Photoluminescence Properties of Copper Oxide Nanoparticles: Effect of Solvents

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Abstract. Using copper sulphate pentahydrate and sodium hydroxide pellets Copper Oxide (CuO) nanopowder is synthesized via solid state co-precipitation technique. The as-prepared CuO nanopowder is characterized by XRD, FESEM, UV–Vis absorption and photoluminescence Spectroscopy. XRD studies reveals that CuO nanoparticles are in monoclinic structure with crystalline size is found to be around 15 nm estimated from Scherrer formula. FESEM measurement shows that particles are in almost irregular shape and some nanorod like structures are obtained. The UV–Vis absorption and photoluminescence measurements are made in different solvents. A strong quantization with varying band edge in different solvents is found from UV–Vis absorption measurements. From photoluminescence spectra it is seen that the intensity of emission as-well-as emission peak wavelength changes with solvent.

INTRODUCTION

Recently, metal oxide nanoparticles, in particular Copper Oxide nanoparticles have attracted attention due to diversified applications. Copper oxide is p-type semiconductor comes in two forms; Cu₂O (Cuprous oxide) and CuO (Cupric Oxide). CuO extensively finds application in gas sensors, electrode materials, magnetic storage media and field emission emitters[1-7]. Its narrow band gap and because of excellent photochemical and photoconductive properties makes it a promising candidate for solar cell[5-8]. The optical properties of CuO are sensitive for both composition and structure of the nanomaterial. Further, fluorescence emission changes with shape, size, structure, morphology and chemical composition of the semiconductor nanomaterial. Although great amount of work have been reported on synthesis, structural and other properties, but less attention is paid to photo physical properties of CuO nanoparticles.

In the recent past, different chemical and physical methods have been employed to synthesize CuO nanoparticles with different size and shapes such as chemical co-precipitation [9], microwave irradiation[10], sol-gel[11], hydrothermal[12] and sonochemical[13], combustion[14]. The solid-state co-precipitation is a novel method as compared to conventional methods; moreover it is quick and simple, cost effective and less energy consumption.

In the present study, we have synthesized CuO nanoparticles via solid state co-precipitation method using copper sulphate pentahydrate and sodium hydroxide as a starting material. To the best of our knowledge this method has not been used to synthesize CuO nanoparticles so far. The technique is modest and quick. The main aim of the present work is to investigate the effect of various solvents on optical properties of CuO nanoparticles.

EXPERIMENTAL

Copper sulphate pentahydrate (CuSO₄.5H₂O), Sodium hydroxide (NaOH) pellets and absolute alcohol (Ethanol) are of analytical grade (SD fine chemicals) and used without further purification. First, Copper Sulphate Pentahydrate ( 0.01 mol (2.496gm)) was grinded for 20 minutes by using mortar and pestle. Then mixed with 0.02 mol (0.800 gm) of sodium hydroxide pellets and the mixture was grinded for 2 hours. During the process blue colored copper sulphate pentahydrate turns into a black precipitate. To remove residual impurities, the final product was washed several times with deionized water and ethanol. Obtained precipitate was dried at 80°C for an hour in
hot air oven. At the end the black colored CuO powder was obtained. The as prepared CuO nanopowder is characterized through XRD, FESEM, UV-Vis absorption and fluorescence emission spectroscopy.

RESULTS AND DISCUSSION

Figure 1 depicts the X-ray diffraction pattern of as prepared CuO nanoparticles. All the diffraction peaks of the sample can be indexed to a monoclinic phase and are matched with the JCPDS No 48–1548[15]. The broad peaks witnessed in the diffraction pattern indicate the size of particles is of nanometer scale. We have also calculated the average crystallite size by using the Scherrer equation; 

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where the symbols have their usual meaning. The average crystalline size of CuO nanoparticles from the intense peaks is found to be around 15 nm.

![Figure 1. XRD pattern of CuO nanoparticles](image1)

Surface morphology of as prepared CuO nanopowder is studied using Field Emission Scanning Electron Microscopy. Figure 2 shows the FESEM image of as prepared CuO nanoparticles. It shows particles are in almost irregular shape and some rod like structures are obtained. The close analysis gives the diameter of rod like structure to be around 40 nm.

![Figure 2. FESEM image of CuO nanoparticles](image2)

Figure 3 (a) shows the absorption spectra of as prepared CuO nanoparticles. Curves a-e respectively, represents the absorption intensity in ethanol, propanol, butanol, pentanol and hexanol. The maximum absorption is found to be 372 nm in ethanol, 340 nm in propanol, 330 nm in butanol, 265 nm in pentanol and 324 nm in hexanol. Using Tauc relation, 

\[(\alpha h\nu)^n = B (h\nu - E_g)\]

we have also estimated the direct band gap of the nanoparticles. The symbols have their usual meanings. In Figure 3(b) curves (a-e) shows the plot of \((\alpha h\nu)^2\) as a function of energy of photons in different solvents. The estimated energy band gap found to be 3.31 eV in ethanol, 3.50 eV in propanol, 3.37 eV in butanol, 4.0 eV in pentanol and 3.41eV in hexanol. It may be noted that the values are higher than its bulk
counterpart. Further, it is seen that the band edge and hence the band gap changes with the solvent. This is attributed to solute solvent interaction which affects the quantum confinement.

![Figure 3](image1.png)

**FIGURE 3** (a) UV–Visible spectra of CuO nanoparticles in various solvents and (b) taut plots. Curve a-e respectively, represents in (a) absorption intensity and in (b) taut plots in ethanol, propanol, butanol, pentanol and hexanol.

Fluorescence emission (FL) spectra of as prepared CuO nanopowder were recorded in various solvents dissolved by ultrasonicator and excited with optimized wavelength 290 nm. Figure 4 shows the fluorescence emission spectra of as prepared CuO nanopowder in various solvents. Curves a-e respectively, represents FL spectra in ethanol, propanol, butanol, pentanol and hexanol. The peak emission is found to be at 358 nm in ethanol, 351 nm in propanol, 353 nm in butanol, 359 nm in pentanol and 348 nm in hexanol. This near band edge emission originates from the electron-hole recombination[16]. Further, it is found that, the intensity as well as the emission peak wavelength changes with solvent. The varying intensity and peak position may be due to varying polarity of the solvent and dielectric constant.

![Figure 4](image2.png)

**FIGURE 4.** Fluorescence Spectra of CuO nanoparticles in various solvents. Curve a-e respectively, represents fluorescence intensity in ethanol, propanol, butanol, pentanol and hexanol.

**CONCLUSION**

In conclusion, we have synthesized Copper Oxide nanoparticles by solid state co-precipitation process. The method is simple and quick. The nanopowder is characterized by XRD, FESEM, and optical properties are studied. XRD studies confirm the formation of CuO nanoparticles in monoclinic crystalline phase with particle size around 15 nm estimated from Scherrer formula. The FESEM measurement demonstrates that the particles are of unequal shape and some rod like structures are observed. The optical properties of CuO nanoparticles are studied. The UV–Vis absorption measurements shows strong quantization with varying band edge in different solvents. From photoluminescence spectra we find the intensity of emission and emission peak wavelength changes with solvent, revealing the solute solvent interaction.
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REFERENCES