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Preparation Doped CuO Thin Film and Studies of Its Antibacterial Activity

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In this work, Mn doped CuO thin films were prepared by using spray pyrolysis method. Different volume ratios of Mn (0%, 2%, and 4%) were used to dope CuO in order to form Mn–CuO thin films. These films were annealed in furnace at temperature 400 °C for 3 h. The characteristics and structure of films were then examined using X-ray diffractometry and scanning electron microscopy analysis. The X-ray diffractometry pattern showed that all films were polycrystalline having anatase phase only, and the films with different doping ratio exhibited characteristic peaks of anatase crystal planes ($\bar{1}11$) and (111) at 35.6° and 38.73° direction, respectively. The scanning electron microscopy observation of the CuO film doped with 2% Mn revealed a smoother surface compared to the other prepared films. The antibacterial properties of Mn doped CuO thin films showed the reduction in growth of *E. coli* and *S. aureus* which increased significantly at high concentration of Mn doping level (2% and 4%, respectively) as compared with undoped CuO with 0% concentration of Mn thin films.

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PACS/topics: spray pyrolysis method, CuO, antibacterial properties of CuO

1. Introduction

Thin films are layers of any material deposited over different substrates to improve and achieve new properties that give better applications for some materials. Recently, the use of thin films has become very extensive because it presents different properties and applications of CuO thin films has grown. These include the reactive sputtering, chemical vapour deposition (CVD), sol–gel, and thermal oxidation [1]. Among all these, spray pyrolysis technique has stoichiometry in multi-component system and splendid control of chemical uniformity. Cupric oxide (CuO, tenorite) is a monoclinic p-type semiconductor with a narrow band gap of 1.2–1.5 eV at room temperature with lattice parameter $a = 4.6837$ Å, $b = 3.4226$ Å, $c = 5.1288$ Å and $\beta = 99.54°$ [2]. On account of their potential uses in many technological fields, copper oxide (CuO) has been established as a number of applications like gas sensors, solar photo voltaics, and lithium ion electrodes, etc. [3]. Copper oxide, in its metal or ions forms, shows excellent antimicrobial activity against a number of microorganisms including bacteria, fungi, algae, and viruses, and yet is relatively safe for humans [4]. Only a few studies have reported a significant role of copper as bactericidal agent [5]. It shows a significantly higher bactericidal activity in comparison to bulk CuO microparticles. CuO structures were reported as potential antibacterial agents by other groups as well. Trapalis et al. [6] and Akhavan et al. [7] reported CuO–SiO_2 composite thin film and CuO/$Cu(OH)_2$ nanostructure, respectively, generated on copper foil as effective antibacterial against *E. coli* bacteria when the bacterial suspension drop was tested on these surfaces. Perelshtein et al. [8] have reported antibacterial CuO-cotton textile against *E. coli* and *S. aureus*. Gao et al. [9] reported strong antibacterial activity of CuO nanostructures comparable to established antibiotics as well as their photocatalytic potential. However, the growth of new resistant strains of bacteria and fungi has led to the searching of new bactericides and fungicides that can effectively reduce the harmful effects of microorganisms [4]. In this work thin films of CuO with different amount of Mn were successfully prepared via spray pyrolysis method and the structural properties were reported by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition to the antibacterial activity, Mn-doped CuO thin films were also examined against *E. coli* and *S. aureus*.

2. Experimental work

2.1. Preparation of thin films

In this work, spray pyrolysis method is used to prepare CuO thin film with 0.1 M of $CuCl_2 \cdot 2H_2O$. 0.1 M of $MnCl_2 \cdot 4H_2O$ aqueous solution was used to prepare Mn doped CuO with different volume ratios (0%, 2%, and 4%). The resulting solutions were mixed by using a magnetic stirrer till the formation of dark blue and clear solutions, without any suspension of particles. Then, the films were sprayed onto glass substrates which was heated previously to 300 ± 5 °C, the carrier gas was a compressed air, and the solution flow rate was ≈ 3 ml/min while the gas flow rate was 30 l/min. The distance between the nozzle and the substrates was kept at 25 cm. The film thicknesses were measured by laser interference. This method is based on interference of the laser beam reflected from thin film surface and substrate. After deposition, the prepared films are annealed in furnace at temperature 400 °C for 3 h. To avoid excessive cooling of substrates, successive spraying process was used with

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time period of 3 s and then stoppage time of 30 s and so on. The crystalline structure of the deposited films was examined by using X-ray diffractometer (Shimadzu XRD — 7000) with Cu $K\alpha$ radiation and the wavelength was 1.5406 Å.

2.2. Antibacterial activity test

The antibacterial activity of pure CuO and different amount of Mn doped-CuO thin films, respectively against the bacteria *E. coli* and *S. aureus* was studied using the antibacterial drop test [10]. Both bacteria samples were cultured in an LB medium at 37 °C for 24 h. The cultured bacteria samples were diluted to reach approximately the concentration of bacteria corresponding to the MacFarland scale (10^7 CFU/ml, CFU — colony forming units). As shown in Fig. 1, two groups of samples, each containing three thin coated films, prepared in different conditions of deposition method, were placed in sterilized Petri dishes. Then 100 μl of bacterial suspension was added on each thin film. The samples were left at room temperature in sterilized hood and exposed to UV light for 5 h in the antibacterial test. After this time period the bacteria-containing drops were washed from the glass surfaces using 1 ml of phosphate buffer solution (PBS). Then, 100 μl of each bacteria suspension washing was dispersed on an nutrient (N.) agar culture medium. The numbers of colony bacteria in the Petri dishes were counted after incubation for 24 h at 37 °C.

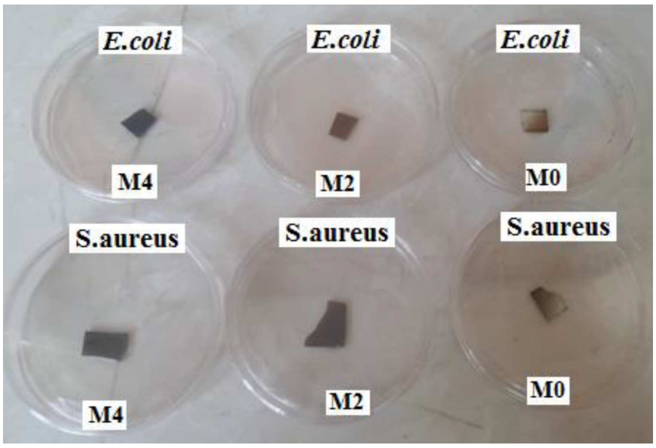

Fig. 1. Illustration of the antimicrobial test for the glass deposited with a thin film.

The antibacterial activities of films against *E. coli* and *S. aureus* bacteria can be obtained from survival rate of bacteria to estimate the precise value of CFU can be defined by a simple formula shown in Eq. (1) as follows [11, 12]:

$$\text{survival rate} = (Y/X) \times 100\%, \tag{1}$$

where X and Y are the CFU before and after exposure, respectively.

3. Results and discussion

3.1. XRD analysis

The phase composition and the crystalline size of pure CuO and doping CuO samples were evaluated by XRD analysis. In Fig. 2 the XRD pattern presents pure CuO (0%) and CuO doped with 2% and 4% of thin films of Mn. It was found that all the films were of polycrystalline structures having anatase phase only. From diffraction patterns, it was observed that the films with different doping ratio exhibited characteristic peaks of anatase crystal planes ($\bar{1}11$) and (111) at 35.6° and 38.73° directions, respectively. These results comply with the standard CuO XRD data. The mean crystal size D of the film was estimated from Scherrer's Eq. (2):

$$D = \frac{0.94\lambda}{\beta\cos\theta}, \tag{2}$$

where λ is X-ray wavelength, β is angular line width of half maximum intensity, and θ is Bragg's angle.

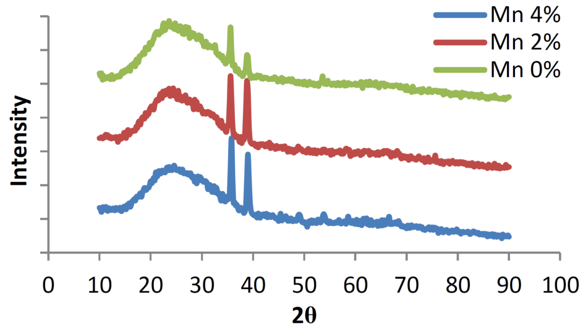

Fig. 2. X-ray diffraction pattern of pure CuO 0% and CuO doped with different content of Mn 2% and 4% thin films.

TABLE I

Doping ratios vs. crystallite sizes.

Doping ratio	($\bar{1}11$) crystallite size [nm]	(111) crystallite size [nm]
0%	24.3	16.4
2%	17.26	17.63
4%	20.18	18.56

The value of mean crystal size was in the range of 16–24 nm and it changed slightly with high concentration. The (111) peak intensity increased a little as the doping ratio increased. Therefore, there was an increase in crystal size, while the lowest crystal size appeared when doping with 2% Mn for the peak ($\bar{1}11$). Table I shows the crystal size of the prepared thin films.

3.2. SEM morphology study

Figure 3 shows SEM images of pure CuO and doped CuO with various content of Mn (0%, 2%, and 4%), respectively. It is clear that the particles have a semi-spherical shape with different sizes. From the results, the CuO film doped with 2% Mn illustrates a smoother surface compared with the other films.

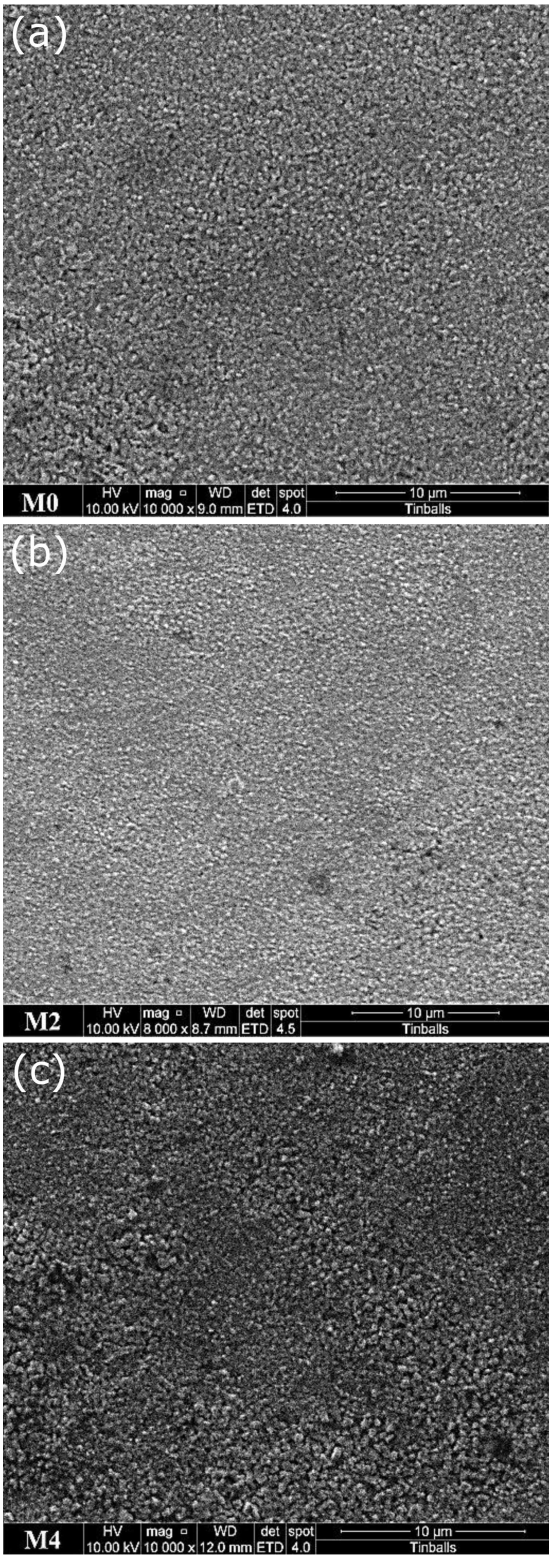

Fig. 3. SEM images of CuO thin films with different doping ratio of Mn: (a) 0%, (b) 2%, and (c) 4%.

This has concluded from the XRD peaks as shown in Fig. 2, where the crystallite sizes presented the same recorded values for the crystallographic planes ($\bar{1}11$) and (111).

3.3. The antibacterial activity of thin films

The antibacterial activity of pure CuO and doped CuO with various content of Mn against Gram negative (*E. coli*) and Gram positive (*S. aureus*) bacteria were examined by the drop test. The results are shown in Figs. 4 and 5, respectively.

The growth inhibition ability of CuO thin films against *E. coli* and *S. aureus* was observed to increase significantly with increase in the Mn doping level (2% and 4%, respectively).

The results reveal that the high concentration of Mn doped CuO 2% and 4% thin films, respectively, inhibited 100% growth of *E. coli* and *S. aureus* completely,

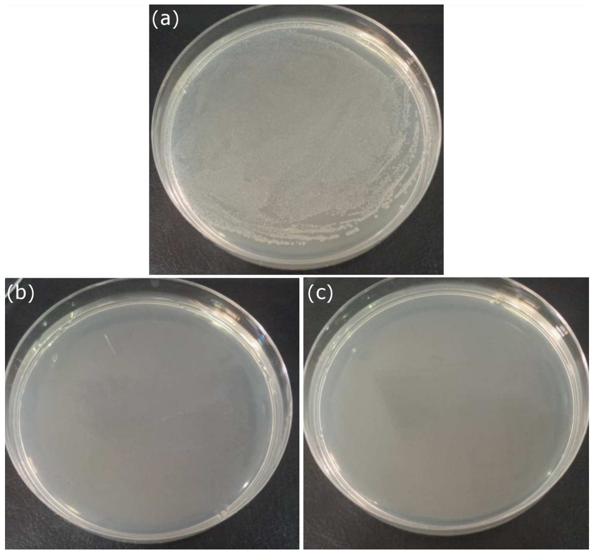

Fig. 4. Photographs of thin films samples against *E. coli* after incubation for 24 h at 37 °C: (a) *E. coli* exposed to M_0 (0%) Mn, (b) *E. coli* exposed to M_2 (2%) Mn, and (c) *E. coli* exposed to M_4 (4%) Mn.

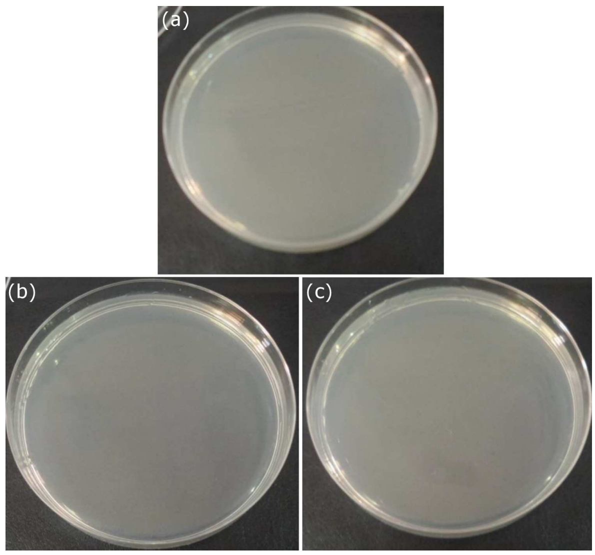

Fig. 5. As in Fig. 4, but for *S. aureus* bacteria.

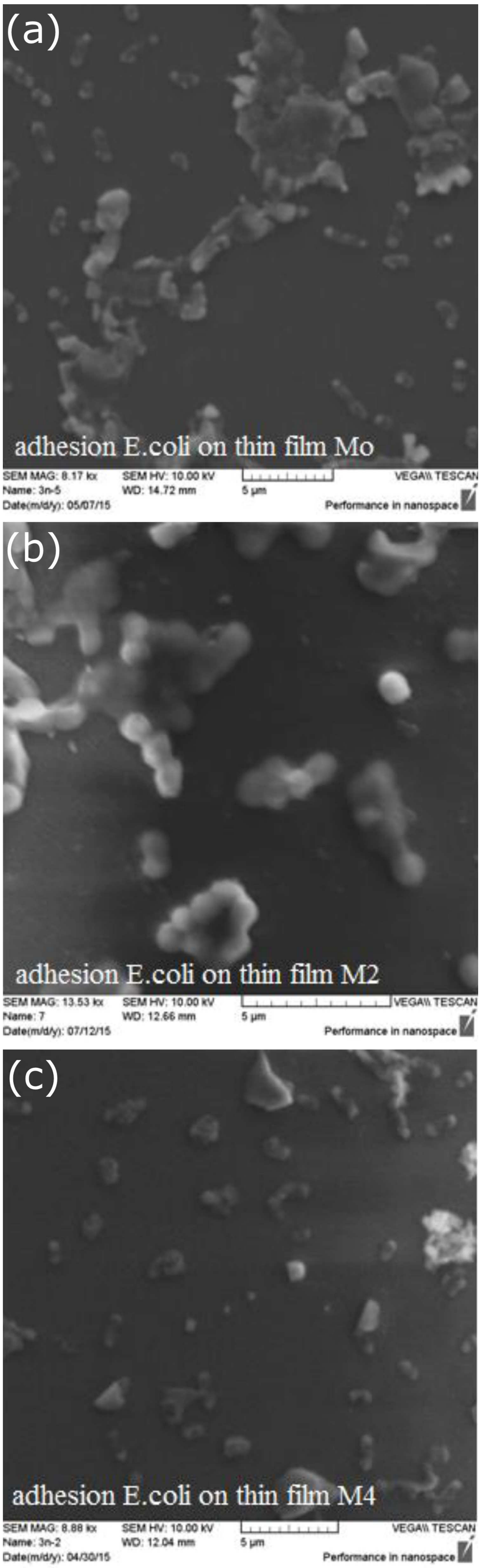

Fig. 6. SEM images of attaching *E. coli* bacteria on thin films samples during the exposition to UV light for 10 h: (a) M_0, (b) M_2, and (c) M_4.

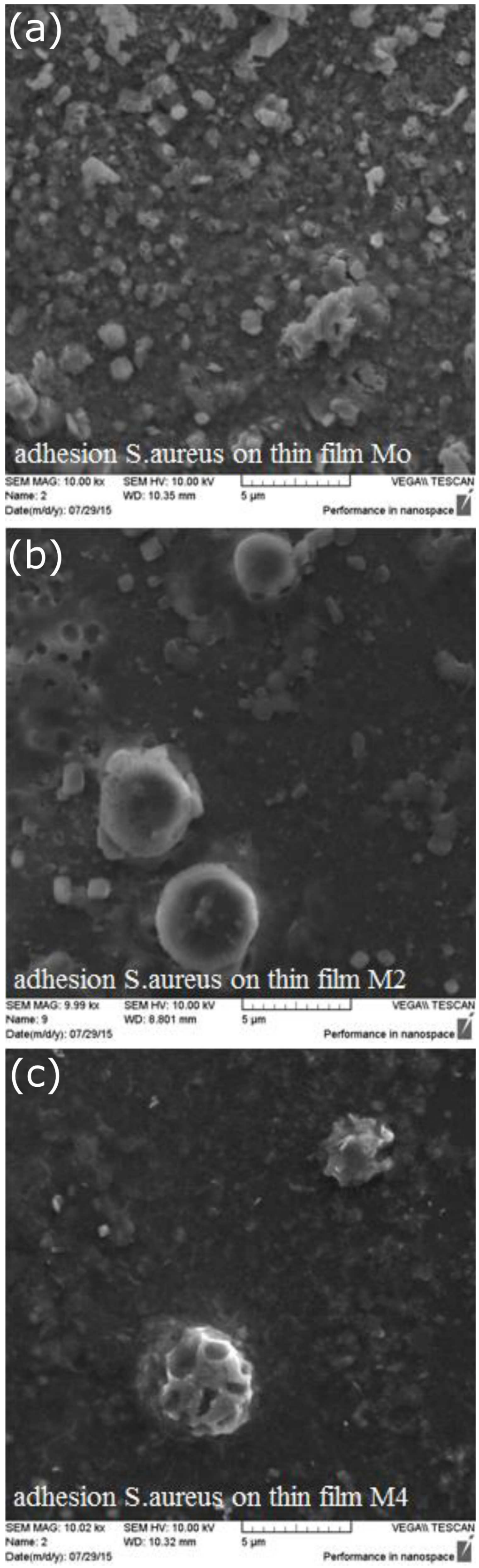

Fig. 7. As in Fig. 6, but for *S. aureus*.

after 10 h of exposed to UV light in the antibacterial test as shown in Fig. 4b and c and Fig. 5b and c, while pure CuO (0%) is found to be more effective against *S. aureus* compared with *E. coli* as shown in Fig. 4a and Fig. 5a, respectively. Since the antibacterial activity of CuO thin film is increased with the increasing Mn dopant concentration. Moreover, this enhanced antibacterial behavior is expected, because of reactive oxygen species (ROS) generated including OH groups by single-electron reduction which does not require UV irradiation [13, 14]. However, photocatalysis using UV illuminated induced oxygen in bacterial cells. Since it has been generally accepted that possible mechanism of antibacterial photoactivity of metal oxides is due to interaction with highly reactive oxygen species (ROS) which would result in oxidative damage of the cell membrane or inside the cells as demonstrate with *E. coli* and *S. aureus* with M_2 and M_4 of high percentage doping of Mn concentrations.

3.4. SEM of bacteria morphology

The SEM images demonstrate the adhesion of Gram-positive and Gram-negative organism's on three types of thin films samples M_0 (0%), M_2 (2%), M_4 (4%) through the exposure to UV light for 10 h as illustrated in Figs. 6 and 7, respectively.

The possible reason of the current result is due to the ROS generation including OH groups during photocatalysis using UV illumination which makes the rough surface of Mn doping CuO thin films very smooth and suitable for attachment to the cells. This demonstrates that thin films (M_2 and M_4) possess high antibacterial properties as compared with M_0 thin film. Since the roughness profile indicates an increase in particle height with Mn doping incorporation, the surface of films become rougher.

4. Conclusions

Spray pyrolysis method was used to prepare CuO thin film with Mn doped CuO with different volume ratios (0%, 2%, and 4%). The structural, morphological, and antibacterial properties were studied as a function of Mn dopant concentrations. From the results of XRD and SEM analysis, CuO film doped with 2% Mn illustrated a smoother surface compared with the other films. High concentration of Mn doped CuO thin films revealed high antibacterial activity against *E. coli* and *S. aureus*, after 24 h. The SEM images demonstrate the adhesion of Gram-positive and Gram-negative organism's on three types of thin films samples due to ROS generation including OH groups during photocatalysis using UV illumination which makes the rough surface of Mn doping CuO thin films very smooth and suitable for attachment to the cells.

Acknowledgments

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