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Optical studies of CuO Nanoparticles using Catharanthus Roseus Plant leaves

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Abstract : We have reported on the synthesis of CuO nanostructures via a complex precipitation method using $NH_3 \cdot H_2O$ as a complexing agent. Synthesized nanostructures were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), Luminescence spectroscopy and UV-Vis-NIR spectroscopy. Structural studies revealed that the formation of CuO nanostructures with monoclinic Crystal structure. The crystallite size of CuO nanostructures was estimated to be ~30 nm using Debye–Scherrer's formula. Morphological analysis by Field Emission scanning electron microscopy showed the formation of CuO architecture. The optical band gap value was estimated to be 1.6 eV using Tauc's plot. The light harvesting efficiency of CuO in dye solution of Catharanthus Roseus plant leaves is also discussed. Photoluminescence spectroscopy has been employed in order to explore the optical emission properties of CuO nano particles.

Keywords : CuO , XRD, Optical band gap, Natural dye, Luminescence.

Introduction

Recent research has shown that the properties of materials depend largely on their particle size, morphology and structure[1]. It is expected that materials with novel morphologies and micro/nano structures could exhibit effective and interesting functions. During the past decade, the metal oxide nanomaterials have acquired much attention owing to their wide potential technological applications in many fields [2-4]. Copper oxide nanoparticles have emerged as potentially powerful materials owing to their various technological applications such as catalysis, magnetic storage media, batteries, solar energy conversion, gas sensing and field emission[5–7].

CuO is a p-type semiconductor material with a narrow band gap of 1.2 eV, and since this gap is smaller than 1.85 eV, its field emission properties are of interest. Moreover, CuO has interesting photovoltaic, electrochemical and catalytic properties.[8–9].These applications can be enhanced by decreasing the particle size and hence a precise control of the size and distribution in the nanometer region is required. Various techniques have been adopted for the synthesis of CuO nanostructures such as sol-gel [10], co-precipitation ,hydrothermal [11], Solvo-thermal [12] and chemical precipitation [13]. To some extent, all the above methods possess some disadvantages. Therefore, developing a simple, inexpensive and robust approach for the rational synthesis of CuO nanostructures under mild reaction conditions is still a challenging task and is highly desired for exploring CuO in device applications.

Organic dyes resemble found in plants, fruits and the advantages of natural dyes is their easy availability, environment friendly, ease of fabrication, low process temperature and low cost of sensitization

material production. Naturally most of the fruits, flowers and leaves show various colours and contain several pigments which are easily extracted and then employed as sensitizer [14].In this investigation, we explore a facile and environmentally benign complex precipitation method using $NH_3 \cdot H_2O$ as a complexing agent to synthesis CuO nanostructure without using any surfactants or organic solvents. The natural dyes were extracted mostly from Catharanthus Roseus (C.R) plants leaves using absolute Ethanol solution. The structural and morphological properties of CuO nanoparticles were investigated using XRD,FESEM and EDXS. The optical properties were investigated by UV–Vis spectroscopy and Photoluminescence measurements using C.R dye Solution.

2. Experimental

2.1 Materials

Copper nitrate (Cu $(NO_3)_2 \cdot 3H_2O$, 99 wt %), sodium hydroxide (NaOH, 96 wt%), ammonia ($NH_3 \cdot H_2O$, 25 wt%) and absolute ethanol (C_2H_5OH, 99.7%) were purchased from Merck, India. All the reagents were of analytical grade and were used without further purification.

2.2 Synthesis of CuO nanoparticles and Preparation of Dye Solution

In a typical procedure, CuO nanoparticles have been prepared as follows: 1.208 g of $Cu(NO_3)_2 \cdot 3H_2O$ was added into 200 ml of distilled water under vigorous stirring to form a homogeneous solution. Then, 25% $NH_3 \cdot H_2O$ was added into the above solution drop by drop under vigorous stirring and kept for 30 min until a stable complex of $Cu(NO_3)_2$ and $NH_3 \cdot H_2O$ was formed (pH = 8). After that, 25 ml of 0.4 $mol \cdot l^{-1}$NaOH solution was dropped slowly into the mixed solution (pH = 11) under vigorous stirring. After reaction, the obtained blue precipitate were washed several times with distilled water and then with ethanol, and dried at 80°C for 24 hours. Finally, the product was calcimined in a furnace with an air atmosphere at 400°C for 2 hours [15].The C.R plant leaves were collected and washed with distilled water. Washed leaves were dried and crushed in a mortar to bring them in powder form. One gram of the C.R powder was then dissolved in absolute ethanol at room temperature in the dark for 24 hrs to extract the dyes (to liberate the dye molecules present in the sample) and the solid residues were filtered out. Filtered Dye solution kept in closed vessel at dark room and the UV-Vis absorption measurements were carried out using 0.5g of the annealed CuO nanoparticles powder was dissolved in 10 ml of dye solution [16].

Table 1 LHE of the CuO nanoparticles in C.R dye solution

Sample	Wavelength , λ (nm)	LHE (%)
CuO nanoparticles powders in C.R dye	310	99.10
	413	98.58
	666	92.19

2.3. Characterization

The structural analysis was carried out by XRD on a Rigaku X-ray diffractometer using CuKa radiation (λ=0.15406 nm). Surface morphology and elemental composition of the samples were analyzed by the energy dispersive X ray (EDXS) spectrometer interfaced to FEI Quanta 200 FEG scanning electron microscope (FESEM).The optical band gap was estimated using a Perkin Elmer lambda 35 UV-Vis spectrophotometer in the wavelength range 300-1100 nm. The room temperature PL spectrum was recorded using a Perkin Elmer LS 45 Fluorescence spectrometer equipped with Xe lamp.

3.Results and Discussion

XRD pattern of CuO Nanoparticles is shown in Fig1. All the diffraction peaks in the pattern can be indexed to the monoclinic structure of CuO with space group C_2/c(15). The sharp peaks indicate the well-crystallized single phase CuO nano crystals and the refined unit cell parameters calculated from the XRD pattern are in good agreement with the standard JCPDS data (a = 4.662 A^0, b = 3.416 A^0, c = 5.118 A^0, and β = 99.546, Card No. 65- 2309) [17,18].The highly diffracted peak is observed at an angle $2\theta = 38.82^o$

$$D = K\lambda/\beta\cos\theta \qquad (1)$$

corresponding to the (002) lattice orientation. Using X-ray diffraction analysis, the crystallite size of CuO structures is determined from the reflection peak width employing Debye-Scherrer's relation given by Eq. (1),

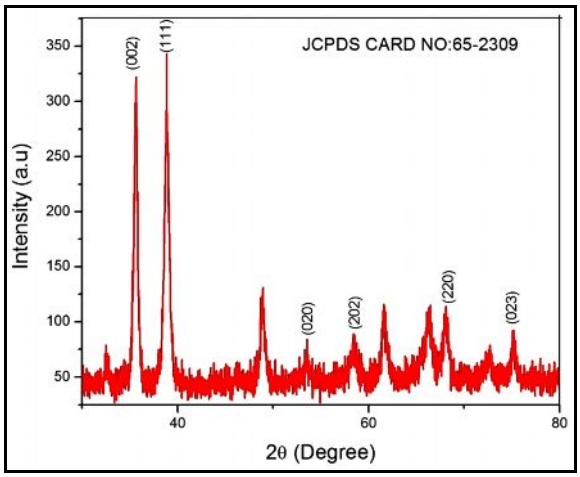

Figure 1 . XRD Pattern of CuO Nanoparticles

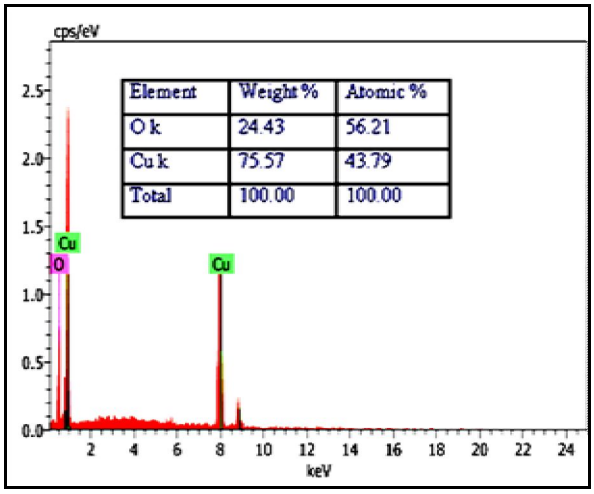

Figure 2. EDAX Spectrum of CuO nanoparticles

Where **K** is the shape factor (0.90), λ is the wavelength of CuKα radiation, β is the full-width at half maximum (FWHM), and θ is the angle of reflection. The mean crystallite size was found to be 30 nm.Energy dispersive X-ray Spectrum (EDXS) was carried out at 20KeV electron energy using SEM and is shown in Fig.2,confirms the presence of Cu and O peaks. There were two peaks relevant to Cu at about 1Kev and 8KeV. The atomic ratio of nickel and oxygen is 43.79 : 56.21 which can be assigned to CuO[19]. Fig 3 (a& b) shows the FESEM images of CuO nanoparticles synthesized via complex precipitation method. It can be observed that the alkaline precursors have substantial impact on the growth of CuO nanostructures. CuO synthesized using NH_4OH as complexing agent showed the formation of CuO nanoparticles. The nanoparticle agglomeration occurs to minimize their surface free energy The morphological properties have a strong influence on the optical and transport properties of the nanostructures [20].

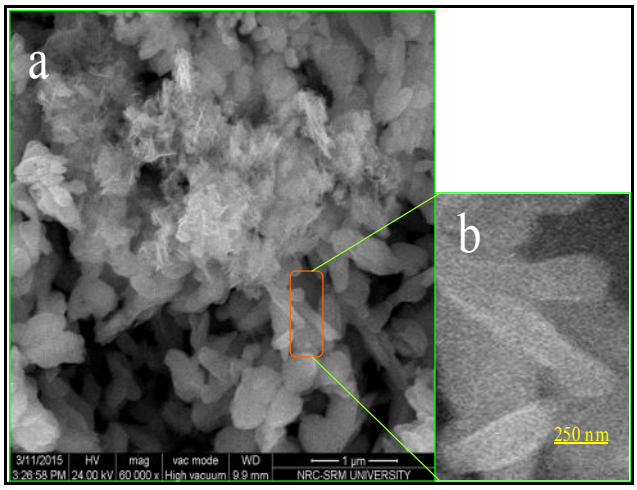

Figure 3. FESEM images of NiO CuO nanoparticles

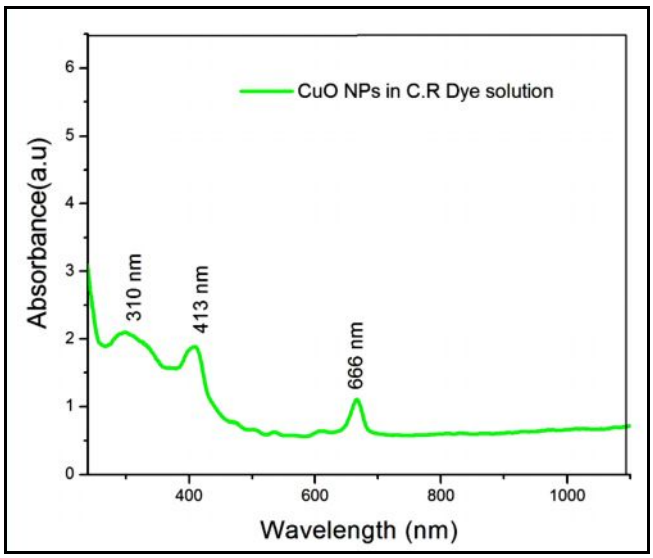

Figure 4. UV-Visible Spectrum of CuO

3.1 Optical Properties

The absorption spectrum of CuO nanoparticles, observed in the UV region, is depicted in Fig. 4. and it was used to study the optical properties of the synthesized CuO Nanoparticles dissolved in T.D dye solution. The value of the band gap for the CuO Nanoparticles was estimated by using Tauc equation 2.

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

where α is the absorption coefficient in cm^{-1}, hν is the photon energy, E_g is the energy gap, A is the energy dependent constant and n is an integer that can take different values depending on the type of electronic transition ,for a permitted direct transition n=1/2 and indirect transition n=2 . The optical band gap of CuO nanoparticles is estimated by using Tauc's plot. The direct and indirect band gap value is obtained by extrapolating the linear portions of the plots hν versus $(\alpha h\nu)^2$ and hν versus $(\alpha h\nu)^{1/2}$ to the energy axis as shown in fig.5 & 6. It is observed that CuO nanostructures exhibit an indirect and direct transition and the band gap value is estimated to be 1.6 eV and 2.5 eV . These values are in good agreement with earlier report. The observed band-gap values are larger than the bulk CuO (1.2 eV), which can be attributed to the well-known quantum confinement (QC) effect resulting from nano sized crystals [21].

3.11 Dye spectral response & Light Harvesting Efficiencies (LHE)

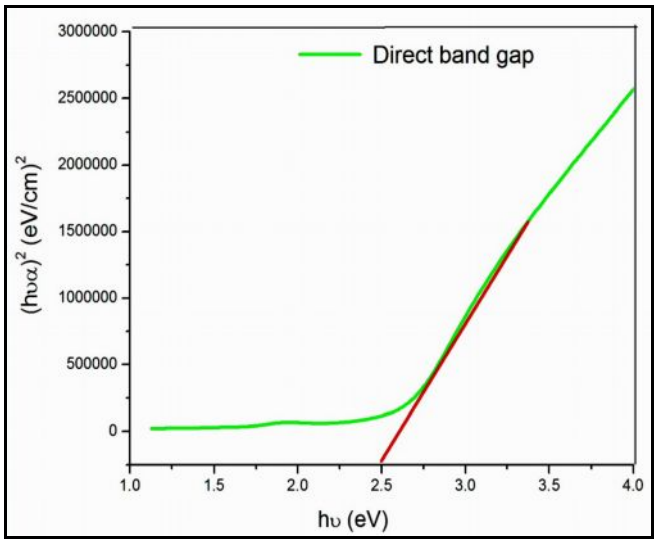

Figure 5. Tauc's plot of CuO nanoparticles (direct band gap)

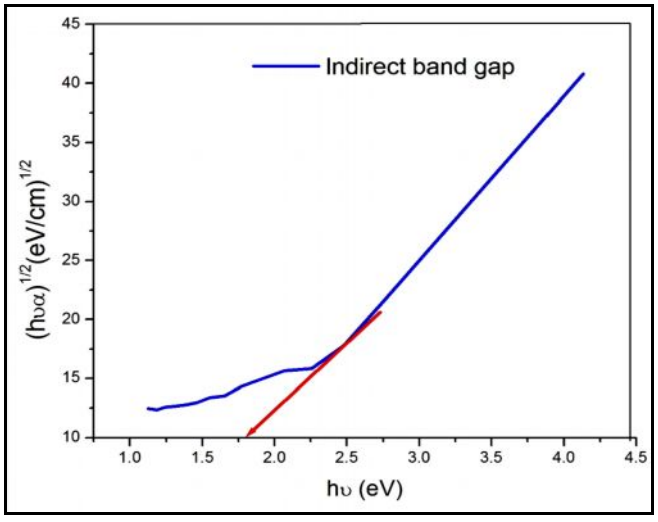

Figure 6. Tauc's plot of CuO nanoparticles (indirect band gap)

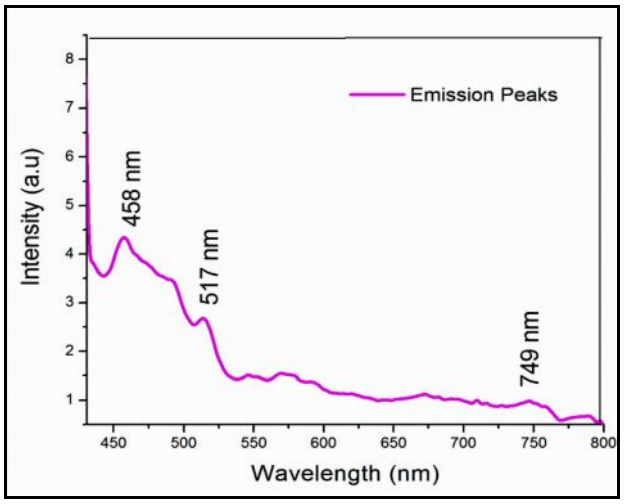

Figure 7. Luminescence Spectra for CuO nanoparticles in C.Roseus Dye solution

The dye spectral response & LHE were calculated from Fig.4. The small absorption peak at 310 nm indicate the presence of CuO in dye solution .The absorption peak is at 666 nm which are indicative of the presence of chlorophyll a. Besides the optical absorption spectra, LHE of the sample were calculated by using the following formula from Eq.3 [22].

$$\mathbf{LHE = (1-10^{-A(\lambda)})\times 100} \qquad \mathbf{(3)}$$

Where A (λ) is the absorbance at a specific wavelength. LHE is maximum at UV-Vis region and minimum at infrared region.

3.2 Luminescence spectra

The room temperature Photoluminescence spectra of CuO nanoparticles are shown in Fig7, at the Excitation of 430nm. The strong emission peaks located at 457nm (2.71 eV) is due to the band edge emission from the new sublevels at 300 K .The emission peaks (IR band) at 749 nm (1.65 eV) ascribed to the specific surface effect, which results in the red-shift of the Fluorescence emission. [23]. Thus, considering these parameters in the design of CuO-based photo-electronic devices is important.

4. Conclusion

In this work, CuO nanoparticles have been prepared by complex precipitation method using $NH_3{\cdot}H_2O$ as a complexing agent and NaOH as a precipitant. UV–Vis spectrum shows the optical properties and light harvesting efficiency of CuO in C.R dye solution and Photoluminescence spectrum revealed that this CuO nanoparticles can be a good candidate for photo electronic devices and its applications in the UV-Vis-IR range and C.R dye solution plays a vital role in increasing light harvesting efficiency. The current synthesis strategy can be extended for the preparation of other technologically important semiconductors.

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