Analytical studies on morphological, optical, electro-optical and Photo catalytic properties of Nano CuO prepared by sol gel method

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Abstract

In this attempt, the popular metal oxide CuO was prepared by the well-known; sol gel technique. The structural and morphological examination was carried out on the fabricated metal oxide and the XRD evaluation results validated the strong amalgamation of monoclinic bravais lattice system. The nano level of the Cu particles was tested and the size determined to be 52-36 nm which was found to be varied with respect to annealing temperatures. The structural modification of nano particle ensemble crystal by the application of temperatures was studied. The Photocatalytic ability was tested and it was evaluated by applying Tri-(chloroisopropyl) phosphate with CuO material. The optical property inducement was recognized in the material by observing UV-Visible characteristics curves. The electric operated optical response between lower and higher wavelength zones in visible region was tested by hyper polarization. The role of compositional bonding elements in the nano material for physical and chemical property response was studied by observing spectral pattern of IR and Raman.

Key words: nano CuO, hyper polarization, IR, monoclinic bravais, Photocatalytic and Raman.

INTRODUCTION

In nanotechnology world, nano sized atomic-amalgamated materials generally possessed specially customized and fanatically tuned unique electro-optical, electro-mechanical, opto-electronic and opto-magnetic properties (Zhao *et al*. 2008; Deraz *et al*. 2010; Farghali *et al*. 2010;) In recent days, transparent metal oxides and transparent conducting metal oxides have fascinated a great deal of notice because of their easy synthesis and great tunable optoelectronic properties. The copper metal is a transition metal that holds many chemical and physical properties. It is normally elastic and ductile, but only a moderately acquiescent material and can be modulated by applying temperatures.

In general, copper oxide is a well-known semiconducting oxide which normally existed in two phases; cupric oxide (CuO) and cuprous (Cu_2O) and they are amalgamated as monoclinic and cubic structure (Espinos *et al.* 2002; Su *et al.* 2008) respectively. Being a low production cost and excellent stability at room temperature, CuO is an important transition-habituate material which is peculiarly enabled incredible properties for wide range of applications such as fabrication of photoconductive and electro-optical devices (Zhu *et al.* 2005; Devi *et al.* 2014). It also behaved as field emission emitters and critical temperature operated high energy superconductors. It is a promising candidate material to act as electrode materials for lithium ion battery and super-capacitors (Samarasekara *et al.* 2006). Because of its catalytic action, it acts as catalyst (Xiang *et al.* 2008) in electro chemical hydrogen storage materials (Xiang *et al.* 2008). Due to its enhanced performance and new functionality characteristics, it is directly used in solar cells (Zhang *et al.* 2014) and gas sensors (Ningthoujam *et al.* 2008). In spite of its wide range of applications in opto-electronic industry, very few works have been traced in the literatures (Manyasree *et al.* 2017; Wang *et al.* 2003). In this paper, experimental results of the structural, morphological, optical and magnetic properties studies are exposed in order to reveal real application of nano CuO.

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MATERIALS AND METHODS

Chemical handling

The Copper chloride ($CuCl_2$), Sodium hydroxide (NaOH), de-ionized water and ethyl acetate were purchased from Sigma Aldrich. All the chemicals were authenticated as an analytical grade and can be used without further purification.

Synthesis

The most appropriate and easy to handle Sol-gel method was employed to prepare copper oxide nano particles. In this methodological synthesis, Copper chloride (0.1M) was taken to dissolve in DI water and then NaOH (0.2M) was mixed in 100 ml of DI water. The mixture was stirred separately for 30 minutes. The NaOH solution was added drop by drop in to the Copper chloride solution by using the burette. Afterward, the mixer was maintained under constant stirring for two hours. Then, the precipitated gel was washed 4 to 5 times by using the mixer of ethanol and ethyl acetate and dried for 10 hrs at 80° C in fine hot air oven. Finally the dried powder were calcined for four odd temperatures such as 300°C, 500°C, 700°C and 900°C for one hour.

The X-ray diffraction studies of prepared nano particles were performed using EXPERT-PRO system with Goniometry PW 3050/60 by CuKá radiation (ë=1.5406 Å). The Photoluminescence spectra were recorded using the F-2500FL model photoluminescence spectrometer ROMVERSION (400001) with different excitation sources. The absorption spectrum was taken from JASCO V-670 UV – VIS-IR Spectrometer. The Vibrational spectra were recorded using FT-IR solid phase KBr pellet techniques.

RESULTS AND DISCUSSION

XRD parametric analysis

The XRD spectral blueprint was recorded at different annealing temperatures 300°, 500°, 700° and 900° C respectively, for the prepared sample of CuO and are shown in Figure 1. According to the patter, the XRD peaks were obtained at 32°, 36°, 38°, 42°, 48°, 58°, 62° and 68° which were assigned for the crystal interplanes; (110), (-111), (111), (-112), (-202), (020) and (-113). Of the all peaks, the first set of (111) and (-111) inverted plane peaks were observed with maximum intensity which represent the strong existence of planes. All other peaks were found with minimum intensity which showed continuation of weak planes. The observed peaks with different intensities confirmed the simple monoclinic lattice pattern amalgamated in the nano CuO crystal. Apart from the major peaks, some other XRD signals were obtained along with the regular pattern which showed the virtual or reciprocal lattice pattern of the present existed CuO crystal. Here, the signals from inverted planes also appeared in the pattern which illustrated that, very appropriate monoclinic crystal system was formed in the synthesis.

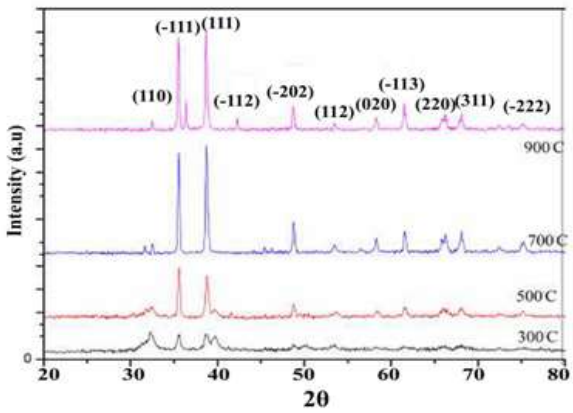

Figure 1. The XRD spectral blueprint of prepared sample of CuO

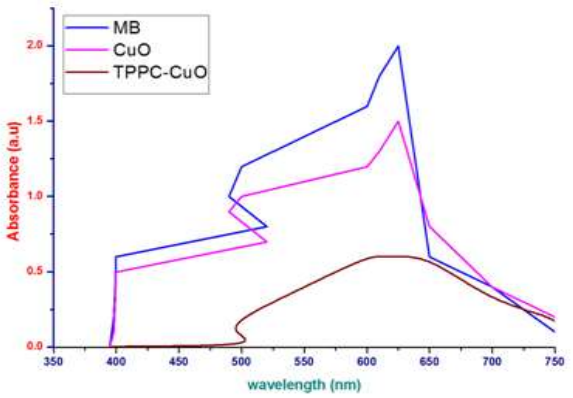

Figure 2. Photo degradation using absorptivity under UV-Visible spectrophotometer

In the case of annealing temperatures, particularly at 300° and 500° C, so many peaks were not present with satisfactory intensity which confirmed that, the crystal planes were not appeared to be amalgamated perfectly. At 700° and 900°C, the XRD crest appeared to be acceptable and they found around agreeable angle of diffracted pattern and these peaks emphasized that, the cubic lattice formation was obtained by the application of annealing temperatures above 600°C. The present monoclinic crystal type was very strong when compared with other bravais lattice and concurrently, it exposes very fanatic physical and chemical properties. According to the assigned planes, the crystal parameters were calculated to be a=4.689Å, b=3.426 Å and c=5.132Å. All the experiential XRD signals predicted that, the present crystal made by nano CuO was pure and free from contamination. According to the Debye Scherer's formula (Manyasree *et al*. 2017), the particle size was measured to be 36 nm

and it was fine size which moderate and definitely the present nano Cu particles will expose its actual property.

Photo catalytic activity analysis

The Photocatalytic process of nano CuO photosensitized with porphyrin was estimated by photo degradation of methyl blue (MB) dye solution illuminated by light with all wavelengths. For that, 2 mg of nano CuO photocatalyst was dissolved in 20 ml of MB solution by sonication process. The mixture was exposed to composed light made by LED illumination for 2 hrs duration. The photo degradation process was monitored by calculating the coefficient of absorptivity using UV-Visible spectrophotometer. The measurement was carried out for entire experiment and the associated graph was portrayed in the Figure 2.

According to the UV-Visible spectra, the photo degradation process was taking place in MB aqueous solution which was induced by present nano CuO photocatalyst. As per the UV-Visible absorption graph, with the photocatalyst, the insignificant degradation of MB molecules could be observed in the irradiation of light. The experimentation with photocatalyst (nano CuO) on MB illustrated that, the self-sensitized photo degradation of MB didn't appear under the experimental conditions. The base curve of photo-process showed that, the photo activity of Tri-(chloroisopropyl) phosphate (TCPP) with CuO was taking place considerably which was 3times greater than that of pure nano CuO. The observed data described that, the porphyrin naturally having capability to absorb light and CuO have wide band gap. This combination with photocatalyst was improving visible light photo activity. The TCPP-CuO photocatalyst illustrated that, the high activity to humiliate MB in aqueous solution underneath light irradiation at all wavelengths. This observation of Photocatalytic activity was supported by the literature (Houas *et al*. 2001; Wang *et al*. 2003).

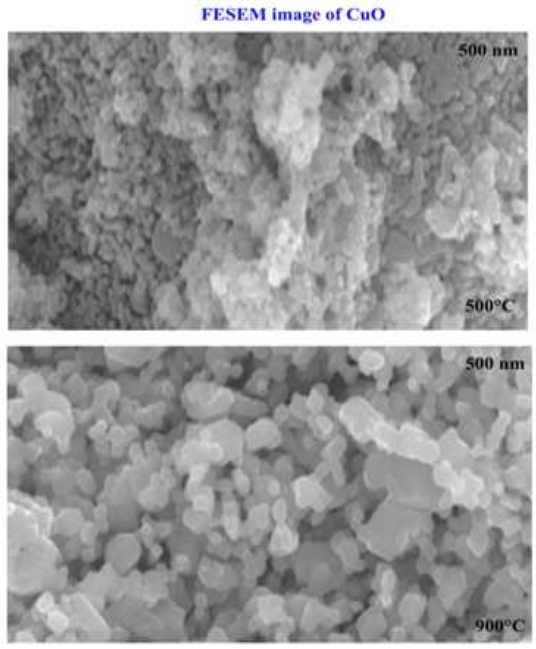

Figure 3. Scanned image of micro surface of nano CuO

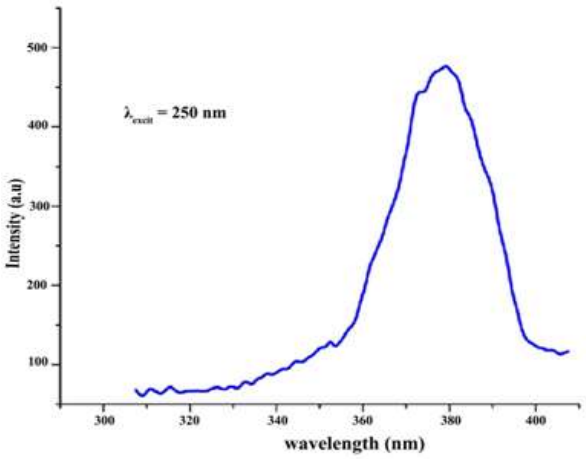

Figure 4. The PL spectra for CuO nano composite

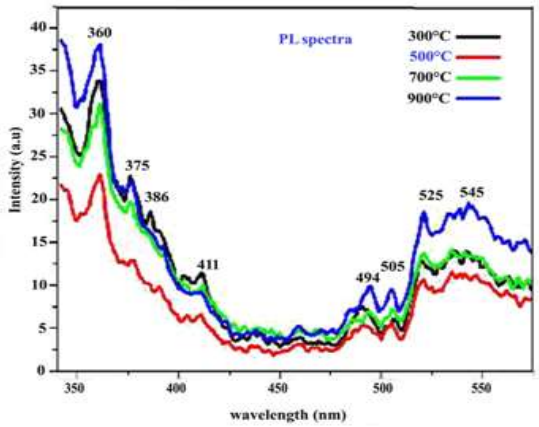

Figure 5. PL spectra at various annealing temperatures

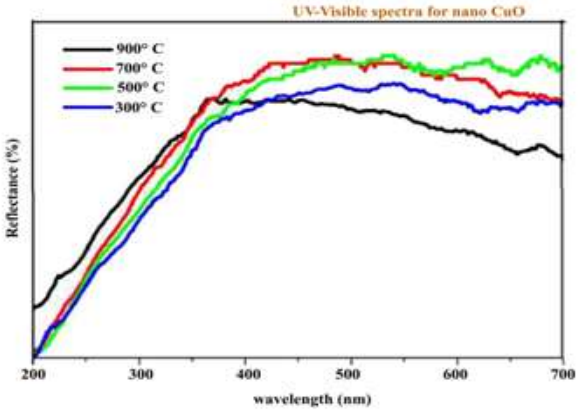

Figure 6. UV-Visible spectra for nano CuO

SEM analysis

The scanned image of micro surface of nano CuO is presented in the Figure 3. As seen in figure, two pictorial diagrams were obtained at two different annealing temperatures such 500° and 900°C. The surface topography and particles compositions in the material were seen in the figure clearly. At 500°C, the amalgamation of CuO nano particles was formally obtained in which the particles assimilation virtually appeared and approximate grain size can be measured. At 900°C, the well defined formation of Cu nano particles was observed. The Figure 3 showed well distinguished nano particles between two temperatures which confirmed the annealing temperature influencing the particle size and morphological amalgamation of monoclinic crystallization. From this observation, it was confirmed that, the method using in this work was found to be efficient to prepare nano particles and proportionately, the Cu nano particles are formed perfectly and efficiently. Such particles will expose its fundamental physical and chemical property surely.

PL examination

The photoluminescence spectra for CuO nano composite was recorded at 250 nm and 300 nm as excitation wavelengths for annealing temperatures such as 300°, 500°, 700° and 900° C and are shown in Figure 4 and 5 respectively. For CuO nano composite at normal temperature, the PL peak was observed at 380 nm with maximum intensity. From this peak, it was found that, the excitation was taking place in the material at 380 nm which was mainly due to the intrinsic characteristics of the CuO in which the interstitial vacancy produced inside the material (Hu *et al.* 2003; Ningthoujam *et al.* 2008).

The Figure 5 showed the series of peaks of parallel graphs which are recorded for the annealing temperatures from 300° to 900° C for CuO extrinsic composite. Here, at all temperatures, the similar peaks were appeared by which it was found that, there was no characteristics shift observed with respect to the annealing temperatures. Instead of that, the intensity of the peaks was increased much due to the annealing temperatures. The PL signals were obtained at 360, 375, 386, 411, 494, 505, 525 and 545 nm respectively for all temperatures. In this graph, the peak intensity was observed maximum from UV region to visible region, particularly, at high frequency of visible region, the PL intensity was found to be maximum and it was clear that, the PL activity of the nano composite was observed to be more in high frequency region. Apart from that, at higher wavelength region, the peaks at 525 and 545 were appeared with additive PL intensity which was due to the enriched PL activity of the

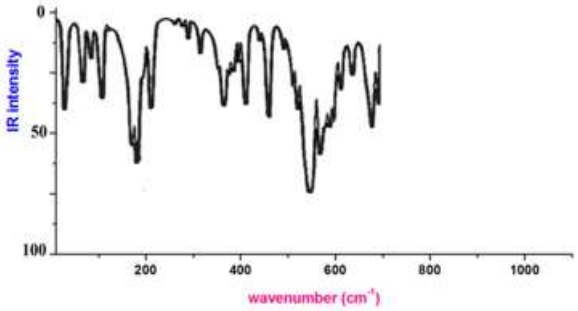

Figure 7. FT-IR spectra

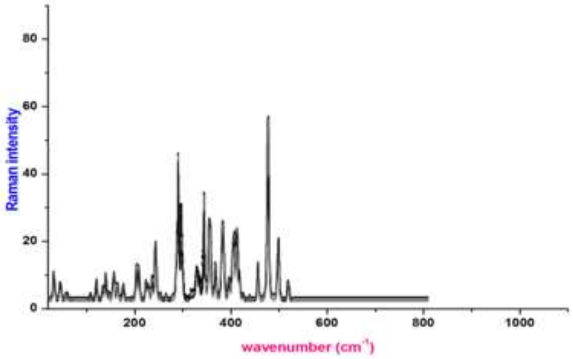

Figure 8. FT-Raman spectra

present nano material. In this case, the PL spectral impression was found on either side of lower and higher wavelength region. From this observation, it was inferred that, the PL activity can be tuned in the CuO material by doping nano impurity.

UV-Visible spectral studies

The UV-Visible spectra were recorded for present nano sample; CuO at different annealing temperatures (300°C to 900° C) in order to study the temperature effect on nano sample and it is displayed in the Figure 6. The UV-Visible spectral pattern is usually measured for identifying the optical characteristics of the nano composite and it was registered in the region of 200-700 nm. Here, the observed spectra illustrated that, at 300°C, the optical response was found to be more than 60% and it was increased more than 75% for nano samples at 500°, 700° and 900° C. The optical response was found to be elevated for higher temperatures which were mainly due to the improvement of the quality of the crystallinity for the present case. Here, up to 300 nm, the optical activity was linearly increased with wavelength and it was saturated from 400 nm up to 700 nm. In this case, the linear optical property was interpreted since the metal was paramagnetic. When the magnetic field is applied on the nano material, the polarizability of Cu-O bonds responded and hyper polarization is taking place. Simultaneously, the linear optical property is changed in to non linear optical property. From this observation, it was found that, the

optical characteristics were found facilitated by electric field and it is tunable.

Vibrational analysis

In order to reveal the vibrational characteristics of the present nano samples, the FT-IR and FT-Raman spectra were recorded in far IR and mid IR region and are shown in Figure 7 and 8 respectively. since all the vibrational spectral finger print of nano metal oxides are observed in far and mid IR, the spectral pattern for present composite was recorded in such region of spectrum. Usually, for the metal oxide, particularly, the Cu-O bond stretching is found in the region 400-850 cm^{1} (Kannaki *et al.* 2012; Tariq *et al.* 2015). Here, the stretching for Cu-O bond was observed at 680 and 550 cm^{1} in IR and Raman spectra. The related Cu-O in plane and out of plane bending vibrations was found at 3410 & 380 cm^{-1} and 210 & 190 cm^{-1} respectively. This vibrational assignment was well agreed with earlier literature (Gopalakrishnan *et al.* 2012). The stretching modes represent the optical phonon modes of Cu-O bonds present in the material and the compositional bonds in the material very precisely pronounced by the presence of characteristics region with strong intensity. In the monoclinic crystal system, the Cu-O bond strongly present in different interplanes and were identified by the strong absorption in IR and polar scattering in Raman spectrum.

CONCLUSION

In this paper, the CuO nano particles were synthesized and the metal oxide formation was successfully made. The morphological and structural studies were carried out by performing the XRD analysis. The optimized results were obtained and the observations made on the examination were validated with the literature. The obtained results of XRD peaks showed the present nano composite was to be monoclinic. The crystal size was measured to range from 52-36 nm by the application of annealing temperatures. The PL studies were carried out for different annealing temperatures and Pl activity of the nano metal oxide was examined. UV-visible spectral pattern was investigated for all temperatures and the optical characteristics of nano material were interpreted. The vibrational characteristics were predicted from metal oxide bond vibrational assignments and the role of bonded system in the physical and chemical properties were studied.

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