

Optical and Morphological Characterization of Sonochemically Assisted Europium Doped Copper (I) Oxide Nanostructures

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Abstract. In the age where application of nanotechnology in our society has proven to be eminent, different routes of synthesizing nanoparticles have emerged. In this study nanoparticles of cuprous oxide (Cu_2O) doped with different amounts of europium was prepared by using solution precursor route approach with the aid of ultrasonic sound. Copper sulphate and europium (III) nitrate pentahydrate was used as source for copper ions and europium ions respectively. X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR) were used to elucidate the cubic crystal structure and organic impurities present on Cu_2O nanoparticles. UV-Vis spectroscopy was used to determine the absorption spectrum of the nanoparticles in the wavelength range of 400nm to 700nm. The bandgap of the undoped and doped Cu_2O were found to fall between 2.1eV - 2.3eV. Scanning Electron Microscopy (SEM) coupled with energy dispersive x-ray was used to observe the dendritic and rodlike morphology and the presence of europium in the synthesized Cu_2O nanoparticles. The observed effect on the absorbance of Cu_2O upon adding Eu and a facile way of synthesizing Cu_2O nanoparticles could bring a positive impact on the production of functional devices for optoelectronic and energy applications.

1. Introduction

Metal oxide nanostructures have profound properties in different fields like optics, optoelectronics, catalysts, biosensors etc. Copper oxides are known for their good room temperature mobility and high minority carrier diffusion length [1,3, and 11]. It is known to have a direct bandgap energy ranging from $\sim 1.8\text{eV} - 2.3\text{eV}$ with its high absorption in the visible region. [5] Knowing this, copper oxide-based materials have been widely investigated due to their potential applications in chemical, photochemical and electrochemical fields [4, 11].

Cuprous oxide or Copper (I) oxide (Cu_2O) thin films can be prepared by several methods such as electrodeposition, sonochemical method, thermal relaxation liquid phase reduction, thermal evaporation, sol-gel, etc. Among these methods, sonochemical assisted techniques will be utilized for preparation of the Cu_2O in powdered form. Sonochemical processing has been recognized as a useful technique for making nanoparticles, nanoemulsions, nanocrystals, biofuels, etc. Sonication is commonly used in nanotechnology for evenly dispersing nanoparticles in liquids. Ultrasound causes chemical reactions through the process of acoustic cavitation – the formation, growth, and implosive collapse of gas bubbles in a liquid. [1].



In comparison with other thin films of oxide semiconductors such as In_2O_3 , SnO_2 , and ZnO [2,6], few data are available on the synthesis of europium (Eu) doped cuprous oxide (Cu_2O) films. With Cu_2O known for its direct bandgap energy and its potential application as solar light absorbers in photovoltaic devices, this study explores changes on Cu_2O in terms of optical and morphological properties upon adding Eu.

2. Methodology

2.1 Materials

The chemicals used in this study were copper sulphate pentahydrate (Sigma-Aldrich). Sodium dodecyl sulphate, ascorbic acid, sodium hydroxide and europium nitrate pentahydrate were used as received and without further purification.

2.2 Synthesis of Doped and Undoped Cu_2O

Nanoparticles of Eu-doped Cu_2O were prepared by using solution precursor route approach with the aid of ultrasonic sound. An aqueous solution of 0.01 M Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) then, 0.1 M of sodium dodecyl sulphate) solution was added to copper solution which formed solution A via sonochemical dissolution for 20 minutes. Aqueous Europium nitrate pentahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was prepared with varying concentration. (0.5%, 1%, 2%, 3% and 5%) and was added to solution A. It was mixed with the aid of ultrasonic sound for 20 minutes and was called solution B. 0.5 M Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) and 1.0 M Sodium hydroxide (NaOH) was added to solution B and the final solution was aged for 24 hours at room temperature. Afterwards, it was filtered and then vacuum dried for three hours at room temperature to produce the doped and undoped Cu_2O .

The study is guided with the aid of XRD (X-ray Diffraction) and FTIR (Fourier Transform Infrared Spectroscopy). After confirming the crystallographic structure of the undoped and Eu-doped Cu_2O , SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-ray Spectroscopy) are used to confirm the formation of nanostructures and confirm that Eu^{3+} is incorporated to the Cu_2O formed. The samples are then subjected to UV/Vis (Ultraviolet-Visible Spectroscopy) to confirm that upon addition of Eu^{3+} , optical absorption of Cu_2O nanostructures is altered or enhanced.

3. Results and Discussion

The study focused on the effects of Europium (Eu^{3+}) when doped to Copper (II) Oxide (Cu_2O). Moreover, the study highlights the effects of Eu^{3+} as a dopant on the optical and morphological properties of Cu_2O .

Pristine Cu_2O and Eu-doped Cu_2O nanoparticles were synthesized using solution precursor approach aided with ultrasonic sound. When copper sulphate pentahydrate is dissolved in water, ions of Cu are formed (Cu^{2+}) which will then be reduced by ascorbic acid. With the addition of NaOH as a source of hydroxide ion (OH^-), copper hydroxide is formed ($\text{Cu}(\text{OH})_2$) which can eventually be transformed to Cu_2O . During this process, some Eu^{3+} will replace Cu^{2+} simultaneously, in the formation of Cu_2O , as a substitutional impurity to form Cu_2O doped with Eu^{3+} . It is known that sonochemical method is used in the experiments to incorporate Eu^{3+} to metal oxides.

The X-ray diffraction pattern of the synthesized sample is shown in Figure 1. The sample used for the XRD was the one with 5% of Eu^{3+} loaded on to Cu_2O . Looking at the diffractogram presented in Figure 1 it was observed that the synthesized Eu- Cu_2O is crystalline in nature with peaks located at 2θ equal to 36.54° , 42.44° and 61.58° each corresponding to planes indexed to (111), (200) and (220) respectively.

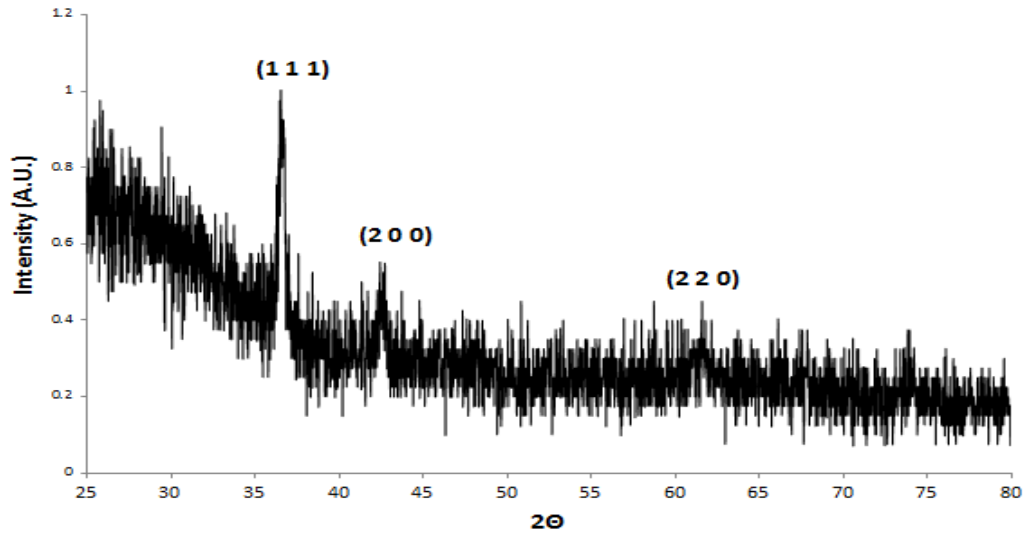


Figure 1. XRD diffractogram of doped Cu₂O

These peaks and indexed planes are in accordance to JCPDS 05–0667. These peaks are also the characteristic peaks of Cu₂O with cubic structure. No other phase, such as europium oxide and other forms of copper oxide were found which indicate the formation of crystalline Cu₂O phase only.

Table 1.2a and 1.2b show the elements present on the undoped and doped samples. EDX was used to determine the incorporation of Eu³⁺ on Cu₂O. A value of -2.58 in the undoped Cu₂O signifies that undoped Cu₂O does not contain Eu³⁺. This negative sign also implies that the signal for Eu detected in the sample is even lower than that of the background. However, a value +0.94 in Table 1.2b mean that indeed Eu³⁺ was incorporated in the Cu₂O crystal. Figure 5 shows the EDX spectra summarized in Tables 1 a and 1b. The resolution limit of the EDX system that was used in the study is 1000 ppm, equivalent to 0.1 wt%.

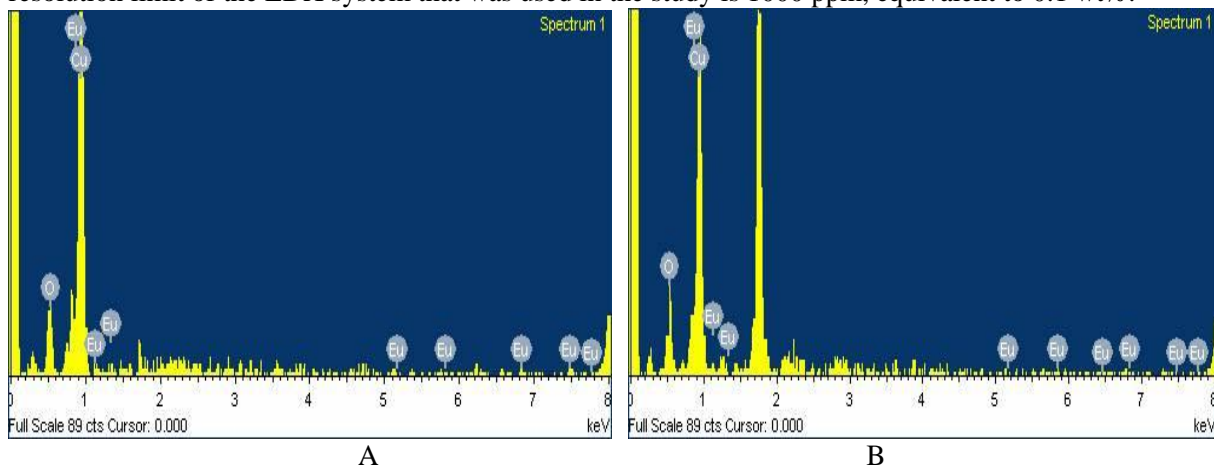


Figure 2. EDX of (A)undoped Cu₂O and (B)Eu doped Cu₂O

Table 1a. EDX Results – Elemental analysis of undoped Cu₂O.

ELEMENT	Weight %	Atomic %
O	13.26	37.38
Cu	89.32	63.38
Eu	-2.58	-0.77

Table 1b. EDX Results – Elemental analysis of doped Cu₂O.

ELEMENT	Weight %	Atomic %
O	18.32	47.27
Cu	80.74	52.47
Eu	0.94	0.26

In this paper, SEM was used to investigate the effect of adding Eu³⁺ ions on the morphology of Cu₂O. This is then paired with EDX to confirm the incorporation of Eu³⁺. These images are illustrated in Figure 3. It can be observed that in this micrograph, aggregates of copper oxide nanoparticles are evident. Voids, canyons and formation of dendritic structures are also evident, signifying a porous microfilm can be produced when it is casted on a substrate. Figure 3 shows the low magnification and high magnification (insets) SEM image of the samples with and without europium.

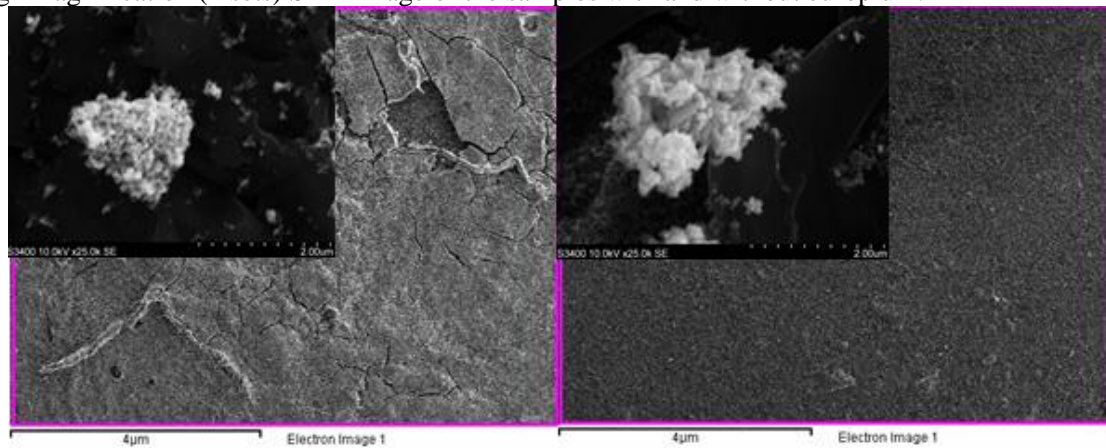


Figure 3. Low magnification of SEM results for left) undoped Cu₂O and right) Eu-doped Cu₂O
 Insets (25000x magnification scale bar = 2μm)

The SEM images obtained at 15,000X magnification are shown in Figures 4a – 4f. At 0.5%wt Eu doped to Cu₂O, as represented Figure 5b the particles are more dispersed, in a dendritic manner, and particles become partly smaller in size with respect to the images obtained from the undoped Cu₂O.

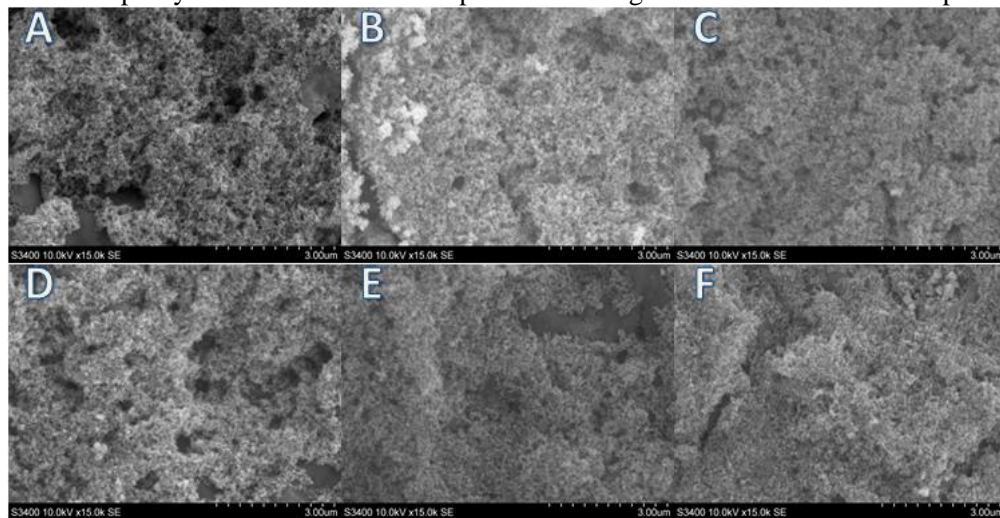


Figure 4. From top to bottom (L-R): (a) undoped Cu₂O (b) 0.5% (c) 1% (d) 2% (e) 3% (f) 5% Eu-doped Cu₂O

At 1%wt Eu doped to Cu₂O, as represented by Figure 4c, voids are visible, but particles are more uniformly sized and are dispersed, still in a dendritic manner, more evenly compared to the undoped Cu₂O. Although a better distribution of particles, agglomeration of particles can be observed, edges of agglomerated particles become distinct forming rod like structures as confirmed by the image shown in the inset image in Figure 3.

UV/Vis was used in this study to compare the effect of the different concentrations of Eu³⁺ on the optical bandgap of doped Cu₂O with respect to that of the undoped Cu₂O. The obtained absorbance spectra of the undoped and Eu-doped Cu₂O are shown in Figure 5. The summary of the computed optical band gap of the doped and doped samples is listed in Table 2. It should be noted that the listed wavelengths in Table correspond to the onset of absorption for each sample. Based on the data gathered from the UV/Vis, it can be inferred that as the amount of Eu³⁺ concentration increases, the E_g decreases, which means that addition of Eu³⁺ favors higher absorbance of visible light. Concentrations of Eu³⁺ ranging from 0.5% to 3% gave a direct linear relationship to the optical bandgap of Cu₂O lower than that of the undoped Cu₂O. This decreased in bandgap to 2.13eV makes it favorable for its potential application as visible light absorbers in photovoltaic devices..

Table 2. Onset of absorption and approximated band gap of doped and undoped Cu₂O.

SAMPLE	Wavelength (nm)	E _g (eV)
Undoped	552	2.25
0.5% Eu-	583	2.13
1.0% Eu-	577	2.15
2.0% Eu-	564	2.20
3.0% Eu-	558	2.22
5.0% Eu-	548	2.26

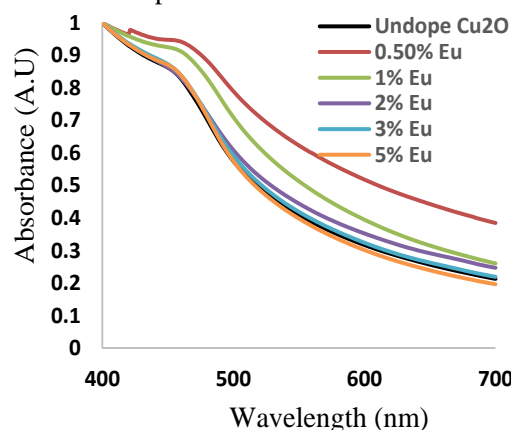


Figure 5. UV-Vis of doped and undoped Cu₂O

4. Conclusion

Undoped and Eu-doped Cu₂O nanoparticles were successfully synthesized via solution precursor route with the aid of ultrasonic sound. The incorporation of Eu³⁺ on Cu₂O did not alter the crystal structure and no formations of other species of copper and europium were observed. The SEM images revealed dendritic nanostructures composed of agglomerated nanoparticles. Optical characterization together with the calculation of bandgap confirmed that the synthesized Cu₂O nanoparticles are absorbing in the visible region. Moreover, the incorporation of Eu³⁺ on Cu₂O decreased the bandgap from ~ 2.25 eV to ~ 2.13 eV. Subsequently, further addition of Eu³⁺ resulted in the increased in bandgap of ~2.28eV. Further studies can be done on the effect of loading more Eu³⁺ on Cu₂O and determine if it could increase its bandgap at higher Eu loading.

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