LINEAR OPTICAL STUDIES OF L-ARGININE SURFACE MODIFIED CuO NANOPARTICLES

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ABSTRACT: We report the synthesis of L-arginine surface modified CuO nanoparticles (NPs) by chemical co-precipitation method. CuO nanoparticles have been characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray (EDX) spectroscopy and ultraviolet-visible (UV-vis) spectroscopy. Structural and morphological characterizations confirm the formation of pure CuO NPs having monoclinic crystal structure with average particle size of 5 nm. UV-vis study show that the band gap energy in case of CuO NPs has been increased up to 2.51 eV.

KEYWORDS: CuO NPs; HR-TEM; XRD; L-arginine; UV-vis.

1. INTRODUCTION

Nanomaterials having particle size in the range of few nanometers show properties which are of scientific and technological importance. Inventions in nanotechnoogy show excellent nonlinear optical properties (NLO) that resulted technological importance to optoelectronic devices. Semiconducting nanomaterials are known to have peculiar shape and size dependent physical, chemical, electrical and optical properties which have potential applications in optoelectronics, electronics, medicine, photonics etc. [1-4]. 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 [5] 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. L-arginine has already been used as a capping agent for the synthesis of nanoparticles [6,7].

In this paper, we report synthesis of CuO nanoparticles (NPs) by using L-arginine as capping agent. CuO NPs have been characterized by various techniques and results are presented.

2. MATERIAL SYNTHESIS AND METHODS

CuO NPs have been synthesized by chemical co-precipitation technique. 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, India. L-arginine was purchased from Sigma Aldrich, USA.

For synthesis of CuO nanoparticles, 3ml $CuCl_2.2H_2O$ stock solution (1M) was poured into 100ml double distilled (dd) water and kept under vigorous stirring for 1h at 100°C. For sample CLR1, 1ml L-arginine solution (1M) which is used as a capping agent was added drop wise into the solution and stirred further for 30min. Finally, NaOH stock solution (1M) was added drop wise till its pH reaches to value 7 that immediately results into black precipitate. The precipitate then centrifuged at 4000 rpm (REMI Model-4RC) for 20 minutes and washed 2-3 times with ethanol. The black precipitate was dried in an electric oven at 100°C for 24 hours and finely ground in an agate mortar to get fine powder. Same process was adopted to synthesize samples CLR2 and CLR3 by adding 2 and 3ml L-arginine respectively. Sample CuO-pure was prepared by same procedure without the addition of L-arginine.

CuO NPs have been characterized by X-ray diffraction (XRD) using Rigaku diffractometer Miniflex II with nickel filtered CuKα radiation (λ=1.5406 Å), high resolution transmission electron microscopy (HR-TEM) using JEM-2100 HR-TEM, Make-JEOL, Japan and EDX using JSM-7000F, JEOL, Japan. Ultraviloet visible (UV-vis) spectroscopy was performed using UV-visible spectrophotometer (BLK-C-SR, Stellarnet, USA) in the wavelength range 200-900 nm.

3. RESULTS AND DISCUSSION

3.1 STRUCTURAL AND MORPHOLOGICAL STUDIES USING XRD, EDX AND TEM

Fig.1 indicates XRD spectra for uncapped and L-arginine capped 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=4.6927Å, b=3.4283 and c=5.137Å, $\alpha= \gamma= 90^{o}$ and $\beta=99.546^{o}$ 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 [8]. Considering the spherical nature, particle size of these NPs are calculated by Debye-Scherrer formula $d = k\lambda / (\beta\cos\theta)$ (where k is a constant (k=0.93) and β is width of the diffraction peak at half maxima) and mentioned in table 1. It is seen that particle size of CuO NPs decreases with increase in the concentration of L-arginine. An EDX spectrum (Fig.2) confirms purity of prepared samples. HR-TEM micrograph (Fig.3) clearly attests formation of CuO NPs with uniform near spherical structure.
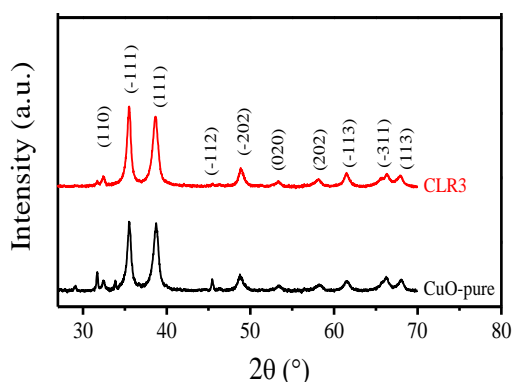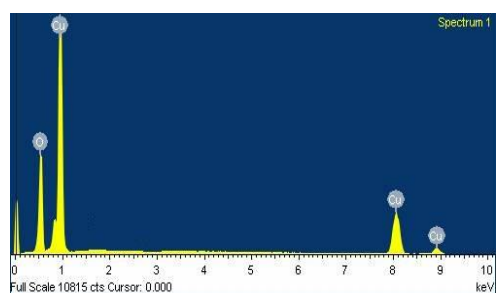

Fig. 1 *XRD pattern of CuO NPs*

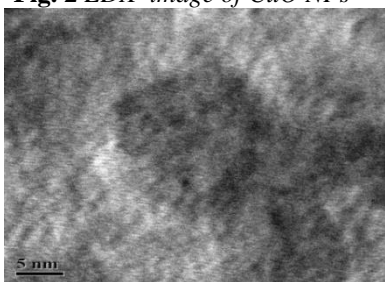**Fig. 2** *EDX image of CuO NPs*

Fig. 3 *HR-TEM micrograph of CuO NPs*

3.2 LINEAR OPTICAL STUDIES USING UV-VIS SPECTROMETRY

Fig.4 shows absorption spectra for uncapped and L-arginine capped CuO NPs samples (CuO-pure, CLR1, CLR2 and CLR3). 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 [9]. 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 quantised and novel optical properties emerge due to movement of excitons in the constrained region. Maximum absorption takes place at 388, 371, 363 and 351nm for the samples CuO-pure, CLR1, CLR2 and CLR3 respectively. Blue shifting of the maximum absorption wavelength is thus obvious. CuO NPs capped using highest concentration of L-arginine shows strong blue shift and reduced particle sizes are obtained as indicated by quantum confinement effect [10,11]. However, absorption intensity goes on decreasing and absorption bands become narrow as particle size decreases. This indicates that L-arginine effectively modified the surface of CuO NPs by annealing surface states. Low density of surface states might have caused less and selective absorption.
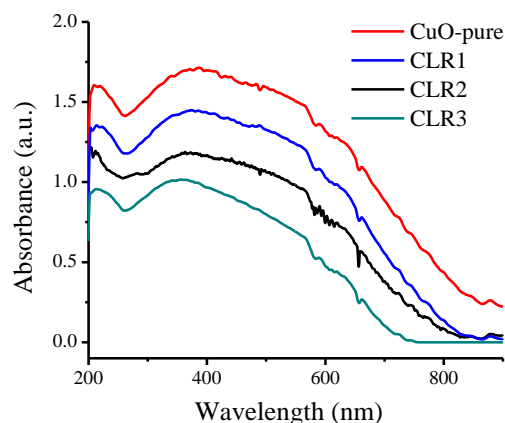

Fig. 4 *Absorption spectra of CuO NPs*

The optical band gap (E_g) of CuO nanoparticles is calculated using the equation; $\alpha = A*(E_g - h\nu)^n / h\nu$ where, α is absorption coefficient, E_g is band gap, A* is constant and n is equal to 1/2 for direct transition and 2 for indirect transitions [12]. The band gap energy is obtained by extrapolating the linear portion of the plot to the energy axis. The plot of variation of $(\alpha h\nu)^2$ vs. photon energy (hν) for all CuO NPs samples is shown in the Fig.5. Good blue shifting of the optical band gaps have been observed as the particle size

decreases for highest concentration of L-arginine. As obtained particle size for CuO NPs is in the range of Bohr exciton radius which is 6.6-28.7 nm [13] for present case, this regime is treated as strong confinement regime [14]. 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, is bulk band gap energy, is the exciton binding energy, and n is the quantum number [15]. The particle size for all samples is calculated from UV-vis spectra by using effective mass approximation (EMA) [16]. The EMA 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 [17]), and m_e^*, 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.5 are listed in table 1.
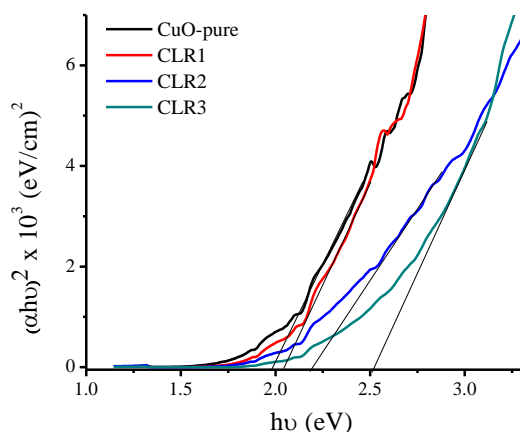

Fig. 5 V*ariation of (αhv)2 vs. photon energy (hv) of CuO NPs*

Table 1 Particle size and band gap energy of CuO NPs

Sample code	Particle size (nm)		Energy gap (eV)
	XRD	UV-Vis	
CuO-pure	20	9	1.9
CLR1	-	5	2.05
CLR2	-	4	2.19
CLR3	7	3	2.51

4. CONCLUSIONS

Pure and L-arginine surface modified CuO NPs with average particle size of 5 nm have been synthesized by chemical co-precipitation technique. XRD, TEM and EDX studies confirm the formation of uniform, pure CuO NPs having monoclinic crystal structure. UV-vis studies show that the samples show strong blue shifted excitonic absroption for highest concentration of L-arginine and band gap energy upto 2.51 eV have been obtained. Particle size and band gap energy of all CuO NPs have been calculated by effective mass approximation analysis.

5. ACKNOWLEDGMENTS

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