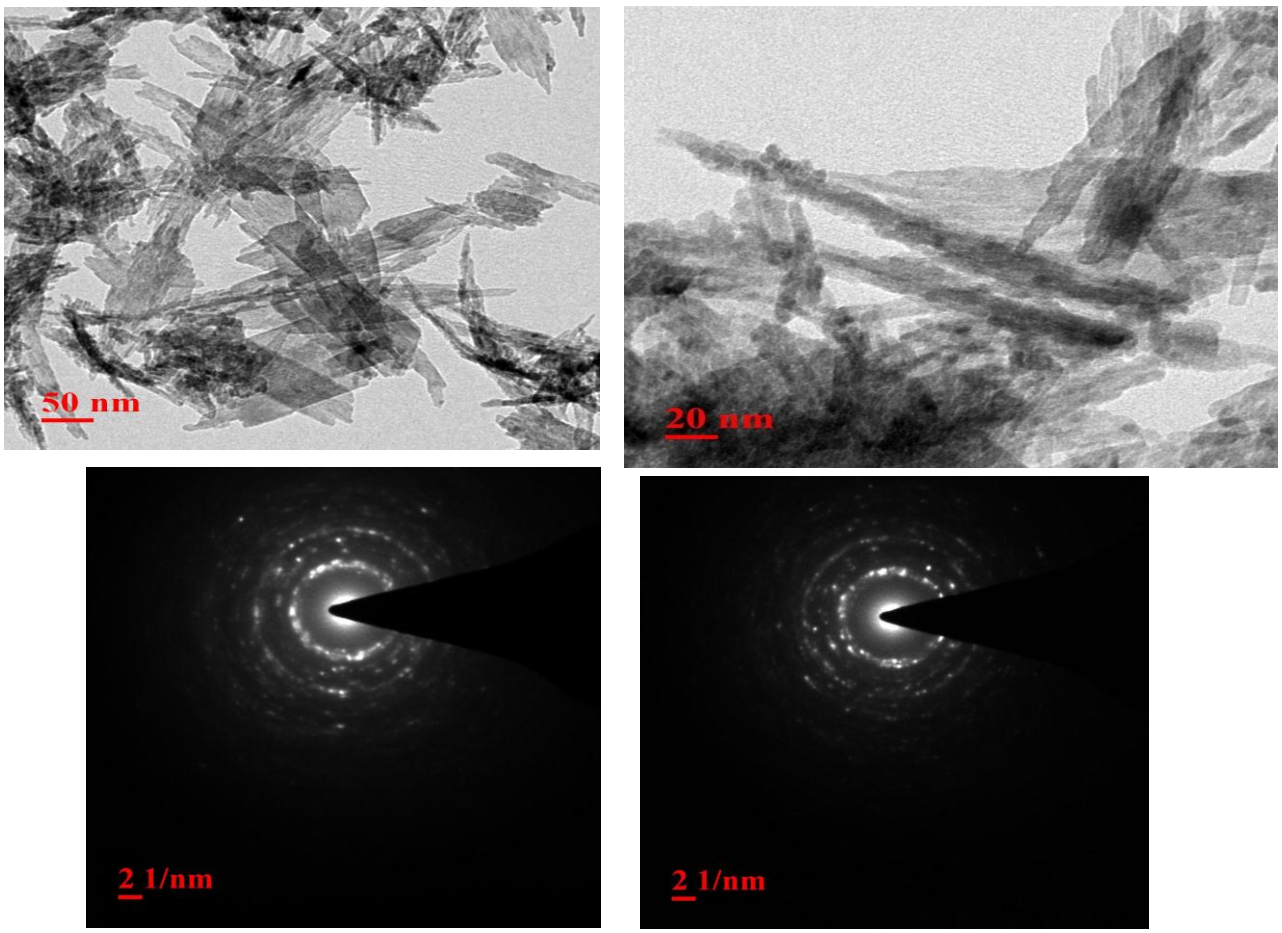


Fig 5: TEM micrograph of CuO and selected area electron diffraction pattern

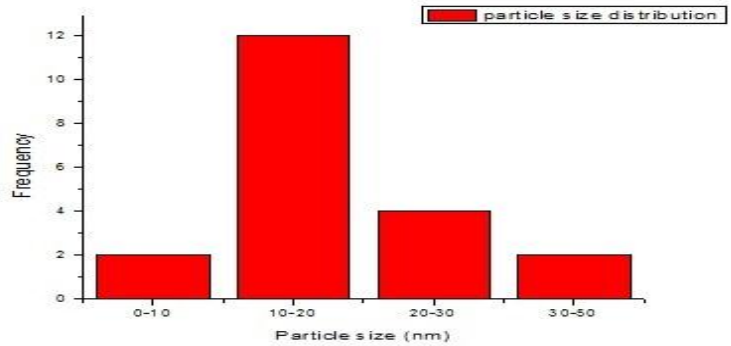


Fig6 :TEM Histrogram for Particle size distribution

3.5- Energy Dispersive X-ray Analysis (EDX)

Energy-dispersive X-ray spectroscopy (EDX), sometimes called energy dispersive X-ray analysis (EDX), is an analytical technique used for the elemental analysis or chemical characterization of a sample; it relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its spectrum.

EDAX spectrum of CuO nanoparticles plot identifies the elements corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. The higher a peak in a spectrum, the more concentrated the element is in the spectrum. The dried powder of the sample was analyzed on Energy Dispersive X-ray Analysis (EDAX or EDS) technique. The peaks have confirmed the presence of Copper and Oxygen. The average atomic weight percentage ratio of Cu & O.

El	A.N	Series	unn. C [Wt. %]	norm. C [Wt. %]	Atom. C [At. %]	Error (1 Sigma) C [wt. %]
Cu	29	K-series	87.18	87.18	63.14	2.66
O	8	K-series	12.82	12.82	36.86	0.43
		Total:	100.00	100.00	100.00	

Table 1: Composition analysis of EDX

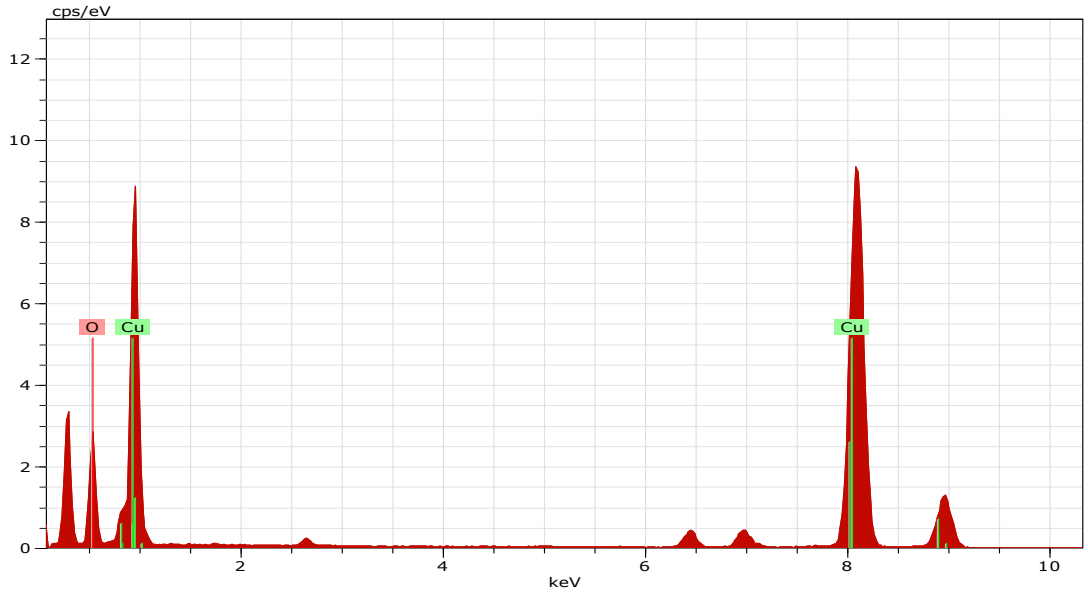


Fig 7: graph of EDX (composition of elements)

From the above table, it can easily be seen that the chemical composition of copper and oxygen in copper oxide nanoparticles are **63.14%** and **36.86%** respectively. Corresponding to that composition error in table is also 2.66% and 0.43% for copper and oxygen respectively

4- APPLICATION

catalytic Reduction of p-Nitrophenol using Copper Oxide Nanoparticle: In this reaction, the reduction of p-Nitrophenol to p-aminophenol using copperoxide nanoparticles as a catalyst with sodium borohydride ($NaBH_4$) at mild conditions i.e. temperature at almost 25^o celcius for 20 minutes. The product formed by this reaction is identified by thin layer chromatography (TLC). It tells us about whether our reaction proceeded or no formation occur. When our precursor and reaction product spots are placed on silica gel plate or TLC plate and further we put it into iodine chamber. Then if these spots varies with different speed it means reaction succesfully occurs. In contradict to this if both spots are varies with same speed or not varying it means no reaction takes place.which occurs in without catalytic reaction. The dark spot indicates the precursor and light one stands for the resultant drop. P-Aminophenol is a building block compound. Prominently, it is the final intermediate in industrial synthesis of paracetamol. Treating P-aminophenol with acetic anhydride gives paracetamol.

Fig 8: silica gel plate or TLC**.**

5- CONCLUSIONS

Nanoparticles of copper oxide were successfully synthesized by using chemical reduction route. The study suggests that synthesis route is low cost, environmental friendly and can be prepared in simple laboratory equipment in ambient condition. UV spectra confirms the occurrence of nanoparticles. Raman spectroscopy gives the peaks corresponding to copper and oxygen by which we primary confirmed that CuO nanoparticles are present. XRD spectra confirmed the formation of single phase CuO nanoparticles of long fibrous shape.crystalline size was found from XRD is **16.7 nm**. TEM result corroborate well with XRD results. An catalytic activity of using CuO nanoparticles was confirmed with $NaBH_4$ (strong base) for reduction of nitro group to amino group using TLC technique.

6- FUTURE SCOPE

In presented paper, we synthesized CuO nanoparticles. Prepared sample are characterized by UV-visible, Confocal Raman spectroscopy, XRD,TLC,TEM with EDX. In future we will synthesized nanoparticles of different doped materials with certain required conditions to get minimum size or more accuracy with some additional activity corresponding to that material. We can also find out toxicity behaviour. We can also work on its different properties.

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