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Fabrics and Medical Devices (Catheters) Coated with Zn-doped CuO Nanoparticles Kill Micro-organisms and Provide a Healthy Environment

Indra Neel Pulidindi[1], Vatsal Jhaveri[2], Suresh Selvaraj[3], Prakash Vaithyanathan[4,*]

†Dedicated to the living encyclopedia of Catalytic science, Professor Balasubramanian Viswanathan on his 83rd birthday on 15th September 2024.

Abstract

These days, drug resistance by microorganisms is a major challenge in the field of medicinal chemistry. Most of the familiar antibiotics turnout to be of no impact in curbing the proliferation of microorganism (bacteria, virus and fungus). To address the issue of multi-drug resistance (MDR) and extremely drug resistance (EDR) in microorganisms that cause various health complications, like the dental decay, biofilm formation, foul smell, delayed wound healing, aggravation of wounds, apart from many others. Professor Aharon Gedenkan's group has come up with a land mark paper in the year 2013 that was published in Small (Wiley Publishers). The breakthrough reported in the paper is on the sonochemical synthesis of Zn doped CuO nanoparticles (NPs) and exploiting the same for antibacterial applications. Zn doped CuO NPs showed four orders of magnitude higher antibacterial activity compared to the undoped system (CuO NPs) prepared under analogous conditions. Interestingly, the material showed such exceptional antibacterial activity even upon depositing the NPs on cotton fabric. This means that all the bedding and clothing material used in hospitals can be replaced with Zn doped CuO coated fabrics (blankets, curtains, pillow covers and many more) to kill the bacteria effectively and in doing so the spread of many diseases can be controlled.

Keywords: Zn doped CuO, sonochemical synthesis, anti-bacterial activity, antimicrobial activity, public health

INTRODUCTION

There is an ancient saying that "health is wealth". Another proverb says – "A sound mind in a sound body". These wise sayings signify the need of good health. These days all around we see pollution, scarcity of resources, malnutrition, spread of several, bacterial, and viral diseases. Moreover, several famous bacteria, namely, *Escherichia coli* regular strain as well as the multi drug resistant (MDR) E. coli), *Staphylococcus aureus*, *Streptococcas mutans*, *Staphylococcus epidermidis*, *Proteus mirabilis*, *Klebsiella pneumonia*, *Enterococcus faecalis*, and *Pseudomonas aeruginosa*, are a source of infections and causing health hazard. To address this issue Professor Aharon Gedanken's group developed an effective anti-bacterial material, namely, Zn doped CuO ($Cu_{0.88}Zn_{0.12}O$) that showed remarkable (four orders of magnitude higher) antibacterial activity compared to the undoped system prepared under analogous sonochemical conditions [1-16]. In addition, the mechanism of action of the Zn doped

*Author for Correspondence
Viswanathan Balasubramanian
E-mail: bviswanathan@gmail.com

[1]Scientific Consultant, Jesus' Scientific Consultancy for Industrial and Academic Research (JSCIAR), Tharamani, India
[2]Chemical Engineer, Ammonium Sulphate Plant, Gujarat State Fertilizer Company Ltd., Vadodara, India
[3]Associate Professor, Department of Science and Humanities, ACE Engineering College, Ghatkesar, Secunderabad, Telangana, India
[4]Science Teacher and Innovator 50, L.B road, Adyar, Chennai, India

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CuO in killing the bacteria has been elucidated using classical analytical techniques like the differential scanning calorimetry (DSC), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and electron paramagnetic resonance (EPR) spectroscopic techniques. This review on the topic “public health” thus focus on the synthesis, characterization and antibacterial activity of the Zn doped CuO nanoparticles exploited in day to day medical applications such as medical devices (catheters) and fabrics.

SONOCHEMICAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ZN DOPED CUO NANOPARTICLES ($CU_{0.88}ZN_{0.12}O$)

Sonochemical irradiation has been a proven field to produced nanomaterials (metals, metal oxides, carbon nano materials and doped systems and many more) apart from being a promising device for effectively coating surfaces (fabrics and metal surfaces and biological systems like artificial teeth) with potential nanomaterials with antibacterial and antiviral properties leading to safety in public health infrastructure. To address the issue of multi drug resistance (MDR) and extremely drug resistance (EDR) in micro-organisms, Professor Gedanken et al., have developed a sonochemical pathway to produce Zn doped CuO nanoparticles ($Cu_{0.88}Zn_{0.12}O$), systematically characterized them using various classical analytical techniques like XRD, DSC, SEM, TEM, EDAX and EPR to gain knowledge on their structure as well as the origin of the antibacterial activity.

The XRD pattern of Zn doped CuO produced via sonochemical route is shown in Figure 1 (a) and Figure 1 (b). The same image shown in Figure 1 (a) is enlarged in Figure 1 (b) for the Zn doped CuO system. In addition to the XRD pattern of the Zn doped CuO, the XRD traces of other metal oxides like the ZnO (bulk) and CuO (bulk) procured from Sigma Aldrich, Israel were shown for comparison. In addition, the XRD trances resulting from the ZnO (nano) and CuO (nano) prepared in the sonochemical route under identical conditions (same concentration of either Zn^{2+} or Cu^{2+} or both) were shown in Figure 1 (a). The essential feature of the XRD pattern of the Zn doped CuO is that it is pure, meaning, it has only single phase of monoclinic CuO. No additional, independent phase of ZnO is present along with Zn doped CuO. Such phase purity is very much necessary to study in detail the origin of the antibacterial activity solely originating from the Zn doped CuO system. Such phase purity is achieved owing to the unique trick of the trade known to chemists, i.e., to play with the relative mole rate of the Zn^{2+} and Cu^{2+} precursors. When the mole ratio of the Zn^{2+} and Cu^{2+} precursors is 1:3, such Zn doped CuO ($Cu_{0.88}Zn_{0.12}O$) with the single phase, namely, monoclinic CuO is observed. Any increase in the amount of Zn^{2+} species during the synthesis will result in the appearance of an individual phase of the hexagonal Wurtzite phase of ZnO, which is not wanted. Thus by carefully choosing a specific mole ratio of Zn^{2+} and Cu^{2+}, the derived Zn doped CuO can be obtained. No more than 12 % of the Cu^{2+} in the CuO lattice can be replaced by Zn^{2+}.

Having learned this from XRD, further characterization of the doped system ($Cu_{0.88}Zn_{0.12}O$) was carried out suing HR-TEM (Figures 2a and b), HR-SEM (Figure 2 c) and EDAX (Figure 2 d, e and f) as shown in Figure 2. The figures are self-explanatory. Thin slices (lamelle) of Zn doped CuO were seen in the HR-TEM images. The HR-SEM image showed smooth surface of the particles of Zn doped CuO. The uniform distribution of the elements, namely, Cu, Zn and O, in the doped system were seen in the EDXA (Figures 2 d, e and f).

MECHANISM OF ANTIBACTERIAL ACTIVITY OF ZN DOPED CUO ($CU_{0.88}ZN_{0.12}O$)

Zn doped CuO NPs showed exceptionally high antibacterial activity compared to the undoped system CuO NPs prepared under identical conditions. The four orders of magnitude higher antibacterial activity of the doped system, $Cu_{0.88}Zn_{0.12}O$, was attributed to the structural defects, dislocations, co-existence of the amorphous phase of the Zn doped CuO apart from the crystalline phase of Zn doped CuO as well as due to the presence of the oxygen vacancies. All these defects are responsible for the generation of reactive oxygen species (ROS). Reactive oxygen species have the ability to kill the bacterial. Thus the exceptionally high killing ability of the Zn doped CuO system was attributed to the far far higher amounts of the ROS generated in the $Cu_{0.88}Zn_{0.12}O$ compared to the undoped system.

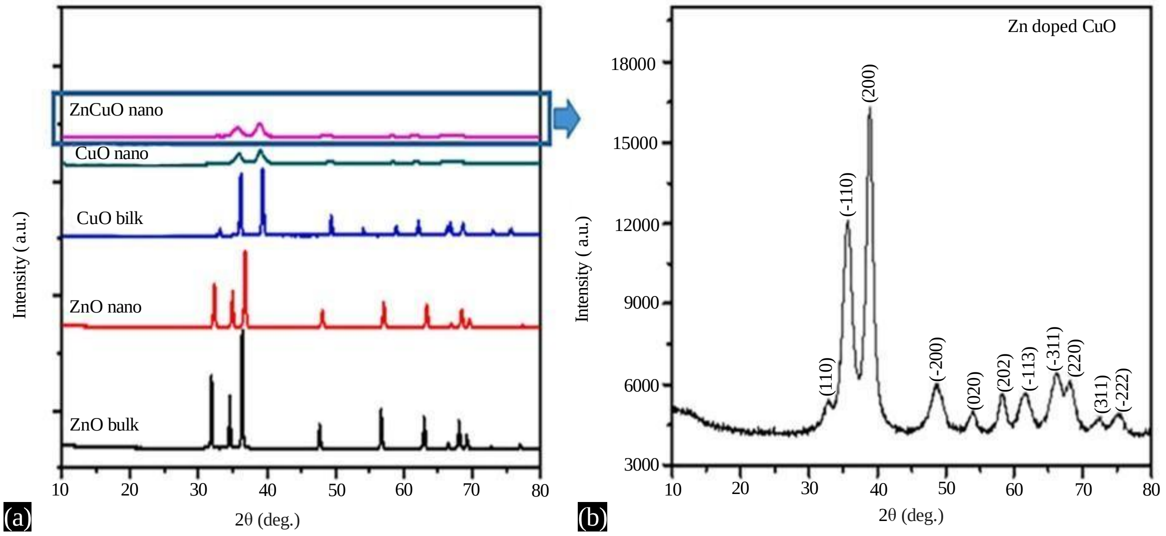
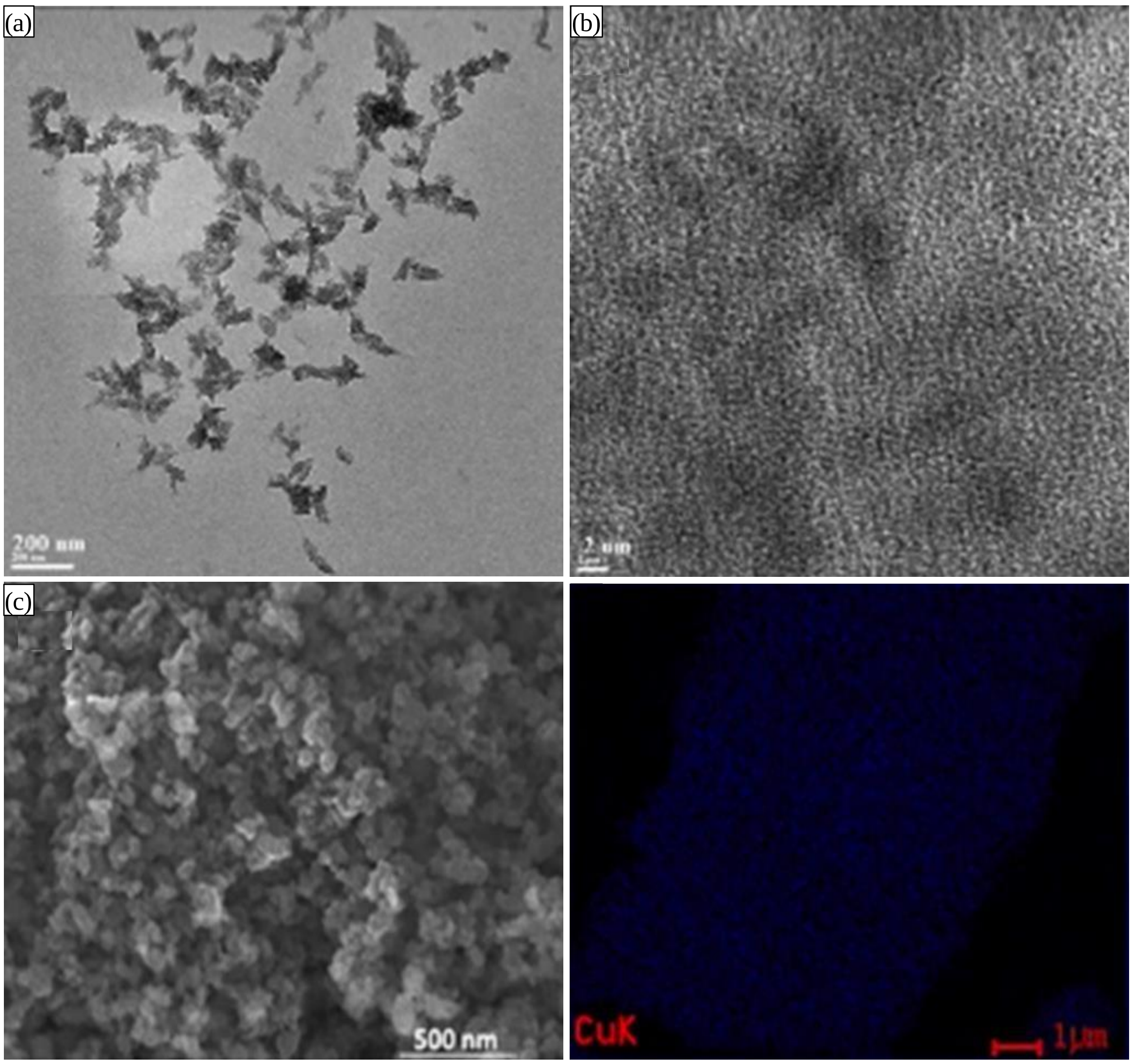


Figure 1. (a) X-ray diffraction (XRD) pattern of ZnO (bulk), ZnO (nano), CuO (bulk), CuO nano and Zn doped CuO nano; (b) Zn doped CuO nano [enlarged version of the same pattern shown in Figure 1 (a)] [reproduced from reference 2 with permission from the Elsevier].



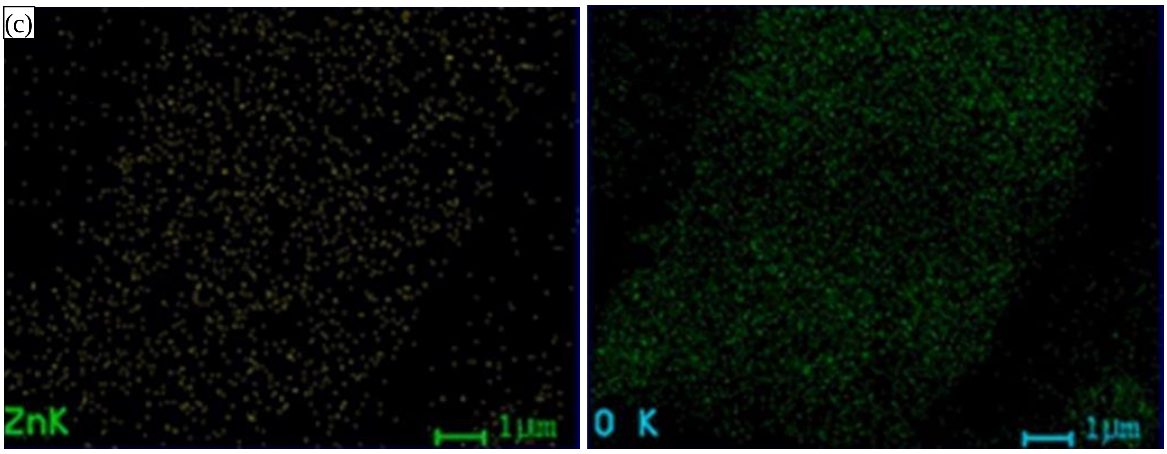


Figure 2. High resolution transmission electron microscope images of Zn doped CuO (a and b); high resolution scanning electron microscope image of Zn doped CuO (c) and the energy dispersive X-ray analysis (EDXA) of Zn doped CuO (d, e and f). [reproduced from reference 2 with permission from the Elsevier].

EPR is an elegant technique to probe the structure and dynamics of ROS. Three kinds of ROS, namely, hydroxyl, super oxide anion radical and singlet oxygen radicals were observed in the EPR using the spin-trapping technique. The Spin trapping technique captures the short-lived radicals and enables their quantification. Using such spin-trapping techniques it was found that nearly 40 % of ROS are hydroxyl type radicals in nature. These ROS species will cause injury to the bacterial cell membrane and cause the cell rupture and proliferate into the internal structure of the cell and kill the cell through the generation of ROS. The structural defects in the $Cu_{0.88}Zn_{0.12}O$ systems, and the ROS generation ability and the bacterial killing function are directly proportional. Such ROS generation ability of the Zn doped CuO is observed in aqueous suspensions, as well as in coated systems like cotton fabrics coated with CuO and in catheters coated with ZnO. Thus the sonochemical technology for the generation of Zn doped CuO NPs and their deposition on various substrates has to be kept for generations.

CONCLUSION

The unique potential of the sonochemical method for the synthesis of Zn doped CuO nanoparticles ($Cu_{0.88}Zn_{0.12}O$) with phase selectivity was demonstrated. The Zn doped CuO system showed exceptionally high antimicrobial activity due to the structural defects. The structural defects are an assent that equipped the materials, $Cu_{0.88}Zn_{0.12}O$, with the special ability to generate reactive oxygen species (ROS) that are detrimental to bacteria including the multiple drug resistant (MDR) and extremely drug resistant (EDR) strains. Use of Zn doped CuO in hospitals provide safe environment curbing the proliferation of micro-organisms and accelerates the healing procedures.

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