ULTRAVIOLET-VISIBLE STUDIES OF L-VALINE CAPPED CuO NANOPARTICLES

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Abstract

In this paper, we present synthesis and ultraviolet-visible (UV-vis) analysis of L-valine capped CuO nanoparticles (NPs). Pure and L-valine (1, 2 & 5 mol%) capped CuO NPs have been obtained by simple co-precipitation technique. 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 and uncalcined samples were characterized by UV-vis study which attested the formation of NPs by witnessing blue shift in the absorption spectrum. Uncalcined samples show highest blue shift and thus effect of temperature is obvious. Optical band gaps have been obtained from Tauc plots and particle sizes were calculated using effective mass approximation technique.

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

1. Introduction

Nanotechnology is playing a vital role in day to day life on account of high surface to volume ratio and quantum size effect. These nanomaterials have applications in various thrust areas e.g. optics, fiber optics, sensors, actuators, optoelectronics, nonlinear optics, etc. Among these, semiconducting nanoparticles (NPs) are one of the focusing areas [1-3]. Nano crystalline CuO semiconductor is one of the best promising materials as it has potential applications in optics and optoelectronics. CuO is a p-type semiconductor having direct bulk energy gap of about 1.85 eV [4] at room temperature. The energy band gap can be increased in the nano regime and optical properties of such materials can be tuned for specific applications. Role of Amino acids in general and L-arginine in particular has already been studied as a capping agent for the synthesis of nanoparticles [5-10]. In this paper, we report the synthesis of CuO NPs using L-valine as capping agent. NPs have been calcined and their optical and morphological properties have been studied and results are presented here.

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 ($CuCl_2.2H_2O$, 99.99%), sodium hydroxide pellets (NaOH, 99%) and ethanol were procured from SD-fine Chemicals, Mumbai. L-valine was purchased from Sigma Aldrich, USA.

2.1 Synthesis of uncapped and L-valine capped CuO Nanoparticles:

Stock solutions of 1M $CuCl_2.2H_2O$, 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. Initially, CuO nanoparticles were synthesized using L-valine as capping agent. For this, 10 ml stock solution of $CuCl_2.2H_2O$ was added into 150ml d.d. water and stirred continuously for 1h under constant heating at 100°C. The temperature was

maintained above 100ºC throughout the reaction. For the synthesis of sample CV1, 5 ml L-Valine (5 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 CV2 and CV5 were also synthesized in this manner by adding 10ml (10 mol%) and 15ml (15 mol%) stock solution of L-valine respectively. One sample (Sample name: CuO-pure) was also prepared without the use of L-valine as capping agent. All the synthesized samples of CuO NPs have been calcined at 500ºC for 30 mins at the rate of approximately 1ºC/min. Calcined samples have been renamed as CuO-PureC, CV1C, CV2C and CV5C.

3. Results and Discussion
3.1 Optical Studies using UV-vis
Ultraviolet-visible (UV-vis) spectroscopy was performed using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA) in the wavelength range 190-900 nm. All samples (uncalcined and calcined) show broad excitonic absorption in the wavelength range 351-654nm as shown in Fig 3.1 (a & b) [11]. This broad range of absorption may be due to inter band surface states transitions in CuO NPs. When electromagnetic wave interacts with CuO NPs, light absorption takes place by creating electron in the conduction band and hole in the valence band. In the crystal of semiconductor, this electron-hole has columbic interaction to create excitons. When size of the crystals is in nano range, energies are highly quantized and novel optical properties emerge due to movement of excitons in the constrained region. Maximum absorption for all the samples is shown in the table 3.1. Blue shifting of the maximum absorption wavelength is thus obvious. CuO NPs capped using highest concentration of L-valine shows strong blue shift and reduced particle sizes are obtained as indicated by quantum confinement effect. This indicates that L-valine effectively modified the surface of CuO NPs by annealing surface states.

The energies of the possible optical transitions can be obtained through the relation $E_n = E_g - E_{exc} + (\hbar^2\pi^2 n^2 / 2MR^2)$; where, M $(= m_e^* + m_h^*)$ the total mass of the e-h pair, R is radius of nanoparticle, E_g is bulk band gap energy, E_{exc} is the exciton binding energy, and n is the quantum number. The particle size for all samples is calculated from UV-vis spectra by using effective mass approximation (EMA). The EMA [12] formula can be stated as:

$$E_g = E_{bulk} + h^2 / 8r^2[(1/m_e^*) + (1/m_h^*)] - e^2 / 4\pi\varepsilon_0\varepsilon_r\gamma_e$$

where, E_g is band gap energy of NPs, E_{bulk} is energy gap for bulk semiconductor (=1.85eV for bulk CuO), m_e^* and m_h^* are effective electron mass ($0.65m_e$) and effective hole mass ($1.75m_e$). γ_e is Bohr exciton radius, ε_r is relative dielectric constant (7.11), ε_0 is dielectric constant of vacuum and r is the radius of NPs. Particle sizes calculated and band gaps determined from Fig are listed in table following table 3.1.
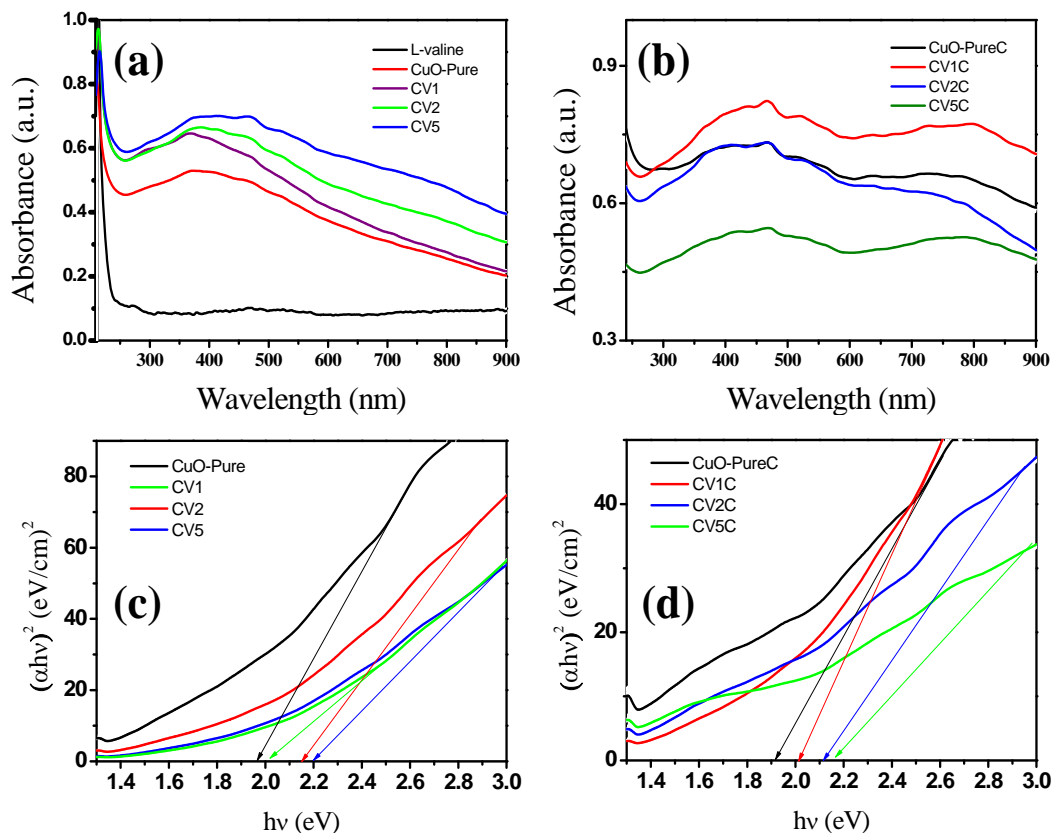
Fig 3.1 Absorption spectra (a & b) and Optical band gaps (c & d) of uncalcined and calcined CuO NPs

Table 3.1 UV-vis spectral details of all CuO NPs

Sample Name	Max Absorption (nm)	Optical band gap (eV)	Particle Size (nm)
CuO-Pure	510	1.94	10.00
CV1	475	2.037	5.00
CV2	471	2.151	4.00
CV5	465	2.21	3.00
CuO-PureC	522	1.92	12.00
CV1C	482	2.023	7.00
CV2C	476	2.12	5.00
CV5C	472	2.164	4.00

3.2 Morphological studies using TEM

Fig 3.2 shows HR-TEM micrographs and SAED pattern of CuO NPs. All micrographs confirm the formation of CuO NPs having uniform near spherical shape having average particle size of 10 nm. Particle size obtained from TEM data are found to be in good agreement with UV-vis data.
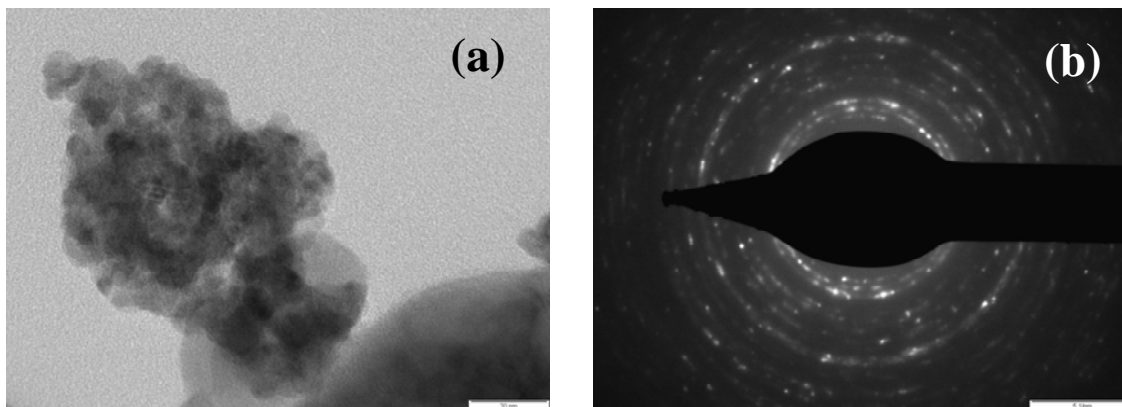
Fig 3.2 HR-TEM micrograph (a) and SAED pattern (b) of CuO NPs

4. Conclusions

In summary, pure, uncapped and L-valine capped CuO NPs have been obtained by wet chemical synthesis technique. TEM images attest the formation of uniform CuO NPs with spherical morphology. UV-vis studies confirm the formation of CuO NPs by witnessing blue shift in the maximum absorption wavelength. Absorption blue shift is less in case of calcined NPs. Particle sizes have been calculated by EMA approximation and optical band gap engineering is validated for L-valine capped CuO NPs.

5. References

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