The Size, Morphology, Electrochemical Measurement and Optical Properties of Cuo Nanocrystals Using New Oxide Source by Sol-Gel Technique

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ABSTRACT

Spherical shaped CuO nanocrystals were successfully synthesized by sol–gel technique. Triethanolamine (TEA) used as a capping agent to control the size, morphology and optical properties of the CuO nanocrystals. Evolution of structure, surface morphology and optical absorption analysis of these nanocrystals were studied using UV–Visible spectrophotometer (UV–Vis), X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS). UV–Visible technique used to measure the band gap of TEA capped CuO nanocrystals having good optical property compared than uncapped CuO nanocrystals in the synthesized samples. The FT-IR study of transmittance peaks at 502 cm^{-1},603 cm^{-1} and 674 cm^{-1} were Cu-O stretching mode, and 677 cm^{-1} has been Cu-O monoclinic phase of the uncapped CuO nanocrystals. In addition the transmittance peaks at 502 cm^{-1}, 583 cm^{-1} have been Cu-O Stretching mode and 784 cm^{-1} are Cu-O monoclinic phase of the Triethanolamine capped CuO nanocrystals.

Introduction

Over the past decade, the field of nanotechnology has undergone great developments, resulting in new procedures for the controlled synthesis of a broad variety of nanoscale materials and measurement of their exclusive properties. The optical, electronic and catalytic properties of the nanostructure. These properties and their generally high surface-to-volume ratio has led to their use in several analytical applications [1]. With thousands of different engineered nanomaterials (ENMs) is of key importance for the acceptance and achievement of a sustainable technology to the profits of humans and the environment [2-3]. While transition metal oxide nanocrystals are used with great success to get better the efficiency of semiconductors and sensors [4-6]. In recent studies, Nanoscale metal oxides have attracted a great deal of research interest because of both fundamental and technological [7].

The work has been already done on cuprous oxide or Cuprite (Cu_2O) and cupric oxide or tenorite (CuO), with a band gap of 1.85eV - 2.21 eV respectively [8-10]. In our work we have synthesized CuO with Coumarin using the sol-gel technique. In the recent works, different methods have been proposed to synthesize CuO nanoparticles such as thermal oxidation, electro-deposition, hydrothermal treatment, high-temperature combustion and sol-gel technique [11-17]. Therefore, sol-gel synthesis combining with a capping agent is a powerful, simple and effective route for the controllable synthesis of CuO nanoparticles [18]. A variety of organic additives in aqueous solutions are also known to control the preferred orientation, grain size, surface morphology and the chemical composition [19] such as Coumarin, saccharin, citric

acid, EDTA, malonic acid and tartaric acid [20]. Among them, Coumarin is known as an additive that not only refines the grains, but makes the grain size distribution more uniform as well [21]. It is well known that the properties of nano-crystalline depend on both the size and morphology of the nanocrystals or nanoparticles. Many investigations are still carried out to improve the characteristics of CuO materials [22].

In the present work, a simple method was designed to prepare CuO nanocrystals with a capping agent like Triethanolamine (TEA) by the sol - gel technique at 80 °C. Commonly nanocrystals synthesis depends upon the temperature and stirring rate. Increases the temperature as well as reducing the stirring rate. Triethanolamine (TEA) as capping agent to study their effects on the size and morphology of CuO nanocrystals. The present investigation occurs to synthesize a new oxide source Coumarin with CuO nanocrystals obtained by the Sol - gel method. Coumarin ($C_9H_6O_2$) is an aromatic compound (1, 2 benzopyrone or α-benzopyrone) acquires from natural products. It is one of the most active classes of compounds exhibiting a wide spectrum of biological activity. The molecular structure of a capping agent (TEA) with the reacting group as shown in Table 1. Coumarin is important natural occurring and synthetic compounds which show several relevant applications.

Experimental details

The chemical reagents used in the experiments were analytical grade, purchased from Merck India Ltd., AR grade and used without further purification. A Sol–gel technique used copper acetate monohydrate and Coumarin to synthesize CuO nanocrystals. In a typical synthesis, copper acetate

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monohydrate [Cu (CH₃COO)₂ .H₂O] and Coumarin [C₉H₆O₂] were dissolved in distilled water to prepare the precursor solution of 0.2 M, 0.3 M. 100 ml each of the precursor solutions were added slowly into the copper acetate solution. 0.005 M of Triethanolamine (TEA) in 0.66 ml of solution was added slowly into the copper acetate solution. The mixed solutions were constant stirring for 5 h at 80° C. After 5 hours a dark green colored gel was obtained. The sol–gel stirred for 5 h before being matured in a hot air oven at 150 °C for 2 h to evaporate excess solvent. The product was washed with ethanol, repeated this process for 5–6 times and further dried at 150° C. Finally, a pure black colored powder was collected as a sol–gel product.

Results and Discussion

UV-Visible spectrum of CuO nanocrystals

The optical properties of the synthesized uncapped and TEA capped CuO nanocrystals dispersed in liquid ammonia. The band gap energies of the absorption characteristics of the nanocrystals were recorded in the wavelength range of 200– 900 nm. The uncapped and TEA capped CuO nanocrystals were broad absorption peak centered at 384 nm and 396 nm respectively. The weak absorption peaks are 610 and 635 nm of the uncapped and TEA capped CuO nanocrystals. Further, the corresponding cutoff wavelengths are 463 and 504 nm observed for the uncapped and TEA capped CuO nanocrystals respectively as shown in Fig 1. The band gap calculated by equation (1)[23]

$$E = \frac{h*c}{\lambda} \ eV \tag{1}$$

The calculated band gap values of the uncapped and capped TEA CuO nanocrystals are 2.6 eV and 2.4 eV respectively. Therefore, we have concluded that depending upon the absorption peaks centered increases probably the band gap of the nanocrystals decreased [24]. Finally, we conclude that TEA capped CuO nanocrystals having good optical property compared than uncapped CuO nanocrystals.
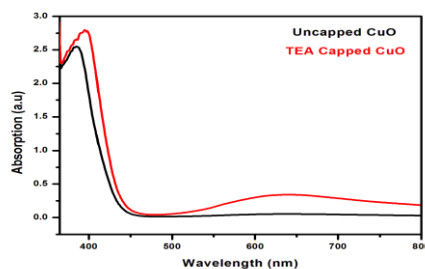

Figure 1. UV-Visible Spectrum of uncapped and TEA capped CuO nanocrystals

Photoluminescence studies

Photoluminescence (PL) spectrum of uncapped and TEA capped CuO synthesized samples were recorded in the range of 240-900 nm at room temperature. The fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical band gap [25]. As seen, a narrow and weak emission band around 420 nm and 495 nm, using an excitation wavelength of 250 nm was recorded for the uncapped and TEA capped CuO nanocrystals. Meanwhile, a comparison between uncapped and TEA capped CuO nanocrystals clearly revealed that there are two distinct emission bands in their Photoluminescence spectra. The uncapped CuO nanocrystals were sharp, narrow and symmetric located at about 492 nm and 396 nm. In addition, TEA capped CuO nanocrystals were sharp, narrow and

symmetric located at about 495 nm and 420 nm respectively. A sharp emission peaks at 492 nm and 495 nm of the uncapped and TEA capped CuO nanocrystals were observed in violet to blue region supports the blue-shift behavior of the peak position, in comparison with bulk CuO as shown in Fig 2. This observed blue-shift behavior is attributed to the enhanced quantum confinement effect due to decrease in the dimensions of the nanostructures. The uncapped and TEA capped CuO nanocrystals luminescence blue bands at 491 and 495 nm are caused by transition vacancy of oxygen and interstitial oxygen. However, the uncapped and TEA capped CuO nanocrystals photoluminescence intensity according to the 492 (4.2 a.u) and 495 (4.5 a.u) respectively. So, we have concluded, TEA capped CuO nanocrystals having good optical property than uncapped CuO nanocrystals. Optical properties depending upon the band gap value, if the band gap drastically reduces the nanocrystals are a good conductor and optical property material.
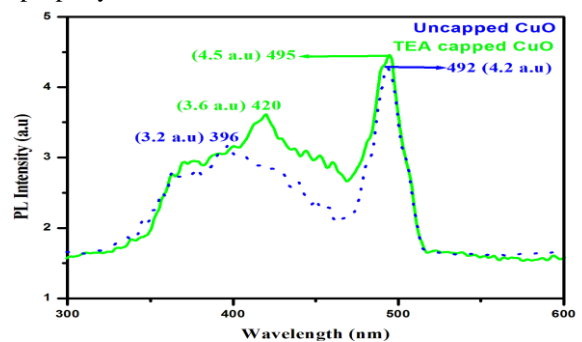

Figure 2. Photoluminescence Spectrum of uncapped and TEA capped nanocrystals

Structural analysis and Particle size calculations

The characteristic X–ray diffraction patterns of uncapped and Triethanolamine (TEA) capped CuO synthesized samples were recorded in the range of 2θ between 20°– 80°. The XRD peak position was consistent with the uncapped copper oxide and the sharp peaks with high intensity indicated the crystalline nature. The peaks observed at 35.02°, 38.55°, 48.74°, 58.13°, 61.66°, 66.27°, 67.80° and 74.65°. These peaks were assigned to the (-111), (111), (-202), (112), (020), (-113), (022) and (220) of the monoclinic structure of uncapped CuO nanocrystals. The orientation and the crystalline nature of the prepared uncapped and TEA capped CuO nanocrystals were identified from their corresponding XRD pattern Fig. 3 (a and b) shows the X-ray diffraction pattern of the synthesized samples. The XRD peak position was consistent with the Triethanolamine (TEA) capped copper oxide and the sharp peaks with high intensity indicated the crystalline nature. The peaks observed at 35.14°, 38.40°, 48.77°, 58.05°, 61.50°, 66.05° and 67.88°. These peaks were assigned to the (-111), (111), (-202), (020), (202), (-113) and (022) of the monoclinic structure of Triethanolamine (TEA) capped CuO nanocrystals. The unit cell parameter of the uncapped and Triethanolamine (TEA) capped CuO nanocrystals are, a = 4.684 Å, b = 3.425 Å, and c = 5.129 Å with monoclinic structure, space group C₂/c and volume cell 81.16 Å³ respectively. The strong and sharp diffraction peaks of the uncapped and Triethanolamine (TEA) capped CuO nanocrystals indicate the obtained products are well crystalline in nature. Tables 2 and 3 represent the particle size of synthesized uncapped and Triethanolamine capped CuO nanocrystals.

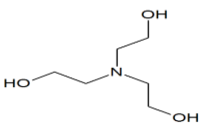**Table 1. Molecular structure of capping agent with reacting group**

Capping agent	Reaction sites	Molecular structure
TEA	Nitrogen (N)	

Table 2. Uncapped CuO Nanocrystals

S.No	2θ (degree)	d spacing (10⁻¹⁰ m)	FWHM (β) (radians)	Miller indices	Particle size (D) (nm)
1.	35.02	1.752	0.0296	[-111]	7.39
2.	38.55	1.037	0.0341	[111]	4.37
3.	48.74	0.781	0.0127	[200]	11.6
4.	58.13	0.780	0.0323	[112]	4.5
					Average particle size = 6.99nm

Table 3. TEA capped CuO Nanocrystal

S.No	2θ (degree)	d spacing(10⁻¹⁰ m)	FWHM (β) (radians)	Miller indices	Particle size (D) (nm)
1.	35.14	1.302	0.0543	[-111]	3.20
2.	38.40	1.422	0.0349	[111]	4.24
3.	48.77	0.876	0.0417	[-202]	3.67
4.	58.05	0.843	0.0268	[020]	5.52
					Average particle size = 4.16 nm

Table 4. Stretching modes in Uncapped and EDTA capped CuO nanocrystal

S. No	Wavenumber (cm⁻¹)		Uncapped CuO Stretching mode	TEA capped CuO Stretching mode
	Uncapped CuO	TEA capped CuO		
1.	512	523	Cu=O Stretching mode	Cu=O Stretching mode
2.	592	602	Cu=O Stretching mode	Cu=O Stretching mode
3.	743	749	Cu=O Monoclinic phase.	Cu=O Monoclinic phase.
4.	3500 - 1300	1026 and 2919	CO_2 and H_2O molecules.	C-H stretching aliphatic groups of TEA

Table 5. Elemental composition of Uncapped and TEA capped CuO nanocrystal

Elements	Atomic percentage (%)	
	Uncapped CuO	TEA capped CuO
Copper (Cu)	47.01	41.05
Oxygen (O)	52.99	58.95

Using Debye–Scherrer's equation, the particle sizes are calculated by four main line widths in XRD spectra uncapped and TEA capped CuO nanocrystals were finding out the particle size as 6.99 nm and 4.16 nm as shown in Tables 2 and 3 respectively. The specific crystallographic planes confirmed that the formation of the uncapped and Triethanolamine (TEA) capped CuO (space group C_2/c) monoclinic phase matches with the standard (JCPDS card No.80-1916).
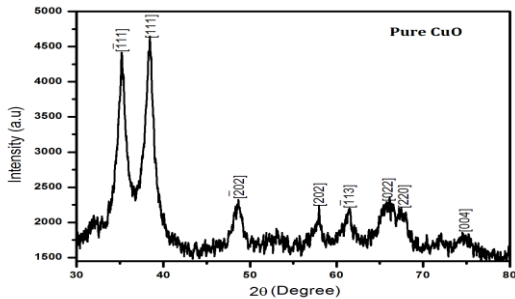

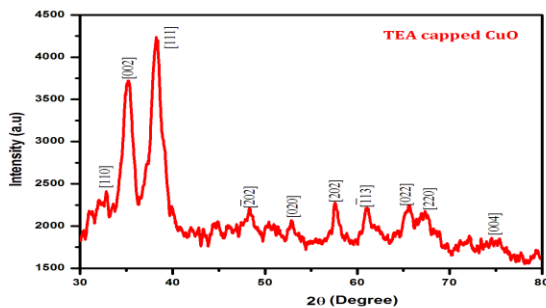**Figure 3 (a). X-ray diffraction pattern of CuO nanocrystals**

Figure 3 (b). X-ray diffraction pattern of TEA capped CuO nanocrystal

FT-IR spectra of functional group analysis

In the present investigation, the FTIR spectrum of low frequency region 400–700 cm^{-1} assigned the vibrational properties of CuO nanostructures correspond to 512 cm^{-1} and 592 cm^{-1} have been Cu-O stretching modes. The stretching modes in uncapped and TEA capped CuO nanocrystal as shown in Table 4. Furthermore, a transmittance peak at 743 cm^{-1} has been Cu-O monoclinic phase of the uncapped CuO nanocrystals as shown in Fig. 4. The broad absorption peak at a frequency 523 cm^{-1}, 602 cm^{-1} and 749 cm^{-1} (0.011a.u.). The maximum frequency observed for uncapped agent is 1080 cm^{-1}. Furthermore, a transmittance peak at 1026 cm^{-1} and 2919 cm^{-1} were C-H Stretching aliphatic groups of TEA. This result suggests that the presence of a capping agent in CuO nanocrystals [28, 29] and shown in Fig.4
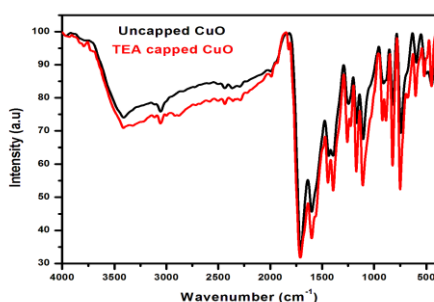

Figure 4. FT-IR Spectrum of Uncapped CuO and TEA capped CuO nanocrystal

Field Emission Scanning Electron Microscopy (FE-SEM) with EDS spectrum

The morphology of the uncapped and TEA capped CuO nanocrystals were analyzed by FE-SEM. FESEM images of the uncapped and TEA capped CuO nanocrystals with the different magnification like X50000, X75000 and X100000. FE-SEM images of uncapped and TEA capped CuO nanocrystals were identified that the rod like morphology and a spherical morphology shown in Fig.5. [A] - [F]. It can be seen that the size of uncapped and TEA capped CuO nanocrystals are in the range of 30.1 nm to 43.5 nm and 22.6 nm to 27.0 nm respectively. Moreover, TEA capped CuO nanocrystals are good morphology and the very narrow range of the particle size.
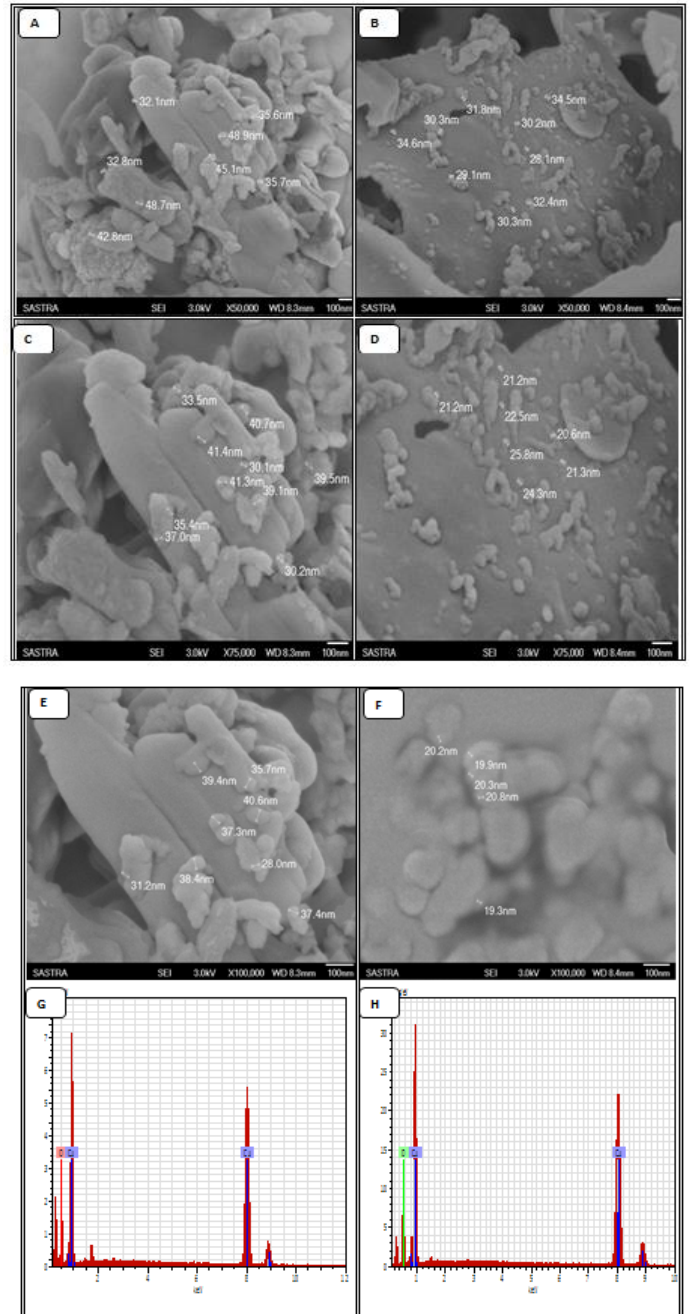

Figure 5 [A-F]. FE-SEM image of Uncapped and TEA capped CuO nanocrystal

Figure 5 [G-H]. EDS Spectra of Uncapped and TEA capped CuO nanocrystal

This happened due to the addition of the TEA as a capping agent. Further, these results confirmed that the

variation of the uncapped and TEA capped CuO nanocrystals. Finally, TEA has a good size controller and good influence of the CuO nanocrystals. EDS spectra of uncapped and TEA capped CuO nanocrystals are shown in Fig. 5. (G) and (H) respectively. These results indicated the presence of CuO in the capped and uncapped agents. The elemental composition of uncapped and TEA capped CuO nanocrystals, which is clearly obtained from EDS analysis Table 5.

Electrochemical measurements were carried out in 0.2 M tetra butyl ammonium per chloride aqueous electrolyte via a three electrode system. The CuO was engaged as the working electrode (WE), a platinum wire counter electrode (CE), and an Ag/AgCl reference electrode (RE). Electrochemical oxidation and reduction of Cu (II) ions with tetra butyl ammonium per chloride as supporting electrolyte. Cyclic Voltammetry (CV) measurements were performed within a potential range of -1.4 to 1.4 V versus Ag/AgCl at a scan rate at 50 mV s-1. From the CV curve of the anionic potential (Ipa) and cationic potential (Ipc) values of the pure CuO nanoparticles are 0.25 V and -0.10 V respectively as shown in Fig 6. It shows a pair of redox peaks, which is attributed to the Cu (II) /Cu0 redox couple. These resulted potential values are indicated as reversible electrochemical reactions of pure CuO nanoparticles. In addition, cationic potential peak corresponds to the reduction of CuO into Cu0, and the anionic potential peak arises from the formation of CuO. In addition, CV measurements of pure CuO nanoparticles are the cationic peak, which appeared at -0.10 V but TEA capped CuO nanoparticles are suppressed the cationic peak after the addition of the TEA capping agent. In this case, Ipc appeared in 0.53 and currently -1.9 μA reveals a rapid, irreversible electro catalyst compared than the pure CuO nanoparticles as shown in Fig 6.
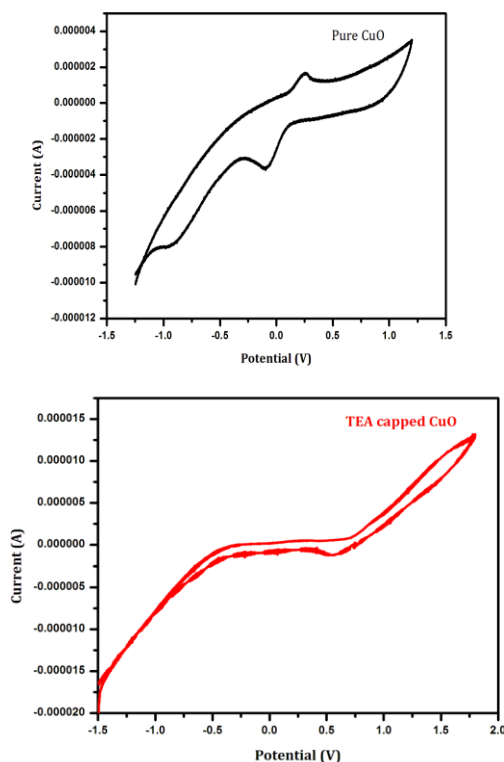

Figure 6. Cyclic Voltammetry of Pure and TEA Capped CuO

Conclusion

In this paper, Capped and Uncapped CuO nanocrystals were synthesized by a sol-gel technique using TEA as a capping agent. From CV results, CuO nanoparticles based electrode exhibited reasonably good electrochemical reaction for the electro catalytic activity. The interaction of the TEA reaction sites with Cu2+ ion of the copper acetate in the sol-gel medium is the possible for the change in the morphology of the resulted nanocrystals. TEA capped CuO nanocrystals having good optical property than uncapped CuO nanocrystals. FE - SEM images of uncapped and TEA capped CuO nanocrystals were identified that the rods like morphology and spherical morphology. TEA has a good size controller and good influence of the CuO nanocrystals accordingly the resulted nanocrystals. Finally, this research work can potentially use in the application of catalysts, gas sensors, field emission devices, lithium-ion electrode materials, electrochemical cells and solar cells.

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