Structural and Morphological properties of Lithium Doped Copper Oxide Nanoparticles

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Abstract — The developments of nano size metal oxide particles are concerted because of their notable advancements and its idiosyncratic nature. Metal oxide nanoparticles have proven heed due to their unique physical and chemical properties differing from bulk. Among all the metal oxides, copper oxide nanomaterials have attracted more attention due to its distinctive properties in the field of catalysis, optoelectronics, sensing and solar cells. Monoclinic copper oxide nanoparticles have enthralled due to its wide range of applications in multifarious fields. Pure copper oxide and lithium doped copper oxide nanoparticles were synthesized using energy efficient and rapid solution combustion technique were glycine is employed as a fuel. Samples are characterized by X-ray diffraction (XRD) and FTIR. The surface morphology of these nanoparticles was carried out using high resolution scanning electron microscopy (HR-SEM). Nanoparticles have many active sites as compared to the bulk, because of its large surface to volume ratio. The advantages of producing nanoparticles by this method are swift, versatile and cost effective.

Keywords—copper oxide; solution combustion synthesis; optoelectronic devices.

INTRODUCTION

The exotic properties of nanoscale metal oxide particles have encouraged wide ranging research activity on their heterogeneous application [1]. In the field of green chemistry, nano metal oxide catalyzed reactions has avowed as captivating and environmentally enticing methods of organic synthesis. Among the known varieties of metal oxides, copper oxide nanoparticles (NPs) possess remarkable physiochemical properties such as small particle size, large surface area, significant reactive morphology and surface active sites. CuO nanoparticles are of great interest due to its potential applications in a wide variety of areas including electronic and optoelectronic devices, such as photo conducting and photo thermal [2], electrochemical cells [3], gas sensors [4], and solar cells [5]. The monoclinic copper
oxide is known for its size-dependent chemical properties and due to their interactive properties like their large surface to volume ratio. In the present study lithium has been incorporated with CuO and its effect on structural and morphological features have been studied.

EXPERIMENTAL PROCEDURE

Pure CuO nanoparticles were synthesized by solution combustion method [6] with analytical grade chemicals, copper nitrate Cu(NO$_3$)$_2$.3H$_2$O was used as an oxidizer and glycine as a fuel and their required amounts were dissolved in double distilled water. The Lithium dopant was added in 1% in nitrate form with the solution. Stoichiometric composition of the redox mixture was calculated based on the principles of propellant chemistry, keeping the O/F ratio to unity. Aqueous solution is prepared in flat bottom flask and stirred constantly for 45 minutes. The mixture was then kept on the mantle to evaporate excess water and to auto-ignite with the rapid evolution of large volume of gases to produce fine powder. As-prepared powder was heat treated at 400°C for 2 h to remove the nitrate impurity. Finally, the precursors were annealed at 800°C for 1 h. After this duration, the annealing was put off and cooled to room temperature. Hence pure and well crystalline powder was obtained. The obtained material was grounded and was characterized for the structural and morphological properties.

Structural studies of these samples were carried out by XRD powder X-ray diffractometer in the 2θ range using Cu K$_\alpha_1$ radiation (1.54056Å). The XRD patterns were compared with standard ICDD files of CuO (89-5895) The Morphology of the powder was studied using scanning electron microscopy (SEM). FTIR absorption behavior of the synthesized samples was obtained using Perkin-Elmer Spectrum FTIR spectrometer with scanning range 4000–400 cm$^{-1}$.

RESULTS AND DISCUSSIONS

Structural analysis: X-Ray diffraction

The distinctive XRD pattern of the pure CuO and 1% Lithium doped CuO nano particles annealed at 800°C is shown in fig.1a,b. The peak positions of the sample exhibited the monoclinic structure of CuO which was confirmed from the ICDD card No (89-5895). Further, no other impurity peaks was observed in the XRD pattern.
The crystalline size was calculated using the Scherrer formula [7],

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of X-ray radiation, \( \beta \) is the full width at half maximum (FWHM) of the peaks at the diffracting angle \( \theta \). Crystallite size is calculated for pure copper oxide and reported as 32 nm. Simultaneously, the peaks become narrower as the dopant is introduced resulting in the increase of crystallite size. The variation of crystallite size and lattice parameters with Lithium dopant of 1% concentration was calculated and the results are presented in Table 1.

**Table 1. Estimated lattice parameters and crystallite size**

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CuO</td>
<td>4.461</td>
<td>3.125</td>
<td>5.058</td>
<td>32</td>
</tr>
<tr>
<td>CuO + 1% Li</td>
<td>4.788</td>
<td>3.434</td>
<td>5.106</td>
<td>40</td>
</tr>
</tbody>
</table>
Morphological study: FESEM

Fig. 2 (a) Pure CuO, (b) Li doped CuO annealed at 800°C

Fig.2 (a) (b) shows the SEM micrograph of CuO nanoparticles annealed at 800°C and shows SEM micrograph of 1% Li doped CuO nanoparticles annealed at 800°C. Crystallite size increases with the Lithium dopant concentration. Average particle sizes obtained from SEM images were found to be 30-40 nm. The SEM image of pure CuO reveals that the powder agglomerated with polycrystalline particles. The pores and voids were caused due to the amount of gases that escaped during combustion reaction. The process of agglomeration takes place because of an increase in the rate of nucleation of the particles at higher temperatures. When the pure CuO is doped with 1% of lithium and annealed at 800°C, the surface area of the grain increases slightly and contributes multi facets.

FTIR Analysis:

Fig. 3. FTIR spectra of (a) Pure CuO (b) Li doped CuO
The FTIR spectra of pure and alkali metal doped CuO nanocrystallites recorded at room temperature in the range 400-4500 cm\(^{-1}\). Fig.3 shows an obvious transmittance band around 580 cm\(^{-1}\) and 535 cm\(^{-1}\) which were assigned to vibration of Cu(II)-O bands. The broad absorption band at 1712 cm\(^{-1}\) is due to the vibration mode of absorbed water molecules. The shift in transmittance band from 580 to 572 cm\(^{-1}\) and 535 to 521 cm\(^{-1}\) indicates that there is a complexation of CuO and lithium.

CONCLUSION

A simple and swift combustion synthesis method to prepare high-quality lithium doped copper oxide nanoparticles are adopted, in which an aqueous solution of the metal nitrates and glycine is heated to the point of auto ignition. The resultant ash was found to consist of finely divided particles of Lithium doped copper oxide depending on the fuel/oxidant ratio in the precursor. This mixture is readily converted to the desired phase by annealing at 800\(^\circ\)C. XRD patterns showed that the synthesized structures have good crystallinity with monoclinic crystal structure. Using of glycine as fuel in preparation of copper oxide with lithium as dopant affects the structural and morphological properties of these materials. The crystallite size varies in the range of 32–40 nm. FTIR spectra also validate the purity of CuO nanoparticles. SEM analysis shows that the morphology and specific surface area of the samples are influenced by the calcinations temperature and the dopant concentration.

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REFERENCES