



SYNTHESIS AND CHARACTERIZATION OF L-VALINE CAPPED SN DOPED CUO NANOPARTICLES

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Abstract

We report synthesis, structural and linear optical properties of L-valine capped undoped and Sn doped CuO nanoparticles (NPs). Sn doped (1, 2 and 5 wt%) CuO NPs were obtained by chemical co-precipitation method and were calcined at 500°C for 2h. X-ray diffraction (XRD) shows formation of crystalline CuO having monoclinic phase with average particle size of 10nm. Ultraviolet-visible (UV-vis) spectroscopy attests the formation of NPs and strong blue shift in the excitonic absorption has been observed for both uncalcined and calcined NPs. All samples show broad excitonic absorption in the wavelength range 351-654nm. This broad range of absorption may be due to inter band surface states transitions in CuO NPs.

Keywords: CuO nanoparticles, L-valine, XRD, UV-vis.

1. Introduction

Nanostructured materials offer great advantages over bulk materials owing to enhanced properties due to high surface to volume ratio and quantum size effects [1-3]. Metal Oxide or Semiconducting and Metal nanomaterials are known to have peculiar shape and size dependent physical, chemical, electrical and optical properties which can be

engineered as per application requirements [4]. These nanomaterials are widely used in optoelectronics, electronics, medicine, photonics etc. Third order nonlinearity in semiconducting materials is gaining extreme importance because of its potential applications in optical switching, optical limiters, optoelectronic devices, optical signal processing, optical waveguides, ultrafast optical communication systems, optical storage systems, ultrafast NLO devices, etc [5]. Nano crystalline CuO semiconductor is one of the best promising materials as it has potential applications in optics and optoelectronics. Copper oxide is an excellent nanoparticles system for investigating the size induced structural transformations and phase stability. CuO is a p-type semiconductor having direct bulk energy gap of about 1.85 eV at room temperature [6-8]. The effect of doping on properties of CuO nanostructures are being studied widely for many practical applications like an efficient catalytic agent, gas sensing material, lithium batteries, solar cells, optical switches, magnetic storage media, etc [9-12]. Effects of dopant and capping agent on semiconductor oxide nanoparticles have been reported in our previous works [13-18]

2. Materials and methods

Undoped and Sn doped CuO nanoparticles were synthesized by wet chemical method. All chemicals of analytical reagent grade were used as received without further purification. Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.99%),

sodium hydroxide pellets (NaOH, 99%) and ethanol were procured from SD-fine Chemicals, Mumbai. Tin chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99.99%) was purchased from LOBA chemi, India. L-valine was purchased from Sigma Aldrich, USA.

2.1 Synthesis of L-valine Capped and Sn doped CuO Nanoparticles:

Stock solutions of 1M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 2M NaOH and 0.1M L-valine in double distilled water were prepared. Double distilled (d.d.) water was used as a solvent for synthesis of CuO nanoparticles. 10 ml stock solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added into 150ml d.d. water and stirred continuously for 1h under constant heating at 100°C. The temperature was maintained above 100°C throughout the reaction. For the synthesis of sample CSn1, stoichiometric amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ leading to 1 wt% doping of Sn is added to the solution and stirred vigorously. 15 ml L-valine (15 mol%) from stock solution was added drop wise into blue colored copper chloride solution. The resultant solution was again stirred for another 30min. After this, NaOH stock solution was added drop wise into this solution till its pH reaches to 7. The color of the solution changes to black immediately and large amount of black ppt was obtained. The precipitate then washed 2-3 times with d.d. water. The precipitate was then dried for 24h in hot air electric oven. Two more samples namely CSn2 and CSn5 were also synthesized in this manner by adding appropriate amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ leading to 2 and 5 wt% doping of Sn respectively. All the synthesized samples of CuO NPs have been calcined at 500°C for 30 mins at the rate of approximately 1°C/min. Calcined samples have been renamed as CSn1C, CSn2C, CSn5C etc. All samples of CuO NPs were subjected to structural and morphological characterization by X-ray diffraction (XRD) using Rigaku diffractometer Miniflex II with nickel filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). Ultraviolet-visible (UV-vis) spectroscopy was performed

using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA) in the wavelength range 190-900 nm.

3. Results and Discussion

3.1 Optical Studies using UV-vis

All samples show broad excitonic absorption in the wavelength range 351-654nm. This broad range of absorption may be due to inter band surface states transitions in CuO NPs. Blue shifting of the maximum absorption wavelength is obvious. When CuO NPs are doped with Sn, particle size is found to increase with addition of Sn in CuO. This fact is also validated from UV-vis spectra as maximum absorption peak is red shifted as shown in the fig 1 (b).

3.2 Structural studies using XRD

Fig 1 (b) indicates XRD spectra for undoped and Sn doped CuO NPs. All the d-values corresponding to the XRD peaks show the presence of a monoclinic end-centred phase of crystalline CuO with cell parameters $a=4.6927\text{\AA}$, $b=3.4283\text{\AA}$ and $c=5.1370\text{\AA}$, $\alpha=\gamma=90^\circ$ and $\beta=99.546^\circ$ which is in good agreement with the reported values (JCPDS card no. 80-1916). Peak broadening can be seen which confirms the nano crystalline nature of CuO crystals. The intensity of peaks is not significantly changed with increasing concentration of Sn in CuO, which indicates that the crystallinity of the particles is retained. The peaks corresponding to the metallic Sn and its oxides structure have not been detected in XRD. This suggests that Sn has been doped into the lattice at Cu-lattice sites. Considering the spherical nature, particle size of these nanoparticles are calculated by Debye- Scherrer formula $d = \frac{k\lambda}{\beta \cos \theta}$; where k is a constant (k=0.93) and β is width of the diffraction peak at half maxima. The average crystallite size calculated for (-111), (111) and (-202) planes was found to be 10 nm for 5 wt% Sn doped CuO samples respectively.

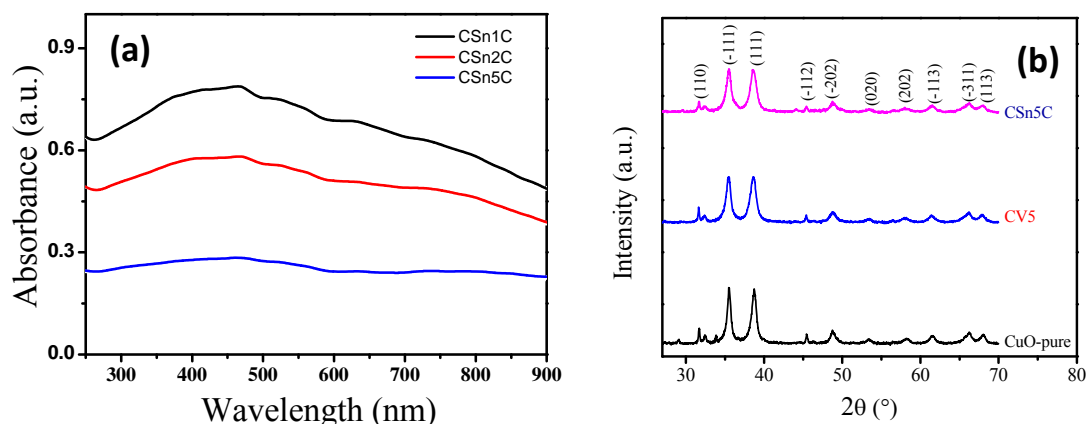


Fig 1(a) UV-vis spectra and (b) XRD Spectra of Sn doped CuO NPs

4. Conclusions

In conclusion, we report synthesis of L-valine capped and Sn doped CuO NPs by co-precipitation method. UV-vis studies attest the formation of CuO NPs by confirming blue shifting of absorption peaks. Absorption peaks are found to be slightly red-shifted with increase in Sn doping concentration. Band gap can thus be engineered. XRD studies confirm the pure phase formation. Sn doped CuO NPs may find potential applications in NLO devices.

5. References

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