



Template Free Synthesis of Copper Oxide Nanoparticles Prepared *via* Precipitation Process

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The present work describes the template free formation of copper oxide nanoparticles *via* chemical solution route with the use of precursor copper acetate hydrate and sodium hydroxide. The XRD reveals that the prepared material is having well crystalline character whereas the morphology of the prepared nanoparticles (size about 30-40 nm) was investigated *via* SEM and it denotes that the observation from XRD is clearly consistent, which have spherical in shape. The TEM was further utilized to confirm the particle shape and size of the grown material, which is in full consistent and exhibit in range 30-40 nm. The FTIR spectroscopy reveal the compositional functional behavior of prepared nanomaterials. Including these analyses, the mass loss with respect to temperature of the grown materials was also observed with TGA. On the basis of microscopic and chemical analysis, we have also proposed the growth mechanism of prepared CuO nanocrystals.

Keywords: XRD, SEM, TEM, Growth mechanism.

INTRODUCTION

Controlled shape and size of nanostructures have great impact and received attention to the scientific community, due to their unique physico-chemical properties such as large surface area; enhance catalytic, optical, electrical, physical, magnetic and biocompatible properties [1-5]. These assets makes prominent material and leads various applications for instance photocatalysis [6], solar cells [7], sensing [8] hydrogen evolution [9], *etc.* Including these applications, nanostructures have various other biological applications such as it can be utilized to control bacterial population, cancer cell inhibition and tissue engineering [3] *etc.* Among various metal oxides, nanostructures of copper oxide, which present in cuprous (Cu₂O) and cupric oxide (CuO) form. The cuprous (band gap about 2 eV) and cupric oxide (band gap of about 1.2-1.5 eV) are a p-type semiconductor with type of II-VI. For the preparation of cupric oxide or copper oxide (CuO) nanostructures, various methods have been such as thermal evaporation [10], chemical vapour desposition [11], plasma enhance chemical vapour deposition [12], surface mechanical attrition treatment [10], metal organic chemical vapour deposition [13], hydrothermal [14], sol-gel [15], spray pyrolysis [16], solution combustion method [17] *etc.* have been utilized to grow the

nanostructures of CuO. The above applied method needs sophisticated instruments with extensive care and difficult to produce inexpensive nanostructures at industrial scale [18]. The chemical solution or precipitation reaction process can solve this problem and produce various types of nanostructures at very inexpensive cost as compared to other thermal or high temperature methods. It can give better crystal quality nanostructures at very low growth temperatures for the bulk production of nanostructures. Towards this direction several reports have been published to grow nanostructures with using various chemicals for the formation of nanoparticles. Deka *et al.* [19] showed the utilization of NaBH₄ for the formation of Cu nanoparticles *via* hydrothermal process at 120 °C for 6 h. Abdulkin *et al.* [20] used variety of capping and reductants materials such as poly(methyl methacrylate) (PMMA), poly(1-vinylpyrrolidin-2-one) (PVP), poly(4-vinyl-pyridine) (PVPy) for the formation of copper and zinc based nanoparticles, NaH₂PO₂, N₂H₄ or NaBH₄. The ethylene diamine tetraacetic acid (EDTA) was used as a capping agent for the formation of copper oxide nanoparticles [21]. The hydrocolloids gum karaya was used a biotemplate material for fabrication of CuO nanoparticles [22]. In another work, reports the use of hydrazine, allylamine (AAm) and polyallylamine (PAAm) chemicals as stabilizing agents for the synthesis of CuO nanoparticles [23].

The present work report the formation of copper oxide nanoparticles without using any template or additives with precursor copper acetate hydrate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$ and alkali sodium hydroxide *via* simple precipitation solution process at a very low refluxing temperature (about 90°C) in 2 h. The general structural evaluation was investigated with scanning electron microscopy and transmission electron microscopy, whereas the crystalline property of the material was examined with X-ray diffraction pattern. Thermal stability of the prepared nanomaterial was observed *via* thermogravimetric analysis. Based on the observations, the chemical reaction and growth mechanism was also proposed.

EXPERIMENTAL

Fabrication or synthesis of template free copper oxide nanoparticles (CuO-NPs): The formation of copper oxide nanoparticles was accomplished with the use of precursor copper acetate hydrate and sodium hydroxide purchased from Aldrich chemical corporation Co. and used without further purification. In an experiment: 15 mM copper acetate hydrate (0.30 g) and 0.2 M NaOH (0.2 g) were mixed in 100 mL of double deionized distilled water under constant stirring, blue colored solution was appeared in a beaker. To this transparent blue colored solution, sodium hydroxide was added as drop by drop and shaken each time for complete mixing. After the complete addition, pH of solution was checked *via* pH meter (cole parmer, U.S.A). Due to increase basicity of the solution, pH was reached upto 12.67. After the complete mixing, the solution was transferred in a two necked refluxing pot and refluxed at 90°C for 2h. As the solution temperature rises, the blue colored solution changes to dark brown colored solution. After refluxing, the precipitate of the salt solution was settled at the bottom of refluxing pot. The formed precipitate was washed several times with alcohol (methanol and ethanol) and acetone and dried at room temperature.

Characterizations of template free CuO-nanoparticles: XRD pattern was used to know the particle size, phase and crystalline property of the precipitated material in range of $35\text{--}65^\circ$ in CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$) with $6^\circ/\text{min}$ scanning speed with an accelerating voltage of 40 kV and current of 40 mA. The general morphology of the prepared nanoparticles was examined *via* SEM at room temperature. For SEM observation, the powder was uniformly sprayed on carbon tape and coated with thin conducting layer of platinum for 3 s. To confirm more clearly, further the powder was analyzed with TEM (JEOL JEM 2010 at 200 kV). Including these, the functional or compositional behavior of the prepared materials was investigated *via* FTIR analysis with using KBr pellets in the range of $4000\text{--}400 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

X-ray diffraction spectroscopy (XRD): The crystalline property of the grown material was analyzed with X-ray diffraction pattern at above parameters. The XRD pattern shows peaks, which are similar to single crystalline CuO without impurities and well matched with the standard JCPDS data card no. 05-661. The XRD spectrum shows no peaks other than CuO, which further confirm that the grown CuO is pure and free from synthetic chemical impurities (Fig. 1) [3].

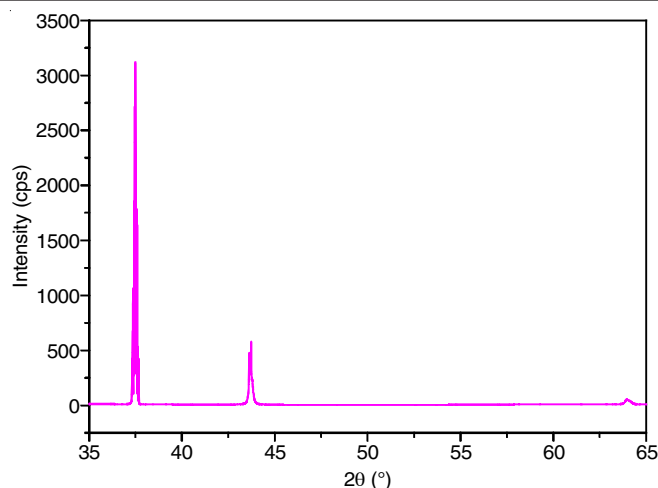


Fig. 1. X-ray diffraction pattern of CuO-NPs prepared in 2 h

Scanning electron microscopy (SEM): To know the general morphology of the grown powder sample of CuO, SEM was utilized and results are displayed in Fig 2. As can be seen from the low-magnification image of Fig. 2(a-b) shows the as-synthesized powder products, having several aggregated molecules of nanostructures in scattered form. When the powder was checked at high magnification (Fig. 2c-d), it confirms that the prepared powder is in the range of nanoscale and possess in a very large quantity. The obtained powder are in a spherical shaped tiny nanoparticles, having around 30-40 nm in range. Some particles are in aggregated form with the accumulation and conjugation of several spheres and triangular shaped structures. From the images (Fig. 2c-d), the surface of obtained particles exhibit smooth, clean and jointed with each other and clearly consistent with the XRD analysis (Fig. 1).

Transmission electron microscopy (TEM): Further the morphological clarification was again analyzed *via* TEM at room temperature at above parameters. Fig. 3 shows the low TEM image of spherical shaped nanoparticles. From TEM image (Fig. 3), it is evident that the size of each nanoparticle diameter is in the range of 30-40 nm, spherical, smooth surface, which is clearly consisted with SEM images (Fig. 2c-d). The size, shapes and crystalline property of grown nanoparticles observed from TEM analysis (Fig. 3) are in consistent with the XRD (Fig. 1) pattern and SEM images observation (Fig. 2).

The FTIR spectrum (Fig. 4) shows the fingerprints of copperacetate hydrate and sodium hydroxide, used for the formation of CuO-nanoparticles. The broad peak between $3600\text{--}3200 \text{ cm}^{-1}$ corresponds to the adsorbed water molecule whereas the asymmetric striching of water molecules centered at 1635 cm^{-1} . A sharp peaks centered at 1562 and 1442 cm^{-1} are associated with C=O and C-O stretching from copper acetate [24,25]. A curved and flat peak around 541 cm^{-1} in FTIR spectrum represents the formation of CuO-nanoparticles. The obtained functional information from FTIR justifies that the nanostructures are having good chemical property and consistant with XRD pattern data.

Thermogravimetric analysis spectroscopy: Thermogravimetric analysis (TGA) is a technique used to measure the changes in sample weight with increasing temperature. The thermal decomposition of as synthesized nanostructures has been examined by thermogravimetric analysis, performed

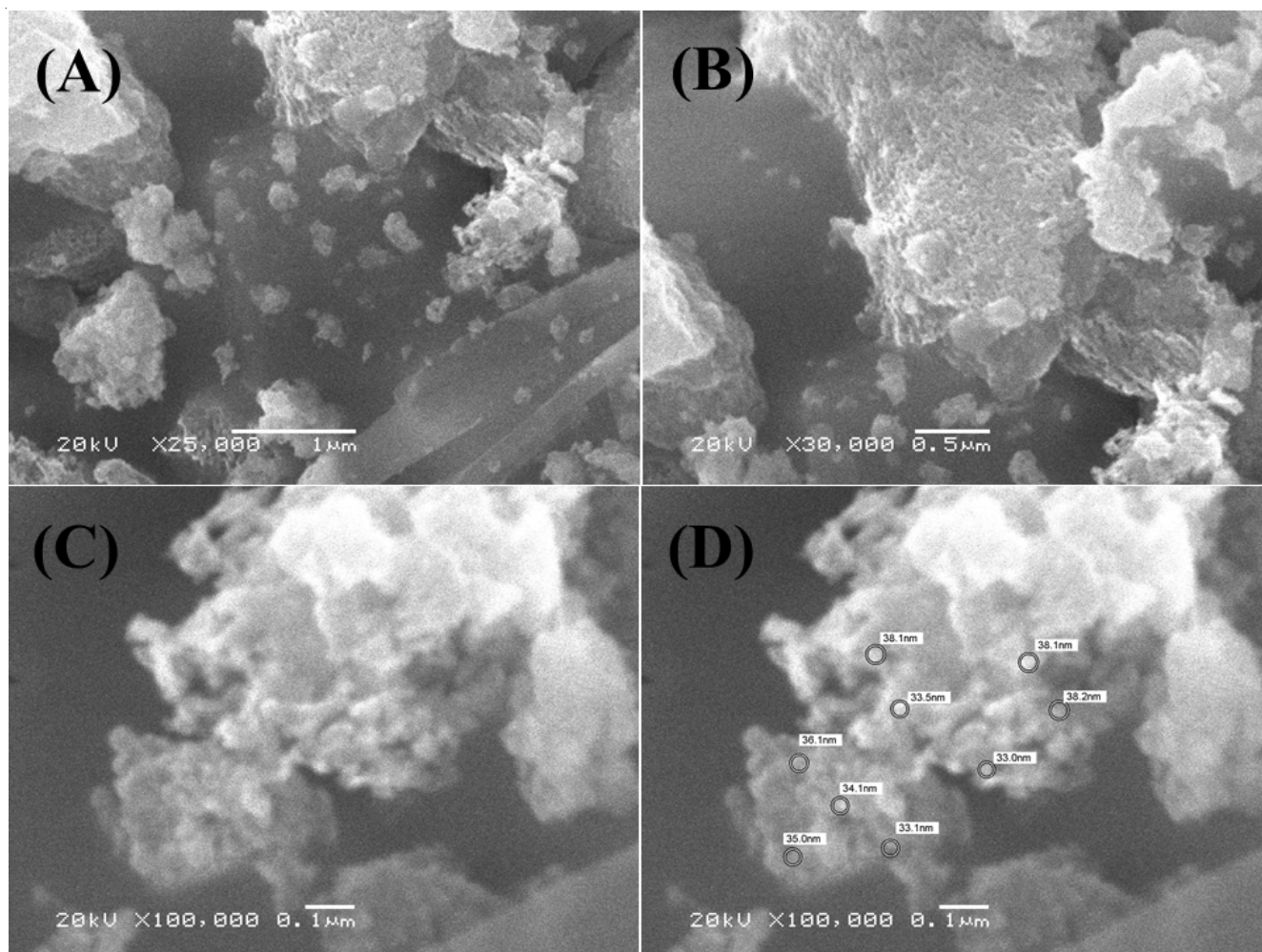


Fig. 2. SEM images of CuO-NPs: (a-b) show the low magnification, whereas (c-d) are high magnification images of prepared material

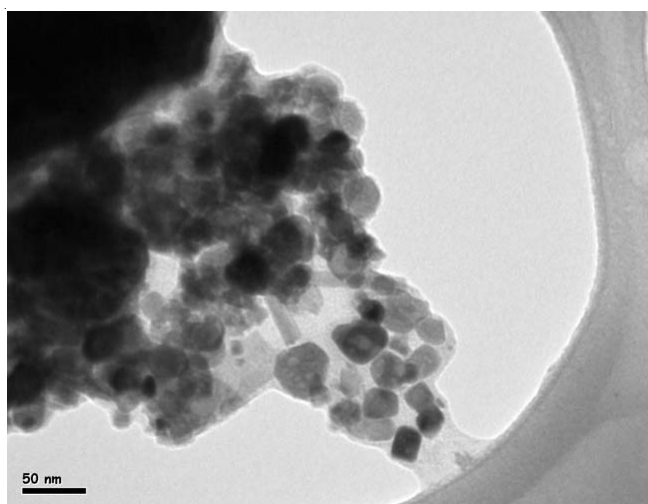


Fig. 3. TEM image of prepared CuO-nanoparticles

under nitrogen flow (100 mL/min), at a heating rate of 20 °C/min. Fig. 5 shows TGA curve of the grown samples of CuO-nanoparticles, which exhibits two step of weight loss between 105- 300 and 520-860 °C, respectively. The total weight loss of these processes determining from TGA curve is around 14 %. The first step starts at 105 °C and is completed at 300 °C with a weight loss of 8.60 %. The second and major one begins

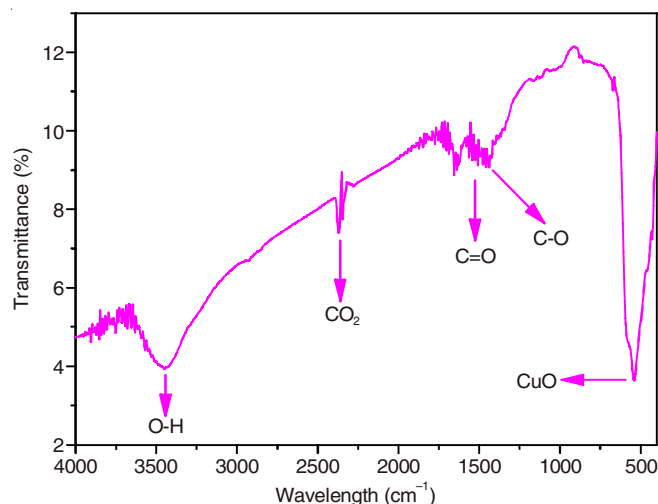


Fig. 4. FTIR spectra of CuO-nanoparticles

at 520 °C and is completed at 860 °C with 5 % mass. This justified that the grown nanostructures are stable at higher temperature.

Possible chemical formation mechanism of template free CuO-nanoparticles: On the basis of present study and used chemical for the synthesis of nanostructures and their materials characterization, we have anticipated a mechanism

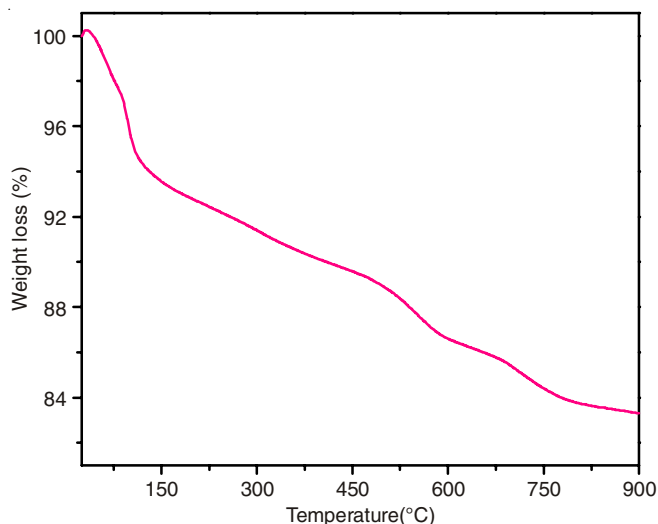
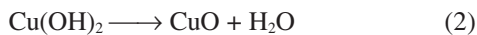
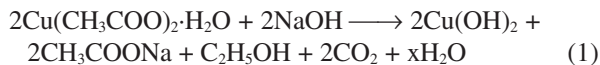


Fig. 5. Thermogravimetric analysis of the decomposition of prepared CuO-nanoparticles

of a chemical precipitation reaction to final formation of nanostructures. It's widely known that the chemical precipitation reaction is formed in liquid medium and can be extensively utilized for a large-scale production of fine oxide materials. When metal salts react with sodium hydroxide solution, forms precipitates in the solution. In the present study, we have mixed copper acetate hydrate and sodium hydroxide. The simple chemical reaction presents the reaction and their byproduct between copper acetate hydrate and sodium hydroxide was carried out.



In an aqueous solution after reaction with copper acetate hydrate and sodium hydroxide, $\text{Cu}(\text{OH})_2$ can be formed (eqn. 1). The copper hydroxide has property to dissolve in aqueous solution in to Cu^{2+} and OH^- ions. Due to continuous formation

of Cu^{2+} ions and OH^- ions form the precursor copper acetate; this finally leads to copper oxide CuO crystallite (eqn. 2). The alcohol and other impurities were removed *via* several times washing of prepared nanostructures. It is assumed that the initially formed $\text{Cu}(\text{OH})_2$ in the solution of copper acetate hydrate and sodium hydroxide nuclei gets aggregated (Fig. 6a-b) and after acquiring sufficient thermal energy from the refluxing pot, forms mixed phases such as small elongated, cubic and trigonal shaped active molecules of CuO . These initial or active CuO nuclei/nanoparticles (Fig. 6a-b) are expected to be the building blocks for the formation of spherical shaped CuO -nanoparticles. These active molecules are generally referred to as primary nuclei. Once these active molecules are formed (Fig. 6c), it grows based on surface energy considerations and rearrange themselves into a complete shaped CuO -nanoparticles (Fig. 6c). The phenomena why the elongated, trigonal and cubic shaped CuO -nanoparticles changes to the spherical shaped nanoparticles may be due to complete saturation of thermal refluxing, which needs further studies.

Conclusion

In summary, the synthesis of copper oxide nanoparticles were successfully done *via* simple precipitation reaction process at a very low refluxing temperature at 90°C in 2 h. The XRD pattern reveals that the prepared nanoparticles are in good crystalline character in nano range size. The morphology and size of the prepared nanoparticles was analyzed *via* SEM and TEM spectroscopy, which further confirms that the particles size of the powder are in the range of 30-40 nm range, smooth and spherical shape. The FTIR and TGA spectroscopy confirms the nanoparticles are having good chemical properties with high thermal stabilities.

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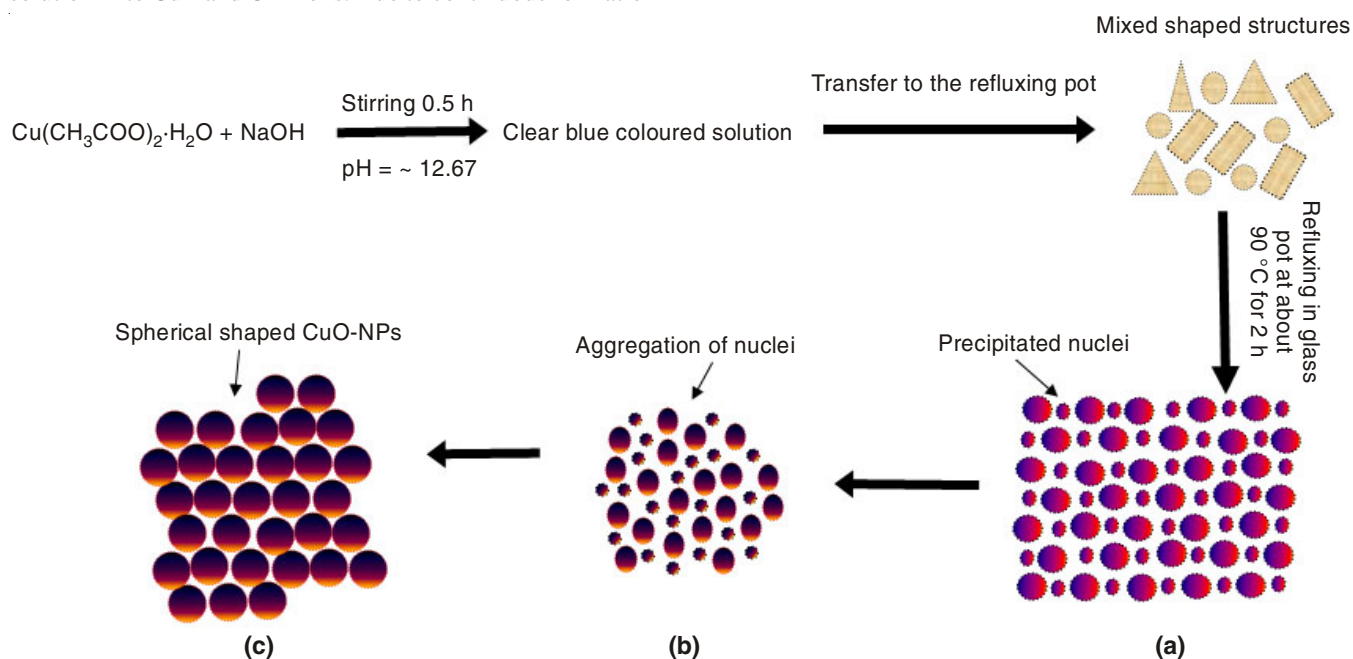


Fig. 6. Possible proposed mechanism for the formation of CuO -nanoparticles

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