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Synthesis and catalytic properties of nano CuO prepared by soft chemical method

ABSTRACT

N. V. Suramwar^{1,2}
S. R. Thakare^{1,*}
N. T. Khaty²

¹*Nanotechnology lab, Department of Chemistry, Science College, Congress nagar, Nagpur, Maharashtra, 440012, India.*

²*Department of Applied Chemistry, Priyadarshini College of Engg. & Tech., Hingna, Nagpur, Maharashtra 440019, India.*

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Well faceted CuO nanoparticles, were synthesized by thermal-assisted dissociation method at reflux temperature in a short period of time. A possible mechanism for synthesis of such highly pure and stable nanoparticles is tentatively proposed by FT-IR study. The large surface area and rich exposed active sites are expected to endow such nanoparticles with excellent performances in catalysis as demonstrated here for the remarkable catalytic activity with respect to the oxidation of alcohol. This interesting result highlights the advantage of such a CuO nanostructure over the bulk counterpart, i.e. the high density of active sites and large surface area, which places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in catalysis. It is the first report on the nanometer-sized faceted CuO acting as a catalyst for an oxidation reaction and simultaneously a good example for the combination of green chemistry and functional materials.

Keywords: *Nanomaterials; CuO; Starch; Catalyst; Sodium borohydride; Alcohol oxidation.*

INTRODUCTION

Manipulation of size, shape, morphology and composition of technologically important materials, within the dimension of nanometers to micrometers, has been a great challenge for material scientists for the last few decades. One-dimensional (1D) nanomaterials, such as nanotubes, nanowires, and nanobelts or nanoribbons have received much attention because they are considered to be the key structural components of future electronic, optical, and mechanical devices. Their unique properties can be harnessed for the design and fabrication of nanosensors, solar cells, field emitters, and transistors. Cu-based nanomaterials have been extensively studied due to their many potential applications.

* Corresponding author:

Sanjay R. Thakare
NanoChemistry lab, Department of Chemistry, Govt. Institute of Science, Nagpur, Maharashtra, 440001, India.
Tel +91 9011097694
Fax +91 9011097694
Email sanjaythakare@yahoo.co.uk

As a well-known p-type semiconductor with a narrow bandgap of 1.2 eV, CuO has been extensively studied because it is an important component of copper oxide superconductors [1, 2]. With regard to its commercial value and interesting properties, CuO has also been widely exploited in a versatile range of applications such as catalysts [3], magnetic storage media [4], field emission devices [5], gas sensors [6], lithium batteries [7], and solar cells [8]. Copper (II) oxide is widely used as a catalyst because of its high activity and selectivity in oxidation and reduction reactions [9-11]. In particular, CuO was valued at one time as a possible alternative to precious metal catalysts such as platinum, palladium and rhodium for reactions involving H₂, such as the oxidation of CO and hydrocarbons, and the reduction of NO_x in automobile exhaust systems. Copper oxide is used in the synthesis of methanol from CO and H₂, and in the water-gas shift reaction [12, 13]. Other groups have reported the preparation of high purity, monodispersed nanocrystalline CuO using sonochemical preparation [14], microwave irradiation [15], and precipitation-pyrolysis [16], with particle sizes ranging from 4 nm to 30 nm, and with both spherical and a circular morphologies [17]. Although great progresses have been made in the synthesis of CuO nanostructures, it still remains a major challenge to develop a facile, one-step route for the synthesis of CuO architectures composed of nanoscale building blocks [18].

EXPERIMENTAL

nanomaterial preparation

In this paper, CuO nanomaterial was synthesized by the chemical dissociation under reflux condition in the presence of stabilizing agent to prepare uniform nonmaterial. This prepared CuO nanomaterial is used as a catalyst in the oxidation of 1-butanol to butanoic acid which overcomes the challenges in term of reaction temperature and recovery of catalyst. All the reagents used in this synthesis were of analytical grade and used without further purification. CuO nanomaterial was prepared by dissociation of copper sulphate under reflux condition. The detailed experimental procedure was as follows. The copper sulphate solution prepared by adding 1 g CuSO₄ in 10 ml of

water which forms the blue copper sulphate solution in water. This blue solution of copper sulphate was added in 100 ml solution having 4 gm starch as a stabilizing agent. The above solution refluxed for 1 hour, during the reflux colour of the solution changes from blue to colorless and then it turns slowly to brick red which indicates the formation of CuO nanomaterial. The nanoparticle is then separated out by centrifuge at 4000 rpm and washed properly with plenty of water for the removal of unreacted chemicals.

Characterization of CuO Nanoparticles

The powder X-ray diffraction measurements were carried out on a PHILIPS HOLLAND, XRD system using Cu K α radiation ($\lambda=1.54056 \text{ \AA}$). The Fourier-transform infrared (FTIR) spectrometer used to collect spectra was a Shimadzu 8001A spectrophotometer. The morphology of the copper nanoparticles was investigated via scanning electron microscopy (SEM, model JSM-5400, JEOL) and transmission electron microscopy (TEM, Philips CM200). The size distribution of copper nanoparticles was obtained by nano-distribution and a zeta potential analyzer (SZ-100, Horiba).

Catalytic Activity

An aliquot of 10 mL of neat 1-butanol is taken in a three-necked round-bottomed flask and 5 mol% catalysts were employed. The flask was then fitted with a water condenser and heated at reflux temperature for 6-8hrs. After that, the solid catalyst was separated simply by decantation/ filtration and the product was analyzed. Then the catalyst thoroughly washed five times with distilled water to remove any adhering reactant/product that might remain on the catalyst surface. The washings are discarded, and the catalyst was dried and recycled to carry out the next set of oxidation reaction. Characterization of the crude sole product is done by co-TLC, and GC-MS studies.

RESULTS AND DISCUSSION

Structural Analysis of CuO

The X-ray diffraction analysis of products was carried out to identify the components of the products (Figure 1). All diffraction peaks are

indexed with the corresponding planes of CuO. No other peak due to possible impurities can be detected, which indicates that the products are of high purity. The XRD spectra showing the intense peak at 35.9 is having plane (111) which is the crystal plane of CuO. The low intensity peaks at 28.2, 42.3, 62.2, and 77.7 which match well with the plane (110), (202), (220) and (113). These are very close to those in the JCPDS File No.5-0661.

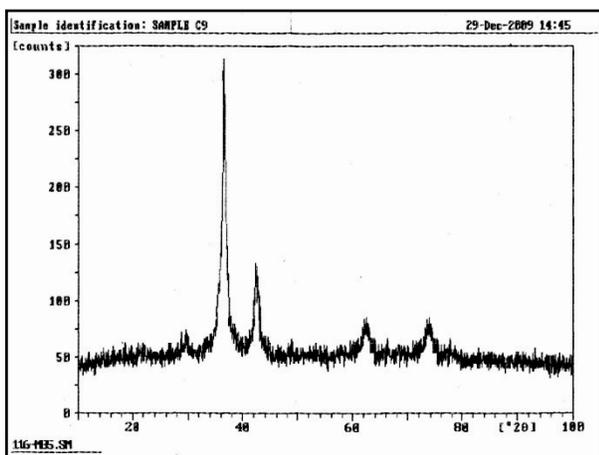


Fig. 1. XRD spectra of Prepared CuO nanoparticle.

This indicates that the prepared CuO material is highly crystalline having characteristic of pure monoclinic crystallites without having any peak due to the possible Cu_2O and $\text{Cu}(\text{OH})_2$ impurity and well arrange in specific orientation. The size of the copper crystallites was estimated from the Debye–Scherrer equation.

$$D = K\lambda\cos\theta / (\beta_{1/2}) \quad (1)$$

Where, K is the Scherrer constant, which is related to the crystallite shape, λ and θ are the radiation wavelength and Bragg's angle, respectively; and β is the full width at half maximum of the diffraction peak. The crystal size of the products as calculated by Scherrer formula is 30 nm. The results of the size distribution analysis (Figure 2) show that the products range from 50 to 80 nm.

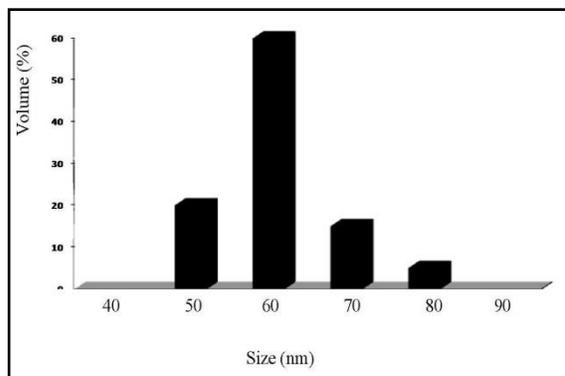


Fig. 2. Size Distribution of CuO nanoparticles.

These measurements correspond with the results from XRD analysis. The SEM (Figure 3a) and TEM (Figure 3b) images of the CuO nanoparticle were taken. The SEM images confirm the spherical morphology of CuO nanoparticles. High magnification images show that the small spherical structures are grown on the surface of the big spherical structures. The resultant morphology is looking like a cluster of grapes.

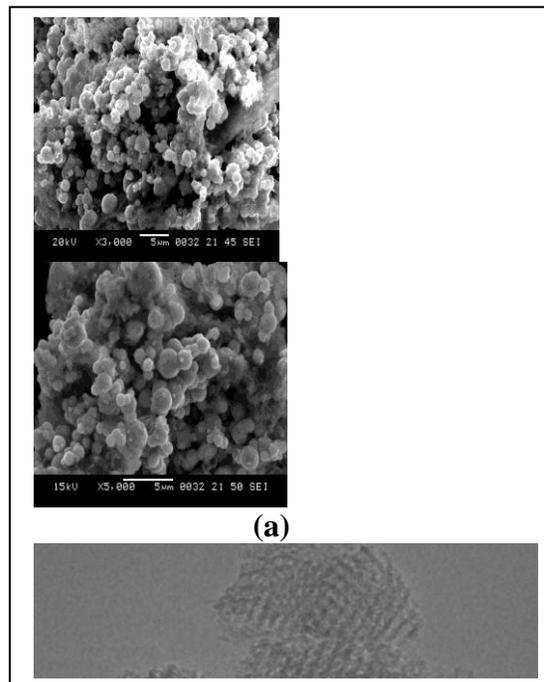


Fig. 3. (a): SEM images of CuO nanoparticles Showing small spherical structures on the surface of bigger one. (b): TEM images of CuO nanoparticles showing particles are well arranged with specific size.

The morphology of the prepared CuO is very interesting and looks like pollen grain. The formation of small structures on bigger one may increase its surface area and indirectly the catalytic activity which discussed in this paper. From TEM images it is confirmed that the particle having size in between 50 to 80 nanometer agrees well with the XRD Analysis. TEM images confirmed the connectivity between the spheres which observed in SEM pictures. The morphological pictures observed in TEM and SEM analysis show that the growth of particles is very well organized. The nuclei formation and growth of particles simultaneously occur and hence it is observed that over the bigger particles the small particles are grown as like a secondary growth occur in biological system of flora. The control growth of particles may be due to the presence of starch molecules. The starch as biological molecule having symmetrical orientation may not allow growing the particles in a random manner. This is may be advantage to use of a biological molecule as a stabilizer of nanoparticles having a specific orientation as well as beautiful morphological nature having tailored properties for specific application. This is happening possibly due to selectivity and sensitivity of biological molecule for which they are popular. In this study FT-IR spectrometry technique is used for understanding the role of the organic molecules. Figure 4 shows the IR spectra of pure starch and CuO nanoparticles coated with starch in the range of 400–4000 cm^{-1} . For pure starch (Figure 4a), the peaks in the range of 670–1000 cm^{-1} are attributed to the C–H bending vibration of –HC–CH– links. The two absorption peaks that appear at 1660 and 1163 cm^{-1} are due to the O–H bending and C–O stretching. The bands observed between 2926 cm^{-1} and 3434 cm^{-1} are characteristic of O–H stretching vibrations. The peaks in the range 1300–1420 cm^{-1} are attributed to the C–H bending vibration of the –HC–CH– links of starch molecules. Also it has been shown weak C–O stretching at 983.8 cm^{-1} which is characteristic of ether functional moiety. Comparing Figure 4a and 4b, all the peaks in Figure 4b which is the IR spectra of CuO nanoparticle coated with starch as a stabilizer are weaker, the stretching vibration of O–H bands at 3434 cm^{-1} gets weaker and the stretching band at 2926 cm^{-1} gets discriminated in the spectrum of CuO coated with starch.

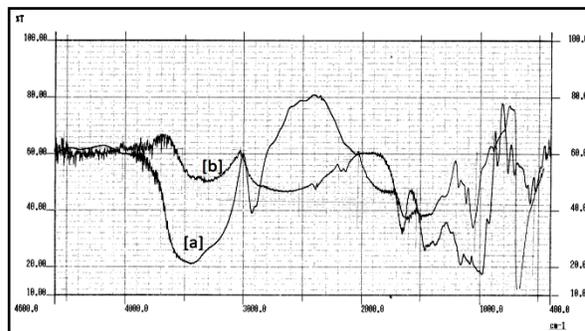


Fig. 4. (a): IR Spectra of pure starch. (b): IR Spectra of CuO nanoparticle

The peaks in the range of 670–1000 cm^{-1} are attributed to C–H bending vibration of –HC–CH– links are shifted to higher wave numbers and some peaks disappeared in the spectrum of CuO coated with the surfactant. The C–O stretching at 983.8 cm^{-1} which is characteristic of ether functional moiety is shifted to higher wavenumber at 1020.5 cm^{-1} . There is sharp peak observed at 610 cm^{-1} in the spectrum CuO nanoparticles which is the characteristics of Cu–O bond formation. These dramatic differences indicate that there is chemical bonding which could have been formed between starch and CuO nanoparticles. The possible chemical interaction between starch and CuO nanoparticles is represented as (Figure 5).

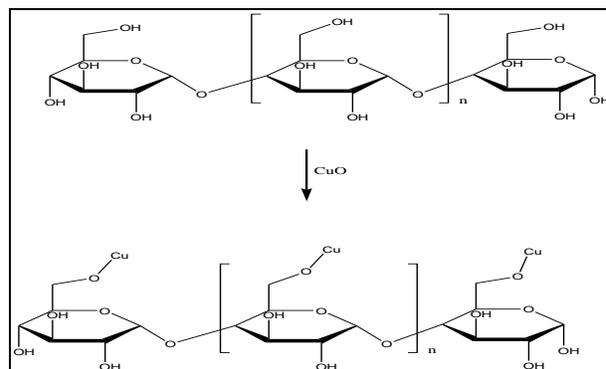


Fig. 5. Possible chemical bonding between CuO and Starch.

Study of Catalytic activity

The above prepared CuO nanoparticles are utilized as a catalyst in the oxidation of 1 Butanol to butanoic acid. GC spectrum of product after 6 hour catalysis reaction is represented (Figure

6). It is observed that the well faceted CuO nanoparticles were good catalyst for oxidation reaction.

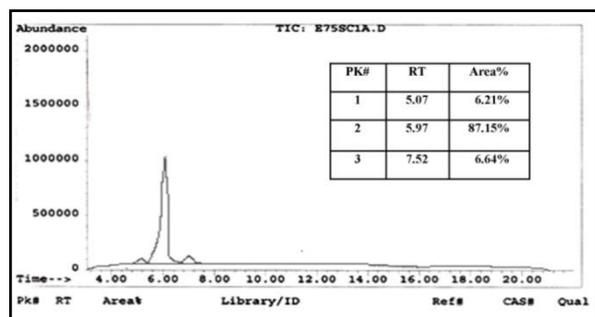
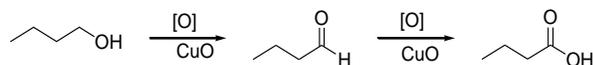


Fig. 6. GC spectrum of Butanoic acid.

This is due to small size and highly active surface area of the CuO nanoparticle. It is assumed that the surface oxygen is involved in the oxidation of 1-butanol. During the oxidation the 1-butanol is first oxidized to butyraldehyde which is further undergoing oxidation to form butanoic acid. We found 87.15% conversion of given 1-butanol to butanoic acid within six hour of time. This is confirmed by m/z value of 89 corresponding to butanoic acid found on the mass spectrum of the given crude product. The gas chromatogram of the given crude product is given in Figure 6 which clearly indicates the peak with retention time of 5.97 and having area of 87.15% which is of butanoic acid. The catalyst is also effective towards the oxidation of lower aliphatic alcohols like methanol and ethanol. The reaction scheme for the oxidation of 1-butanol to butanoic acid is as follows.



The concentration of 1-butanol decreases steadily while that of the butanoic acid increases. The concentration of the intermediate aldehyde increases achieves a steady state and then progressively converts itself into acid.

CONCLUSION

In summary, we have developed a bioinspired and environmentally friendly procedure for rapid reflux temperature synthesis of highly

faceted CuO nanoparticles. Excellent catalytic performance of these CuO nanoparticles demonstrated here with respect to oxidation of alcohols such as Butanol, Ethanol, methanol, etc. This interesting result highlights the advantage of such CuO nanostructures over the bulk counterpart and places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in catalysis. To the best of our knowledge, it is the first report on nanometer-sized CuO acting as a catalyst for an oxidation of alcohol reaction and simultaneously is a good example for the combination of green chemistry and functional materials.

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