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Effect of CTAB on structural and optical properties of CuO nanoparticles prepared by coprecipitation route

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Abstract. CuO (Copper Oxide) nanoparticles were synthesized by a simple coprecipitation route by using copper acetate, sodium hydroxide as precursors and cetyltrimethyl ammonium bromide (CTAB) as surfactant. For the purpose of the study, the surfactant-CTAB treated and non-treated samples were synthesized separately. Both the synthesized samples were studied to understand their structural and optical properties. The formation of CuO and its crystallinity was confirmed by XRD. Further, the optical studies showed a defined blue shift in CTAB treated sample which is clear evidence that the particles undergo confinement when they are nano-regime.

1. Introduction

Researchers have focused on the synthesize of CuO nanoparticles due to its possible applications such as gas sensors, solar cells, storage devices and electrochemical cells [1–3]. CuO, which belongs to the family of transitional metal oxide has the ability to adopt multiple oxidation states and its great natural abundance and nontoxic nature makes it feasible to synthesize. CuO nanoparticles have different properties according to their shape and size and they are synthesized by various methods such as thermal oxidation, electrical position, hydrothermal treatment, precipitation method and gas phase oxidation [4–7].

Z-S Hong et al. synthesized CuO nanoparticles using copper acetate as the starting material through alcohothermalroute and was carried at 110°C and formed nanoparticles ranging from ~3 and 9 nm [8]. Further El-Trass et al. synthesized CuO nanoparticles using the same process and explained a well-defined emission under UV excitation and showed that CuO nanoparticles have narrow size distribution and high dispersion [9]. In addition to that a sharp emission at 365nm and a less intense emission at 470 nm were reported from PL emission spectra. Recently, Sahooli et al. reported the synthesis of mono sized CuO nanoparticles using different solvents by a low cost sol-gel route [10].

In the present study, CuO nanoparticles are synthesized by simple coprecipitation route by using copper acetate as the starting material and sodium hydroxide as precursor and CTAB as surfactant. As per the literature survey, the cationic surfactant CTAB has a long chain structure compared to any other surfactants which is composed of 16-carbon as a long tail and is attached with three methyl groups in an ammonium head group. The electrostatic interaction between the head group of CTAB with the primary CuO will help to confine the particles to be in nano regime.

The present investigation describes the effect of CTAB on altering the properties changes on surfactant treated and non-treated CuO samples prepared by wet-chemical synthesis. The formation mechanism of prepared CuO nanoparticles was also discussed in detail.

2. Methodology
2.1. *Material synthesis*
Analytical grade of copper acetate monohydrate (0.0375 M) and CTAB were added in 50ml of Millipore water. Sodium hydroxide solution (0.001 M) was gradually added to the solution with vigorous stirring till the pH of ~9 achieved. When the resultant solution was stirred for 90 min, the dark greenish powders were precipitated. The product was subjected to ethanol followed by water to remove water soluble impurities. The purified particles were dried for 5 h at 100°C, which gave rise to the formation of CuO nanoparticles.

3. Results and Discussion
3.1. Structural analysis
The XRD patterns of samples with and without CTAB were shown in Figure 1. Both the XRD patterns are identical to the single-phase CuO with a monoclinic structure. The reflections of both the patterns are in good agreement with standard data for CuO (JCPDS 34-0394) and also consistent with earlier reports [11,12]. The broadening of XRD peaks is the clear evidence that the products are nanocrystalline in nature. Comparing both the patterns of with and without CTAB samples (Figure 2), a slight peak shift is observed towards lower 2θ angles.
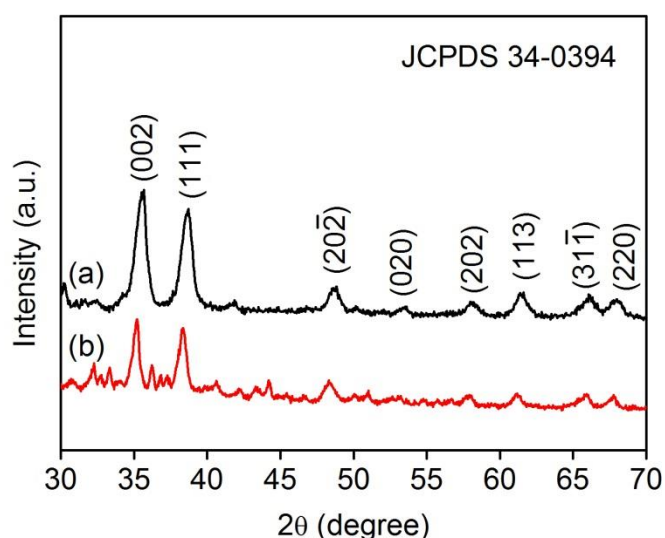

Figure 1.XRD patterns of CuO nanoparticles (a) with and (b) without CTAB

The XRD peak broadening can be caused due to two factors, lattice strain and small crystallite size. These two effects can be distinguished by plotting $\beta \cos\theta$ versus $4 \sin\theta$. Figure 3 shows the Williamson-Hall plot of CuO nanoparticles of with and without CTAB. As the spots of sample with CTAB are more scattered than without CTAB which is the clear evident that the former are more amorphous than latter. From the intercept of both the liner fits, it is determined that the crystallite sizes are 11and 22 nm respectively.
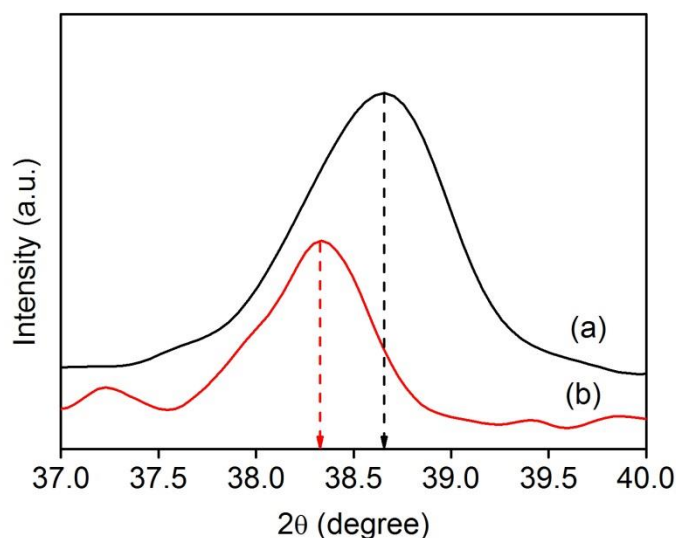
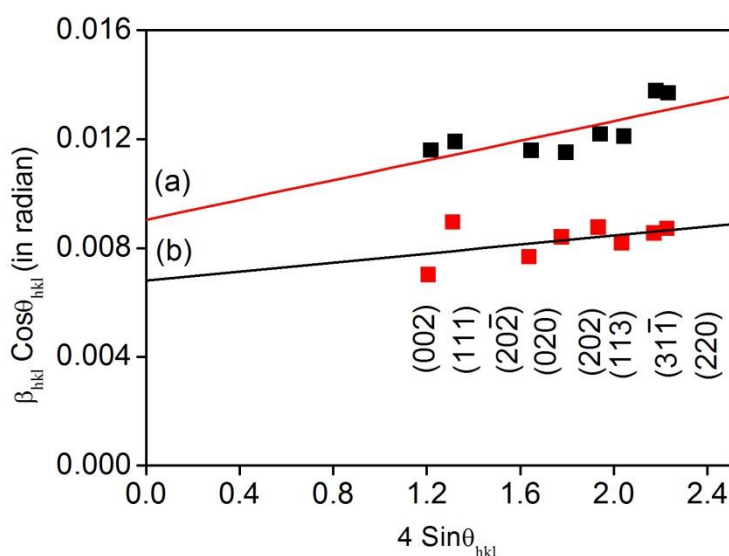**Figure 2.**The peak shift on the diffraction peak (1 1 1) of CuO nanoparticles (a) without and (b) with CTAB


Figure 3. The Williamson-Hall plot of CuO nanoparticles (a) with and (b) without CTAB

3.2. *Formation mechanism*

A potential reaction mechanism is proposed on analyzing the above results. When the copper acetate monohydrate is dissolved in the solvent, it is readily decomposed in to Cu^{2+} and $[(CH_3COO)_2]^-$. In the same way, NaOH decomposes in to Na^+ and OH^- where the excess OH^- ion increases the basic condition of the solvent.

$$Cu(CH_3COO)_2.H_2O \rightarrow Cu^{2+} + (CH_3COO)_2^- + H_2O \qquad (1)$$

$$NaOH \rightarrow Na^+ + OH^- \qquad (2)$$
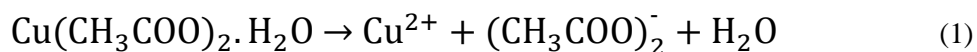
Under the basic conditions, Cu^{2+} reacts with OH^- resulted in $Cu(OH)_2$ which is further transformed to CuO after calcination.

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \qquad (3)$$

$$Cu(OH)_2 \rightarrow CuO + 2H_2O \qquad (4)$$
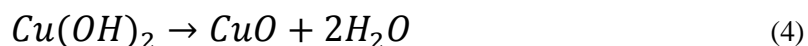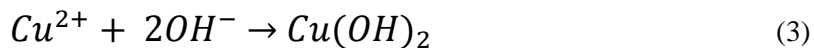
The CTAB won't participate in the reaction but acts as a surfactant in the wet chemical process.

3.3. *FTIR analysis*

From the FTIR spectra of with and without CTAB of CuO nanoparticles in Figure 4, there are some similarities in the bands which is corresponding to the formation of CuO. But the appearance of some bands in the sample with CTAB is the clear evidence that the surfactant made enough impact on the surface of CuO nanoparticles.
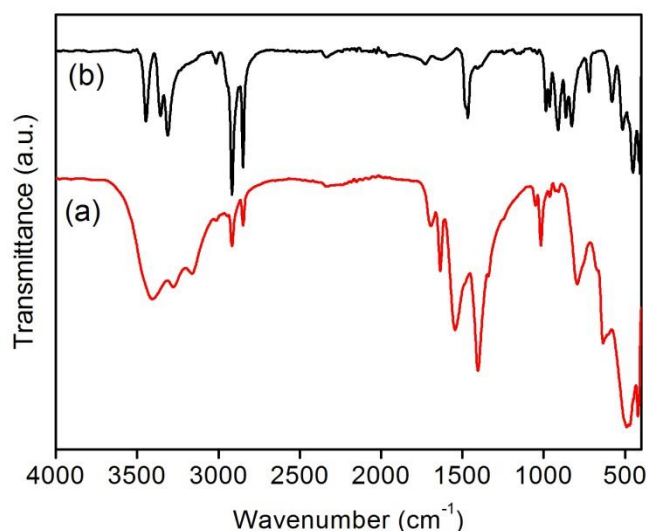

Figure 4. FTIR spectra of CuO nanoparticles (a) with and (b) without CTAB

On comparing both the spectra, the intense band around 3444 cm^{-1} corresponds to the O–H mode of (H–bonded) water molecules. There are peaks at 2916 and 2835 cm^{-1}, are mainly due to the physio-absorbed water molecules present in the solvent. The sharp peaks at 1641 and 1460 cm^{-1} in the sample with CTAB are mainly due to the traces of –CH_2 and –CH_3 symmetric stretching vibrations of the surfactant. The bands observed at 1018, 791 and 630 cm^{-1} are assigned to CO_3^{2-} vibrations where those methylene chains in the CTAB had made intense passivation on the surface of nanoparticles. The spectrum exhibits a broad band at 584 cm^{-1} which is due to the Cu–O mode.

3.4. *UV-vis absorption spectra*

Figure 5 shows the UV–Vis absorption spectra of CuO nanoparticles with and without CTAB. Both the spectra show an intense absorption around 360 nm which is attributed to the recombination of electrons in the conduction band to the holes in the valence band.
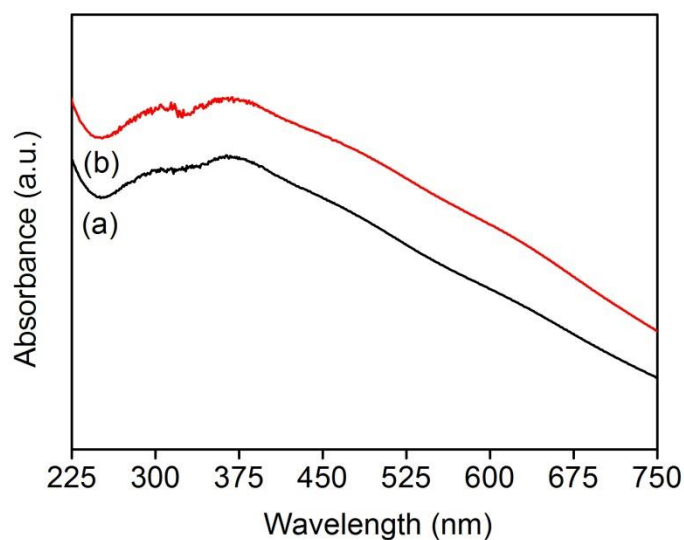
Figure 5. UV–vis absorption spectra of CuO nanoparticles (a) with and (b) without CTAB

The optical bandgap could be calculated by plotting $(\alpha h v)^2$ against energy gap which is shown in Figure 6. It shows that the band gaps of CuO nanoparticles with and without CTAB are 2.14 and 2.01 eV respectively, which is largerthan the value for the bulk CuO (1.85 eV) [12]. The blue-shift observed towards lower wavelength is mainly due to the quantum size effect on the smaller size of CuO nanoparticles.

As the particles size reduces from bulk to nano, there may be significant deviation on the properties of nanocrystalline materials observed compared to bulk properties. Hence the blue-shift of absorption spectra towards shorter wavelength is the evident for the size of CuO particles could be comparable to the Bohr excitonic radius.
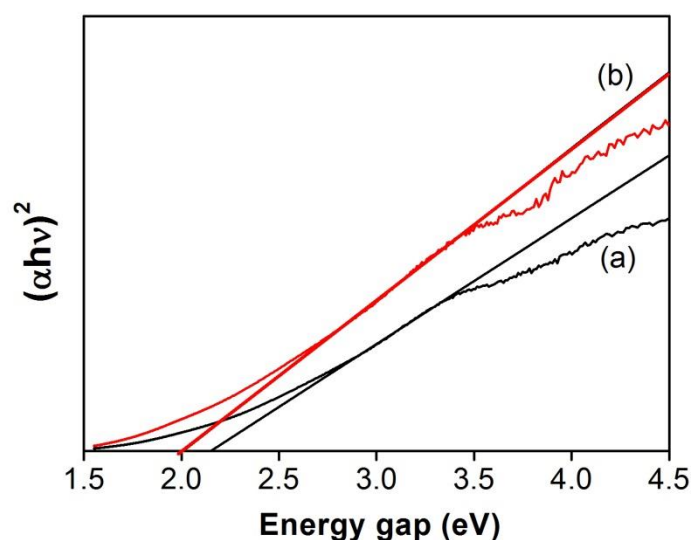

Figure 6. The plot of $(\alpha h v)^2$ as a function of photon energy for the CuO nanoparticles (a) with and (b) without CTAB

4. Conclusions

CuO nanoparticles were synthesized with and without CTAB surfactant by using coprecipitation route at room temperature. The XRD results showed the formation of monoclinic phase of CuO nanoparticles. From the WH plot, the particle size was estimated as 11 and 22 nm respectively for CuO nanoparticles with and without CTAB. It was determined that the CTAB treated sample showed lesser particle size than without CTAB treated sample. The methyl groups available in CTAB made strong adsorption on CuO nanoparticles which was confirmed using FTIR results. Such electrostatic passivation on nanoparticles cannot be expected on any other anionic or neutral surfactants. UV-vis spectra of both the sample showed defined absorption peak around 360 nm. The blue shifted optical bandgap in CTAB treated sample is the clear evidence that the particles undergo confinement when they are nano-regime.

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