

Structural, Morphological and Optical Studies of CuI/CuO Nanocomposites

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Abstract: Copper iodide nanoparticles were synthesized by convention method. The Nano particles prepared was dried at 60°C and then annealed different temperatures like 100°C, 200°C, 300°C and 400°C. It was observed from powder XRD, the sample annealed at 100°C is a pure phase of CuI. From the XRD pattern of the samples annealed at 300°C and 400°C copper oxide peaks were observed in addition to copper iodide peaks. Using Debye-Scherer's relation, the particle size was determined. FTIR, optical, photoluminescence studies and SEM micrographs were recorded for the samples annealed at 300 °C and 400 °C.

Keywords: -- Copper iodide; nanoparticle; annealing; characterization; XRD; SEM; FTIR; Photoluminescence

I. INTRODUCTION

Copper iodide (CuI) is a semiconductor and it has attracted the research community for many years because it has large band gap, negative spin-orbit splitting and has potential solar applications. CuI is used as catalyst in organic synthesis, used in cloud seeding, used to heat in nylon in commercial and residential carpet industries, automotive engine accessories, and other markets where durability and weight are a factor. It is also used as a source of dietary iodine in table salt and animal feed and used in the detection of mercury [1-4]. CuI has many polymorphic forms viz., (i) γ -CuI which crystallizes in zinc blende structure below 390 °C, (ii) β -CuI which crystallizes in wurtzite structure between 390 and 440 °C and (iii) α -CuI which crystallizes in rock salt structure above 440 °C [5,6]. Many techniques like reactive sputtering, pulsed laser deposition, laser assisted molecular beam deposition, polymer assisted reaction, iodination, wet chemical synthesis and sol-gel technique were adopted to synthesize CuI nanoparticles and other forms of nanomaterial [7-13]. In this work, copper iodide nanoparticles were prepared using copper chloride and potassium iodide by aqueous solution method and the prepared sample was annealed at four different temperatures like 100, 200, 300 and 400 °C. The comparative studies of the samples of CuI are subjected to various studies such as XRD studies, FTIR studies, SEM studies, UV-visible spectral studies and PL studies and the results are discussed in this paper.

II. EXPERIMENTAL METHODS

2.1 Synthesis

AR grade chemicals like copper chloride and potassium iodide were purchased commercially. The sample CuI nanomaterial was synthesized by taking copper chloride and potassium iodide in equimolar ratio. 0.5 M of copper chloride salt was dissolved in de-ionized water and 0.5 M of potassium iodide salt was also dissolved in de-ionized water separately in two different beakers. Aqueous solution of sodium thiosulfate was added into copper chloride solution and it was used as the reducing agent. This mixed solution was stirred well using a magnetic stirrer for 1 hour and during stirring, aqueous potassium iodide solution was added drop by drop into copper chloride-sodium thiosulfate solution. After stirring, a brown coloured precipitate was formed and it was filtered using good quality filter papers. The filtrate was dried at room temperature and then dried in hot air oven for 1 hour for 60°C and the dried sample was annealed at different temperatures such as 100 °C, 200 °C, 300 and 400 °C.

2.2 Analyzing techniques

Powder X-ray diffraction patterns of the samples were recorded using XPERT-PRO diffractometer system with CuK_α radiation of wavelength 1.5406 Å. The SEM images were photographed using a scanning electron microscope (Model: JEOL/JSM 6390). The FTIR spectra of the CuI nanoparticles were recorded using a Perkin Elmer spectrometer in the range of 400-4000 cm^{-1} . UV-visible absorbance and transmittance spectra of the samples were

recorded using UV-visible spectrophotometer. Photoluminescence (PL) spectroscopy is used to study the electronic structure of materials and here light is directed onto the sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. This excess energy will be dissipated by the sample through the emission of light, or luminescence and in this work, PL spectra of the samples were recorded using a fluorescence meter in the wavelength range of 350 –750 nm. High resolution surface imaging has been done by scanning electron microscopy (SEM) method and it has the higher magnification, large depth of focus, greater resolution and SEM images were photographed using a Philips XL-40 scanning electron microscopy (SEM) for morphology of the samples.

III. EXPERIMENTAL STUDY

3.1 XRD studies

When X-rays are passed on a crystalline sample, X-rays are diffracted in a pattern characteristic of the crystal structure. In powder X-ray diffraction, the diffraction pattern is obtained from a powder of the material, rather than an individual single crystal. The Bragg's law is the condition for X-ray diffraction (XRD) and here the powder XRD patterns of the prepared samples are shown in the figures 1-3. The reflection peaks of the XRD pattern of CuI nanoparticles in good agreement with the standard JCPDS card No (JCPDS No. 76-0207). The Miller indices assigned to the peaks of the XRD patterns in order are (111), (200), (220), (311), (222), (400), (331), (420) for the given figures 1-2. It is clearly seen that the samples annealed upto 300 °C crystallize in cubic structure with the lattice parameter $a = 6.0434 \text{ \AA}$. The sample annealed at 100°C is a pure phase of copper iodide. The XRD patterns of 300 °C and 400 °C shows copper iodide peaks with the addition of copper oxide peaks. The copper oxide (Fig.3) peaks dominates in the sample annealed at 400 °C. This is in good agreement with the standard values reported by the JCPDS card no.048-1548 and it shows monoclinic phase of CuO. The crystallite size of the particles of CuI was determined using the Debye-Scherrer formula as given by $d = k \lambda / \beta \cos \theta$ where $k = 0.9$ is a correction factor to account for particle shape, β is the full width at half maximum (FWHM), λ is the wavelength of X-rays and θ is the angle of diffraction [14]. The calculated values of crystallite size for various reflection peaks are given in the tables 1-4. The average crystallite of the nanoparticles of CuI are 54.267 nm, 45.1775 nm, 43.3 nm and 42.405 nm respectively for the samples annealed at 100 °C, 200 °C, 300 °C and 400 °C. It is observed that the

crystallite size decreases as the annealing temperature increases

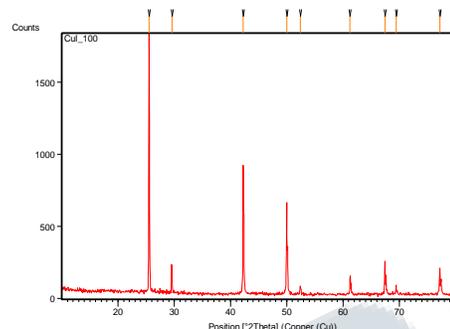


Fig.1. Powder XRD pattern of CuI nanoparticles annealed at 100°C

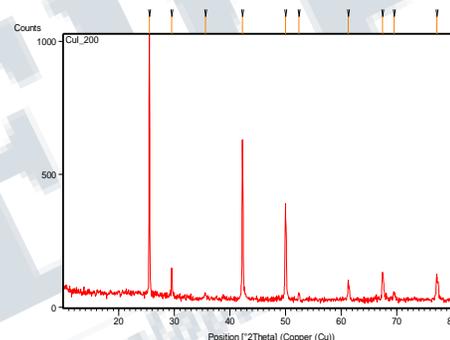


Fig 2. Powder XRD pattern of CuI nano particle annealed at 200°C

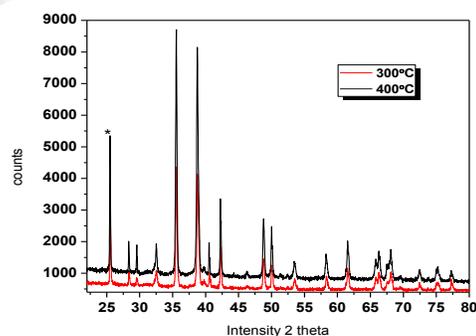


Fig 3. XRD pattern of the CuI sample annealed at 300°C and 400°C

3.2 FTIR studies

FTIR technique is one of the most important and widely used spectroscopic techniques and it helps to identify the functional units, internal structure of the molecules and nature of the chemical bonds of a compound. Absorption of

infrared radiation is confined largely to molecular species for which small energy difference exists between various vibrational and rotational states. When the frequency of the incident radiation coincides with the vibrational frequency of the molecules, absorption of energy takes place. When the molecules return from the excited state to the ground state, the absorbed energy is released resulting in distinct peaks in the IR spectrum. The recorded FTIR spectra of CuI nanoparticles are shown in the figure 4. The peaks in the wave number range 3450-3100 cm⁻¹ are corresponding to the vibrations of OH stretching and this may be due to adsorbed H₂O moisture on the samples. The peaks at 665 and 522cm⁻¹ are the characteristic peaks of CuI Nano sample [15] and these peaks are observed in the FTIR spectra. The peak at wave number 522 cm⁻¹ is assigned to Cu-I stretching vibration. Copper oxide peaks are in range of 500-700 cm⁻¹[16]. The peaks near 1401 cm⁻¹ in the spectra are given assignment as CO stretching which may be due to the adsorbed CO on the samples. The peaks at 3100 and 3400 cm⁻¹ are due to intermolecular hydrogen bonding present in the molecule .Both the CuI and CuO peaks are present in spectra which represents the formation of CuI/CuO Nano composites in the sample.

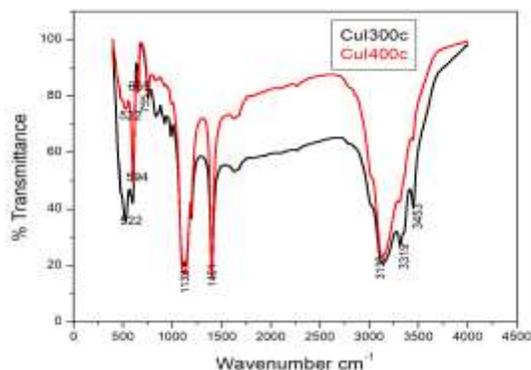


Fig 4. FTIR spectra for the samples annealed at 300 °C and 400°C

3.3 SEM studies

The photographed SEM images are shown in the figure 5. and it is observed that the sample CuI annealed at 400oC shows more agglomeration than the sample annealed at 100 oC. The results show that as the annealing temperature increases, the nature of agglomeration increases. From the SEM micrograph it was observed the formation of CuI nuclei in triangle shaped for the sample annealed at 100oC. This type of shape is reported in CuI thin film prepared by deposition method [17-18]. The size of the nanoparticles

gets decreased when the annealing temperature is increased, because the surface energy is lowered as the size of particles is reduced.

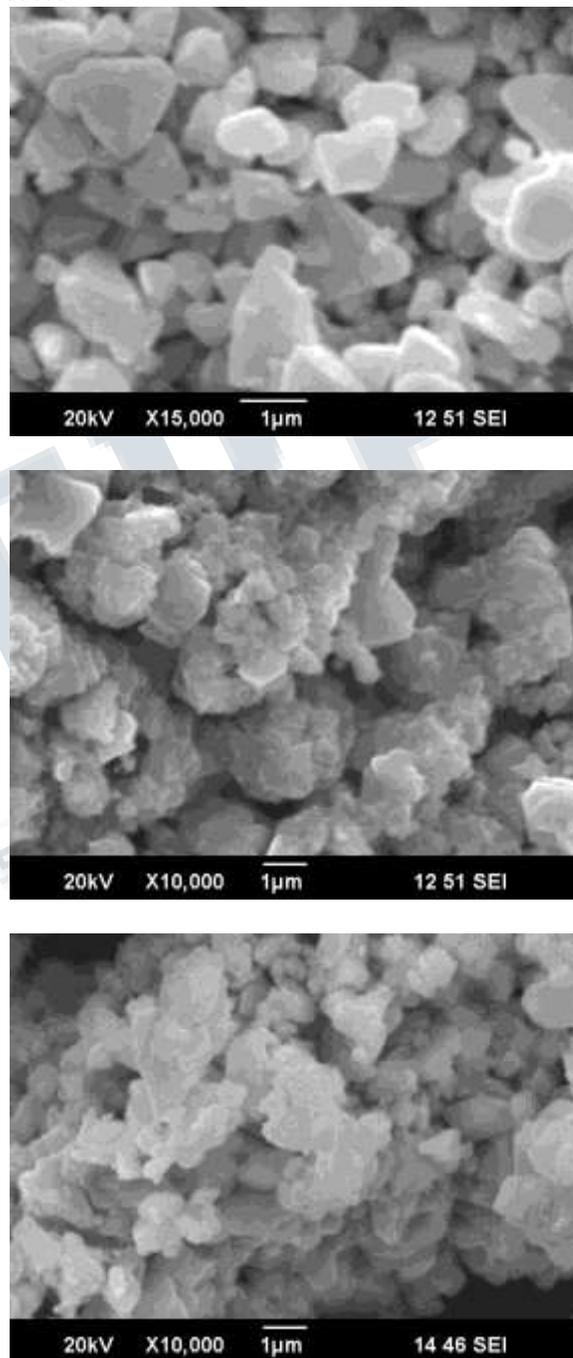


Fig 5. SEM Micrographs for CuI sample annealed at 100 oC 300 oC and 400oC

3.4. UV-visible spectral studies

UV-visible absorption spectrum of the samples were recorded using a spectrophotometer in the wavelength range 190-900 nm and they are shown in the figures 7. The electronic nature and band gap properties of the samples could be understood using these spectra and here absorption is due to the electronic transitions. The peaks at 275 nm and 300 nm. These two peaks are in the uv region The sample shows less absorption and high transmittance in the visible region. It is observed that the peaks at 275 nm and 300 nm are combined to form a broad peak. These values are around in earlier reported values [15]. The shift in the values may be due to both copper iodide and copper oxide nanoparticles in the sample. The second spectra in the figure 8 shows the sample annealed at 400 °C. In this, the peak around 300 nm is completely due to CuO phase in the Nano particle [24].

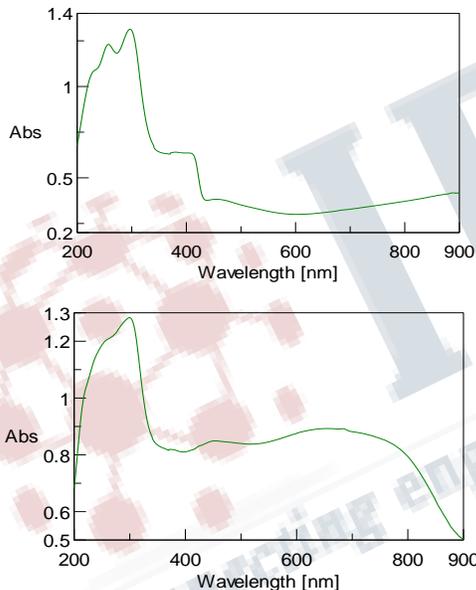


Fig 8. UV absorbance spectra of the samples annealed at 300 oC and 400 oC.

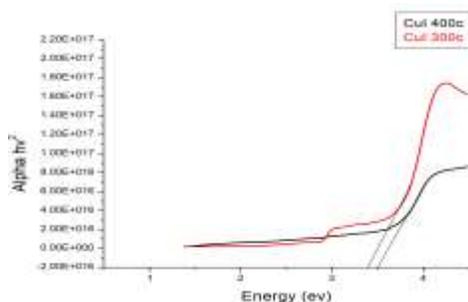


Fig 9. Variation of $(\alpha hv)^2$ with $h\nu$

The optical band gap E_g can be determined by using the formula

$$(\alpha hv)^2 = A(h\nu - E_g)$$

Where A is a constant and $h\nu$ is the photon energy. The functional relationship between $(\alpha hv)^2$ and photon energy for the sample annealed at 300 °C and 400 °C. The E_g value can be obtained by extrapolating the linear portion to the photon energy axis. Figure 9 shows the variation of $(\alpha hv)^2$ with $h\nu$. The extrapolation of these curves to zero absorption coefficient ($\alpha=0$) gave band gaps of 3.4 eV and 3.5 eV for the samples annealed at 300 °C and 400 °C. The 3.4eV band gap is attributed to CuI Nanoparticle but there is a slight difference in reported values which is 3.1 eV [25], the increase in band gap of CuI Nanoparticle may be due to the copper oxide particles in the sample. The sample annealed at 400 °C shows band gap of 3.5 eV which agrees with already reported value [26-27]. This reveals pure phase of copper oxide in the sample.

3.5 PL spectral studies

The nanoparticles of CuI are subjected to photoluminescence (PL) studies using a fluorescence meter and the recorded PL spectra for the sample annealed at 300 °C and 400 °C are shown in figure 6. From the results, it was observed that there are two emission peaks observed at 455(nm) and 684(nm), the peaks originate from the recombination of free excitons and electrons from the conduction bands to the trapped holes. Both CuI and CuO peaks are in the range of 400 nm. [21-22] The peak around 643 nm (1.9 ev) is due to band to band transition of copper oxide and other defects inside the Nano particles [23]. It is also inferred from the spectra that the peak intensity increases for the sample annealed at 400°C.

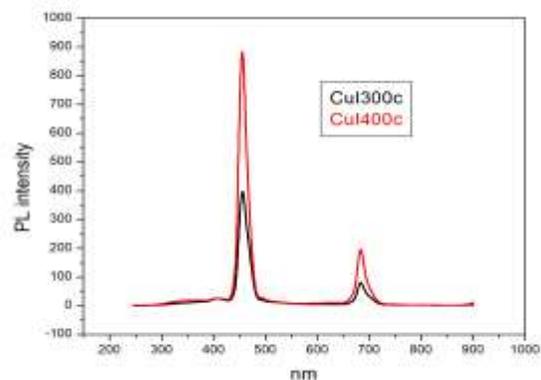


Fig 6. PL Spectrum for the samples annealed at 300 oC and 400 oC.

IV. CONCLUSION

The effect of annealing temperature on the synthesis of CuI Nanoparticle is studied. The change in the structural, morphological and optical characters of the prepared sample has been studied. Powder XRD patterns of the samples show pure gamma-phase of CuI and the samples annealed at 300 °C and 400 °C show CuO peaks in addition to CuI peaks. Using the SEM images, the size and morphology of the samples of CuI were identified. The morphology of the sample changes with higher annealing temperature. From the optical studies it was found the band gap of the sample annealed at 300 °C and 400 °C is found to be 3.1 eV and 3.5 eV. The functional groups of the samples were analysed by recording FTIR spectra and the peaks CuI and CuO on the samples have been noticed. When the samples are excited with UV light of wavelength of 240 nm, visible red light was emitted from the samples

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