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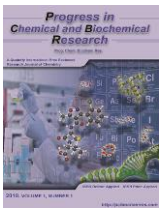

# Facile sonochemical assisted synthesis of $Cu_2O$ and CuO nanoparticles

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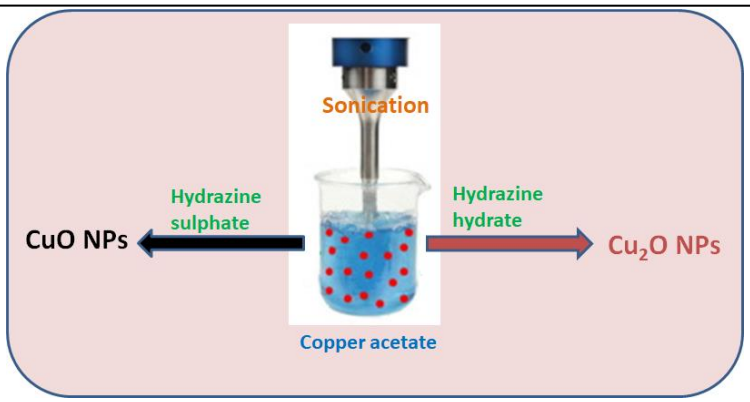
ARTICLE INFO

**Article history:**
Received: 06 January 2019
Accepted: 28 June 2019
Available online: 31 July 2019
Manuscript ID: PCBR-1901-1013

GRAPHICAL ABSTRACT




KEYWORDS

CuO NP
$Cu_2O$ NP
Hydrazine hydrate/sulphate
Sonochemical
DRS

ABSTRACT

This work reports on cupric oxide (CuO) nanoparticles (NPs) and cuprous oxide ($Cu_2O$) NPs synthesized using facile green sonochemical method. Phase analysis, morphology, and crystallinity of the prepared NPs were investigated using X-ray diffraction (XRD), Fourier transform infrared (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDS), and UV-visible diffuse reflectance spectroscopy(DRS). The phase of NPs was tuned as a function of reducing agents. XRD patterns confirmed the presence of pure CuO NPs and $Cu_2O$ NPs. FTIR peak at 621 $cm^{-1}$ confirmed Cu(I)-O vibrations, while CuO vibrations confirmed by the presence of two peaks at 536 and 586 $cm^{-1}$. The FE-SEM results showed that the morphology of the CuO NPs and $Cu_2O$ NPs was highly uniform. EDS confirmed the elemental composition of Cu and O in both CuO NPs and $Cu_2O$ NPs.

## 1. Introduction

Over the last two decades, functional nanomaterials have received great attention for many technological applications including, catalysis, energy, environment, medical, and sensor due to their unique properties at nanoscale [1-5]. Especially, transitional metal/metal oxides nanoparticles (NPs) based materials have attracted much attention due to their unique optical, magnetic, electronic, and catalytic properties [6, 7]. Among these, copper oxides NPs such as CuO NPs and CuO NPs have most widely investigated for many potential applications such as ultraviolet and/or visible light-driven photocatalysis, anti-oxidant, anti-fungal, smart windows, IR detector, gas sensors, batteries, high temperature superconductors and optical limiters [8-11] due to their wide bandgap, high TC, high optical absorption and non-toxic in nature. The physical and chemical properties of

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CuO NPs and $Cu_2O$ NPs are depend on their size, morphology, and phase purity. Therefore lots of efforts have been taken to prepare pure CuO NPs and $Cu_2O$ NPs with different morphology and size. So far, numerous methods are sonochemical preparation, alkoxide-based preparation, microwave irradiation, precipitation pyrolysis and thermal decomposition [12, 13].

In the present work, we report the synthesis of the pure CuO NPs and $Cu_2O$ NPs using copper acetate as a precursor by varying the reducing agents hydrazine sulphate and hydrazine hydrate via sonochemical method.

## 2. Materials and Methods

Copper acetate [$Cu(CH_3COO)_2\ H_2O$], sodium hydroxide (NaOH), hydrazine sulphate ($N_2H_4\ H_2SO_4$) and hydrazine hydrate ($N_2H_4\ H_2O$)were used as received from Merck chemicals, India. Milli Q water was used throughout all synthesis process. All the chemicals were of Analytical grade and used without further purification.

### *2.1 Synthesis of CuO NPs and $Cu_2O$ NPs*

In order to synthesis $Cu_2O$ NPs, 100 mL of 0.25 M [$Cu(CH_3COO)_2\ H_2O$] was ultrasonicated for 10 min, then 100 mL of 0.1 M NaOH was added to the above solution. The reaction mixture was ultrasonicated further for 20 min, then 1M hydrazine hydrate was added drop wise. Afterwards, the reaction system was exposed to high-intensity ultrasonic irradiation powers under ambient air for 30 min. The reddish precipitate was formed and centrifuged, washed periodically with distilled water and absolute ethanol, then dried under vacuum at 60 °C. The same procedure has been adopted to preparation of CuO NPs using hydrazine sulphate as reducing agent. The black colour precipitate was dried under vacuum at 60 °C.

### 2.2 Instrumentation

X-Ray diffraction (XRD) with Cu Kα radiation at 30.0 kV and 30.0 mA over the scan range 2θ, 10-800 at the scan rate of 20 $min^{-1}$ for the diffraction peaks were recorded. FTIR (IR Prestige 21, Shimadzu, Pvt Ltd, Japan) spectra of the samples in KBr pellets were obtained on a Shimadzu spectrometer in the range of 500-3600 $cm^{-1}$. Morphology of the as-prepared NPs was investigated field emission scanning electron microscopy (FE-SEM, model JSM-6610LV, Jeol Asia PTE Ltd, Japan.) equipped with the energy dispersive X-ray spectroscopy (EDS) analysis. UV-Visible diffuse reflectance spectra were recorded by UV-Visible diffuse reflectance spectrometer (Shimadzu, model 2600R).

## 3. Results and Discussion

Pure CuO NPs and $Cu_2O$ NPs phase were prepared by sonochemical assisted method using copper acetate as precursor by varying the reducing agent with high intensity ultrasonics (vibracell, 20 kHz, 50 % amplitude and 100 $W/cm^2$) for 1 h. The reducing agent has played very crucial role in the formation of phase purity of CuO NPs and $Cu_2O$ NPs. The CuO NPs were obtained through copper acetate reacts with hydrazine sulphate and sodium hydroxide undergoes sonication (Equation 1). Due to the abundance of $OH^-$ ions copper acetate was formed the resulting product is black, confirmed the formation of CuO NPs [14].

$$[Cu(CH_3COO)_2]H_2O + N_2H_4\,H_2SO_4 \xrightarrow[\text{Ultrasonics}]{\text{NaOH}} \text{CuO NPs} \quad (1)$$

Similarly, the $Cu_2O$ NPs were obtained through copper acetate reacts with hydrazine hydrate and sodium hydroxide undergoes sonication (Equation 2). These $Cu_2O$ NPs were formed through the $Cu^{2+}$ ions are reduced to Cu+ by hydrazine hydrate as reducing agent in the presence of sodium hydroxide [15].

$$[Cu(CH_3COO)_2]H_2O + N_2H_4\,H_2O \xrightarrow[\text{Ultrasonics}]{\text{NaOH}} Cu_2O\ \text{NPs} \quad (2)$$

The overall chemical reaction occurring in sonochemical synthesis of $Cu_2O$ can be written as given in equations (3-9) [16].

$$[Cu(CH_3COO)_2]H_2O + H_2O \longrightarrow CH_3COO^- + Cu^{2+} \quad (3)$$

$$Cu^{2+} + NaOH \xrightarrow{\text{Ultrasonics}} Cu(OH)_2 \quad (4)$$

$$H_2O \xrightarrow{\text{Ultrasonics}} OH^{\cdot} + H^{\cdot} \quad (5)$$

$$2OH^{\cdot} \xrightarrow{\text{Ultrasonics}} H_2O + O^{\cdot} \quad (6)$$

$$Cu(OH)_2 \xrightarrow{\text{Ultrasonics}} Cu^{2+} \quad (7)$$

$$2Cu^{+} \xrightarrow[N_2H_4\,H_2SO_4]{\text{Ultrasonics}} \text{CuO (Black precipitate)} \quad (8)$$

$$2Cu^{+} + 2OH^{-} \longrightarrow 2CuOH \xrightarrow[N_2H_4\,H_2O]{\text{Ultrasonics}} Cu_2O\ \text{(Reddish precipitate)} \quad (9)$$

Figure 1 displays the XRD patterns of the CuO NPs and $Cu_2O$ NPs. Figure 1a shows the XRD patterns for the precursor (copper acetate) sonicated in presence of reducing agent, hydrazine sulphate. The strong diffraction patterns at 2θ=35.60 and 38.80 were indexed as [002] and [111] planes of monoclinic CuO NPs (JCPDS File No: 45-0937). Figure 1b shows the diffraction peaks centered at 2θ = 36.680, 42.60, 61.760, 73.980 and 77.80 were attributed to (111), (200), (220), (311), and (222) orientation plane of $Cu_2O$ with a cubic phase (JCPDS File No: 5-669). There were no impurity peaks were observed

for CuO NPs and $Cu_2O$ NPs. The average crystallite size of both CuO NPs and $Cu_2O$ NPs were calculated by Debye-Scherrer equation (10) and found to be 27.62 and 24.38 nm respectively.

$$D = 0.9\lambda / (\beta\cos\theta) \quad (10)$$

Where $\lambda$ is the wavelength of X-ray radiation and $\beta$ is the full width at half maximum of the peaks at the diffracting angle $\theta$.

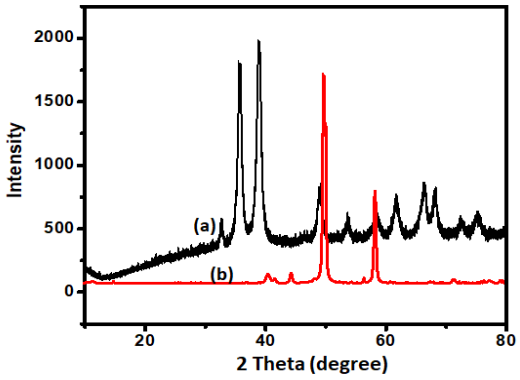


**Fig. 1.** XRD patterns of prepared CuO NPs (a), and $Cu_2O$ NPs (b)

FTIR spectra of CuO NPs and $Cu_2O$ NPs were presented in Figure 2. The two characteristic peaks (Figure 2a) at 586 $cm^{-1}$ and 536 $cm^{-1}$ were due to the Cu(II)-O stretching vibrations confirms the formation of CuO NPs [17, 18]. The characteristic peak at around 621 $cm^{-1}$ is attributed to the Cu(I)-O stretching vibrations in $Cu_2O$ NPs [Figure 2b].

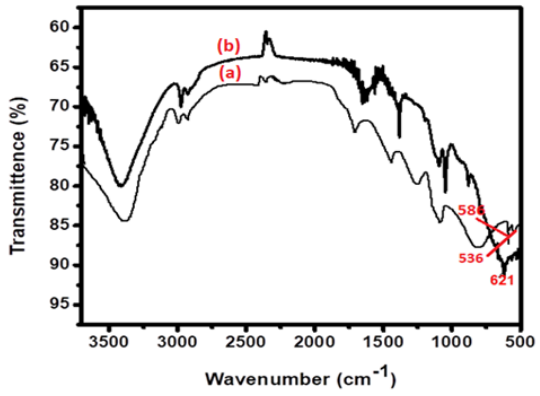


**Fig. 2**. FTIR spectra of a) CuO NPs and b) $Cu_2O$ NPs

The bandgap of as-prepared CuO NPs and $Cu_2O$ NPs were estimated by UV-Visible DRS (Figure 3) and bandgap was calculated using Equation 11.

$$E_g = h\upsilon = hc/\lambda = 1240/\lambda \quad (11)$$

where $E_g$ is bandgap energy, h is planks constant, $\upsilon$ is wave frequency, c is the speed of light and $\lambda$ is the wavelength. It can be seen that the $Cu_2O$ has an absorption edge around 681 nm corresponding to the bandgap of 1.82 eV [19]. However, the CuO indicated optical absorption for a wide range of wavelength at 521 nm. It is known that CuO has a wide range of band gaps in 2.38eV [20].

The representative FESEM images of CuO NPs and $Cu_2O$ NPs were presented in Figure 4. The morphology of CuO NPs rod like structure (Figure 4 (a,b)) while the morphology of $Cu_2O$ NPs was found to be octahedral like structure (Figure 4 (c,d)).

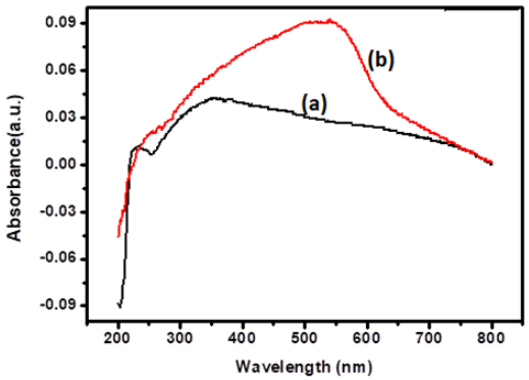


**Fig. 3.** UV-Vis DRS spectra of prepared nanoparticles

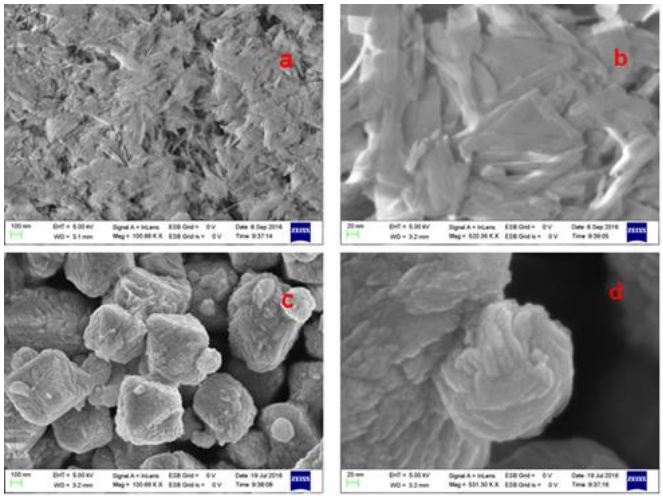


**Fig. 4.** FESEM images of (a,b) CuO NPs and (c,d) $Cu_2O$ NPs

EDS spectra of the CuO NPs and $Cu_2O$ NPs are presented in Figure 5. The presence of copper (Cu) and oxygen (O) in CuO NPs and $Cu_2O$ NPs confirms the formation of CuO NPs and $Cu_2O$ NPs.

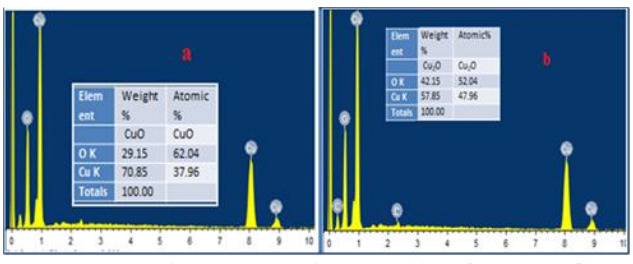


**Fig. 5.** EDS spectra of CuO NPs (a), and $Cu_2O$ NPs (b)

## 4. Conclusion

In this research study, CuO NPs and $Cu_2O$ NPs were successfully synthesized by sonochemical method using copper acetate as precursor at different reducing agents. The XRD and FTIR results confirmed formation of the CuO NPs and $Cu_2O$ NPs. Bandgap of the CuO NPs and $Cu_2O$ NPs were 2.38 and 1.82, respectively. In addition, it was found that the phase purity was critically depend on the reducing agents.

## Conflict of interest

The authors clearly declared that they have no any conflict of interest.

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