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A novel combustion method to prepare CuO nanorods and its antimicrobial and photocatalytic activities

A. Jegatha Christy [a,b], L.C. Nehru [c], M. Umadevi [b,*]

[a] Department of Physics, Fatima College, Madurai — 625 018, Tamilnadu, India
[b] Department of Physics, Mother Teresa Women's University, Kodaikanal-632 509,Dindigul District, Tamil Nadu, India
[c] Department of Physics, Alagappa Univeristy, Karaikudi, India

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ABSTRACT

Copper oxide (CuO) nanoparticles have been prepared by solution combustion method using citric acid as fuel. The structure and morphology of the CuO nanoparticles were investigated by means of X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and energy dispersion spectra (EDS) techniques. The rod like nature and monoclinic crystalline structure of the prepared CuO nanoparticles were revealed from FESEM, HRTEM and XRD. The CuO NPs showed very good antimicrobial activity against *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli* and *Klebsiella pneumoniae*. Photocatalytic activities of CuO nanorods were also investigated.

1. Introduction

The fabrication of transition metal oxides with nanostructure has been the target of scientific interests in recent years because of their unique properties and fascinating applications in optoelectronics and biomedical science. Along this line, synthesis of copper nanoparticles with smaller sizes based on simple chemical reduction is highly demanded. The solution combustion synthesis of metal nanoparticles is being considered to be a promising method to obtain nanosized metal particles as it involves a high level of molecular mixing of the solution components leading to chemical homogeneity of the synthesized product with high purity in a rapid, inexpensive single step operation. The most important fact about solution combustion synthesis is that it is a short duration process and the various gasses formed during the process inhibit particle size growth, which favors the formation of nanosized powders [1].

Copper is a highly conductive, much cheaper, and industrially widely used material and it is unique with the chemical reactivity capable of serving as precursors for the fabrication of conductive structures for ink-jet printing [2] or forming $CuInSe_2$ or $CuIn_xGa_{1-x}Se_2$ semiconducting nanomaterials for photodetectors and photovoltaics [3]. Copper oxide/copper (II) oxide/cupric oxide is a semiconducting compound with a monoclinic structure. CuO has attracted particular attention because it is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties such as high temperature superconductivity, electron correlation effects and spin dynamics. As an important p-type semiconductor, CuO has found many diverse applications in various devices such as gas sensors, photovoltaic cells, batteries, high temperature superconductors etc. In the energy-saving area, energy transferring fluids filled with nano CuO particles can improve fluid viscosity and enhance thermal conductivity. CuO crystal structures possess a narrowband gap, giving useful photo catalytic or photovoltaic properties as well as photoconductive functionalities [4]. Limited information on the possible antimicrobial activity of nano CuO is available. CuO is cheaper than silver, easily mixed with polymers and relatively stable in terms of both chemical and physical properties. Highly ionic nanoparticulate metal oxides, such as CuO, may be particularly valuable antimicrobial agents as they can be prepared with extremely high surface areas and unusual crystal morphologies [5]. The materials like copper, silver, zinc present high antibacterial activity, low toxicity, chemical stability, long lasting action period and thermal resistance compared to organic antibacterial agents [6]. In the present study, CuO nanorods were synthesized by solution combustion method using citric acid as fuel. The antimicrobial and photocatalytic activities of the prepared CuO nanorods were also investigated.

2. Experimental

2.1. Synthesis of CuO nanorods

For the preparation of CuO nanorods, cupric nitrate ($Cu(NO_3)_2$) and citric acid ($C_6H_8O_7$) were taken as starting materials (AR grade). The stoichiometric compositions of the solution components (fuels and oxidizer) were calculated according to the principle of propellant

* Corresponding author. Tel.: +91 4542 241685.
E-mail address: ums10@yahoo.com (M. Umadevi).

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chemistry, keeping the oxidizer (metal nitrate) to fuel (citric acid) ratio as unity [7]. Stoichiometric amount of cupric nitrate was dissolved in deionised water and then citric acid was added into it. The solution was kept in the furnace at 300 °C. Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gasses. After the solution reached the point of spontaneous combustion, it began to burn and released much heat, vaporizing the entire solution instantly and became black powder. Citric acid is oxidized by nitrate and serves as fuel. The expected combustion reaction to form CuO nanorod is:

$$Cu(NO_3)_{2(c)} + 0.611C_6H_8O_{7(c)} \rightarrow CuO_{(c)} + N_{2(g)} + 3.66CO_{2(g)} + 2.44H_2O_{(g)}$$

where 0.611 is the molar ratio of citric acid to cupric nitrate. It corresponds to an 'equivalent stoichiometric ratio' which implies that the oxygen content of copper oxide can oxidize/consume citric acid completely. As a result, CuO product and gasses of CO_2, H_2O and N_2 can be formed directly from the reaction between fuel and oxidizer without the necessity of getting oxygen from outside. Normal atmosphere was maintained in furnace without any inert gas. The temperature outside the furnace is 22–25 °C. The solution was kept in the furnace at 300 °C. With large amount of fumes produced the combustion reaction was completed in 20 min and loose powder was formed which was crushed and ground thoroughly.

2.2. Characterization

The X-ray diffraction patterns were recorded using X-ray diffractometer using Cu-Kα radiation (λ = 0.1542 nm) operated at 50 kV and 100 mA. The experiments were performed with angle of diffraction (2θ) ranging from 20 to 80°. Shimadzu UV-1700 UV–Visible spectrophotometer was used to carry out the optical measurements. The size, composition and atomic structure of the NP's were analyzed by High Resolution Transmission Electron Microscopy (HR-TEM), energy dispersion spectra (JEOL JEM 2100) and field emission scanning electron microscopy (FESEM) (Carl Zeiss sigma).

2.3. Assay for antimicrobial activity of CuO nanorods against microorganisms

The antimicrobial activity of CuO nanorod was evaluated against gram positive *Bacillus cereus* (MTCC-4079), *Staphylococcus aureus* (MTCC-7443), gram negative *Escherichia coli* (MTCC-1721), and *Klebsiella pneumonia* (MTCC-4030). Exactly 0.2 ml of fresh cultures of each organism was inoculated into 5 ml of sterile nutrient broth (Hi Media) and incubated for 3–5 h to standardize the culture to McFarland standards (106 CFC/ml). Three replicates of respective microorganism were prepared by spreading 100 μl of the revived culture on MHA (Mueller Hinton Agar-Hi Media) with the help of spreader. The well was made having a diameter of about 7 mm and 50 μl samples of CuO were added in one well and 50 μl of distilled water as control. The petri plates were kept at 37 °C for 24 h in incubator for bacteria during which its antibacterial activity was evidenced by the presence of a zone of inhibition (mm) surrounding the well.

2.4. Photocatalytic activity

The photocatalytic activity of the samples was evaluated by the photocatalytic degradation of methyl orange (MO) aqueous solution with an initial concentration of 0.1 mM. 0.0125 mM of nano CuO is diluted completely and added with the MO (0.1 mM) solution. After irradiation with ultraviolet light, the reaction solution was periodically taken from the reactor for the determination of the absorbance change of MO with the catalysts. The photocatalytic test was performed at room temperature in natural atmosphere. No detectable degradation of the dye was observed in the absence of the catalysts or without UV irradiation.

3. Result and discussion

The X-ray diffraction pattern of the CuO nanorod is shown in Fig. 1a. The XRD peak positions were consistent with the copper oxide and the sharp peaks of XRD indicate the crystalline nature. The peaks were observed at 2θ = 32.4°, 35.417°, 38.634°, 48. 668°, 53.37°, 58.17°, 61.441°, 66.1°, 67.89°, 72.28° and 75.01° which correspond to (110), (110), (111), (202), (020), (202), (113), (311), (113), (311) and (004) Bragg's reflections of monoclinic structure of CuO respectively (JCPDS:80–1916). The lattice constant values are also calculated and are very close to the standard data. The calculated lattice constants of the unit cells are a = 4.6965 Å, b = 3.4324 Å and c = 5.1329 Å having β = 99.5287°. The volume of the cell is calculated to be 81.6022 $(Å)^3$. The samples exhibit smaller cell volumes than that of bulk. The XRD line width can be used to estimate the size of the particle by using the Debye–Scherrer formula as $D = \frac{k\lambda}{\beta \cos\theta}$ where D is the particle size (nm), k is a constant equal to 0.94, λ is the wavelength of X-ray radiation (1.5406 Å), β is the full-width at half-maximum (FWHM) of the peak (in radians) and 2θ is the Bragg angle (degree). Numerous experiments have shown that strain broadening caused by dislocations can be well described by a special logarithmic series expansion of the Fourier coefficients of Bragg reflection peak profiles. It can be calculated from the formula $\varepsilon_{str} = \frac{\beta}{\tan\theta}$.

A remarkable property of Debye–Scherrer equation is the dependence on the diffraction angle θ. The Williamson–Hall method does not allow a 1/cosθ dependence as in Scherrer equation but instead varies with tanθ. This fundamental difference allows a separation of reflection broadening when both microstructural causes – small

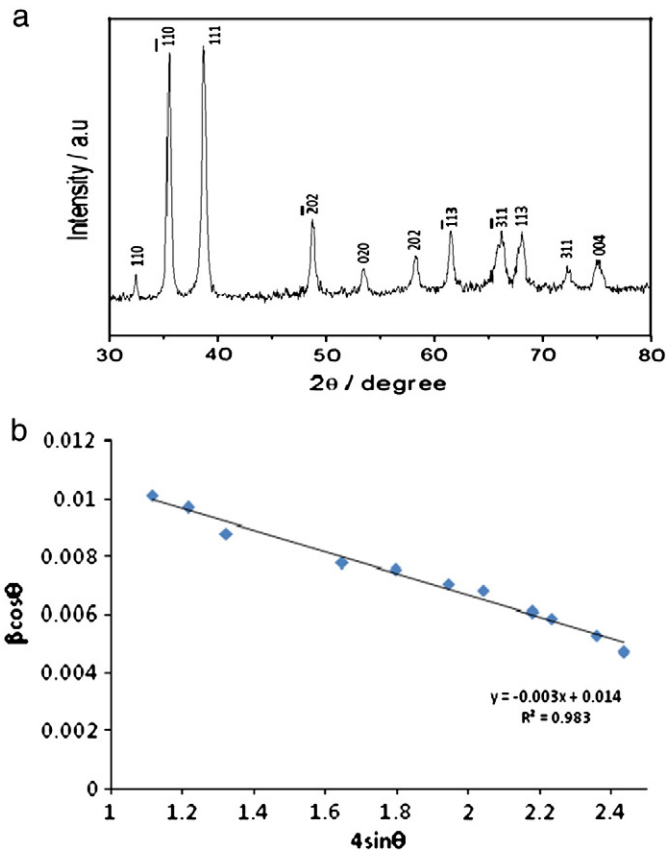

Fig. 1. a) The X-ray diffraction pattern of CuO nanorods; b) The W–H analysis of CuO nanorods assuming UDM. Fit to the data, the strain is extracted from the slope and the crystal size is extracted from the y-intercept of the fit.