

Preparation ZnO:Ag nanoparticles as thin films by Sol-Gel technique for medical application

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تحضير جسيمات نانوية من اوكسيد الزنك والفضة كاغشية رقيقة باستخدام تقنية السائل الهلامي لاغراض التطبيقات الطبية.

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المستخلص:

في هذا البحث, تم تحضير غشاء رقيق من اوكسيد الزنك مطعم بالفضة ومرسب على قواعد زجاجية باستخدام تقنية السائل الهلامي والطلاء بالغطس. التوصيف والتضاد البكتيري للاغشية المحضرة تم تحقيقه. الخواص التركيبية للاغشية المضرة درست من خلال قياسات حيود الاشعة السينية, تجانس وخشونة السطح للاغشية الرقيقة تم توصيفها باستخدام مجهر القوى الذرية, قياسات الخواص البصرية للاغشية المستحصل عليها تم تحقيقها باستخدام مطياف الضوء المرئي وال فوق البنفسجي وايضا اختبارات فعالية التضاد البكتيري ضد بكتيريا اليكوال درست. النتائج اظهرت تضاد بكتيري عند محتوى 10% فضة كانت 70% فعالية وعند محتوى 5% فضة كانت 10% فعالية.

الكلمات المفتاحية: اغشية اوكسيد الزنكوالفضة, تقنية السائل الهلامي, التضاد البكتيري, جسيمات نانوية.

Abstract:

In this research , silver doped ZnO was prepared as thin films deposited on a glass substrate by sol gel technique and dipping coating. The characterization and antimicrobial prepared thin films was investigated. Structural properties of thin films were studied from measurement of x-ray (XRD), homogeneous and roughness of thin films surface was diagnosed by atomic force microscopy (AFM), optical properties measurement for obtained thin films investigated by used Uv-visible spectra and antibacterial activity test against E-coli bacteria were studied. The results showed antimicrobial activity about 70% of 10%Ag content and activity 10% for 5% Ag content studied.

Keywords: ZnO:Ag thin films; Sol-Gel technique; antibacterial; Nanoparticles.

Introduction

In the last few years there has been a growing interest in the improvement of new antibacterial materials has been seen as result to the spread of anti-microbial safe contaminations, which has turned into a significant issue in human health. A conceivable option is the combination of new in organics mixes with antimicrobial properties, since they have the benefit of toughness and in addition synthetic and physical steadiness over regular organics and anti-infection agents mixes [1]. Specifically, antimicrobial films had pulled in awesome enthusiasm since survival of microorganisms on surfaces can bring about the spread of the sicknesses [2] and the hazard danger upon inward breath antibacterial aggravates it's insignificant [3] looked at the powders-based frameworks. For instance, a few antimicrobial semiconductor materials, such as ZnO had been doped with Ag [4], Cu [5] and Pt [6]. Many approaches is the use of a low-cost ZnO matrix, since it has been to a great extent showed its ability to hinder the development of micro organisms, too to go about as a high-extend antibacterial operator [6]. Moreover, it's conceivable to be acquired as films with high sturdiness and improved mechanical properties [2] and additionally high straight forwardness, which makes it in a perfect world for glass-windows [4]. These properties make ZnO alluring in places where high cleanliness it's important [6]. Hence, a different methods were utilized to plan ZnO thin films, for example, radio recurrence (RF)

sputtering process [1], CVD techniques [7], beat laser affidavit [8], shower prolepsis [3], nuclear layer statement [9], compound shower testimony [10] or, then again electro deposition [11]. Most of these systems generally require costly and muddled gear setup. A conceivable option is the sol- gel process, which permits obtaining a strong film by utilizing a sol or a gel as a middle advance, with much lower temperatures than the typically required by conventional techniques, in addition to it is especially proficient in deliver very straight forward movies on various substrates at generally minimal effort [9]. A few endeavors have been led keeping in mind the end goal to acquire sol-gel determined ZnO films, beginning with the utilization of zinc acetic acid derivation as metal antecedent, 2-methoxyethanol or ethanol as dissolvable, and mono ethanolamine or, on the other hand dim ethylamine as stabilizer [10]. In any case, the utilization of 2-methoxyethanol is not recommendable due its high harmfulness, and the ethanol frameworks are not exactly steady. A conceivable option is the joining of a polymer into the zinc-sol arrangement like the poly vinyl pyridine (PVP) [3], which could balance out the sol, as well as could diminish the presented film-worry amid the strengthening strategies, and, as likewise augments increase the thickness of the sol, improves the thickness and decreases the split development. In this work, ZnO antibacterial-films doped with silver were synthesis by the sol- gel

technique and deposition by dipping method. The basic, and in addition the antibacterial properties were assessed against *E. Coli* microscopic organisms.

Materials and Methods:

Zinc acetate [$\text{Zn}(\text{CH}_3\text{COOH})_2$] silver nitrate $\text{Ag}(\text{NO}_3)_2$ are used as main materials, iso propanol as solvent and mono ethanolamine as a stabilizer in this work. First iso propanol were mixed with zinc acetate by a magnetic stirrer for 1 hour at 60°C and then was slowly dropped into the above solution of the mono ethanolamine and we putted it on a magnetic stirrer for 1 hour and then agent for one day. The ratio of zinc acetate and stabilizer was 75% and the molarity of zinc acetate was 0.5 molar, for synthesis ZnO pure, and then doping with Ag at ratio with zinc acetate (5 and 10)%. The substrate cleaned by acetone, methanol and distilled water by used ultrasonic bath for 15 minutes, then dried by N_2 gas. The dimensional the using substrate was (2x2) cm. dipping method used to preparation samples. The sample was dried at 100°C for 5 minutes. After that, the samples were annealed at 450°C , figure (1) indicated the flowchart experimental methods used in the preparation of samples. Table (1) represent all samples were prepared in the experimental work. To calculate the band gap energy used Tauc's relation which is given by in equation [7]:

$$(5)(\alpha h\nu) = A(h\nu - E_g)^n$$

Where α , E_g and $h\nu$ are “absorption coefficient”, “band gap energy” and “photon energy”, respectively. ‘n’ is equal to 2 for “indirect” and 1/2 for “direct band-gap” semiconductor, respectively [5]. To assess the effect on

bacterial development because of the composition of the sol-gel ZnO and ZnO:Ag films, *E. Coli* micro organisms got by a waste water test was utilized, and was refined vigorously in splendid green medium, at 37°C on a turning rotator (120 rpm) with 8 h, and kept up in Eosin Methylene Blue (EMB) agar plates (Becton Dickinson), at a similar temperature over night. Afterward, 50 mL of splendid green stock was included a 250 mL Erlenmeyer flagon, and posterior was vaccinated specifically utilizing a bacteriological circle from EMB agar plates. They got societies were kept up at 37°C over night. At long last, 1 mL from the past immunize framework was added to another Erlenmeyer jar with new medium to finish the antibacterial action examine. The effect on development *E. coli* on films was assessed through the introduction of (1) cm of the ZnO, surfaces doped with different silver substance and the Settlement framing unit (FCU) was evaluated in EMB agar plates. All trials were completed by triplicate.

Table (1) ZnO/Ag sample and thickness

Name of samples	Thickness μm	Ratio of Zn:Ag
S1	0.75	100:0
S2	0.81	95:5
S3	0.79	90:10

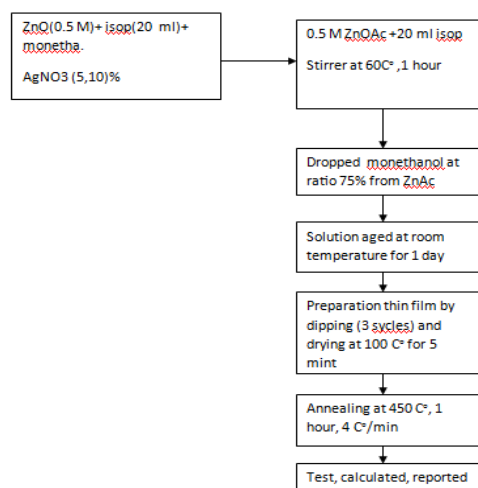


Figure (1) flowchart of preparation ZnO/Ag thin films

Results and Discussion

Figure (2) shows the XRD patterns of ZnO:Ag thin films at two percentage Ag-doped and annealing 450 °C polycrystalline for all samples and its agree with international card (ICDD 39-1451). The (101) plane represent the crystalline trend for all samples and the structure was hexagonal phase for ZnO and the other peaks correspond to FCC metallic Ag phase. Figure (2,c1) shows the pure phase of ZnO has the peaks (101,102,110) planes ,figure(2,c2,c3)shows the phase of the Ag, which it has the peaks (100,002,101) planes. The results showed crystalline structural of zinc oxide was affected by doping process, with all samples preserved the hexagonal phase and the peaks of ZnO is fluctuation around the diffraction angle. The results about structure parameter showed the crystalline size decrease from (31-13) nm with increasing doping of Ag, micro strain decrease from (0.32-0.0076), dislocation density increase from

(1.04-5.91) cm^{-2} and number of crystaled increase from (1.51-20.45) $\times 10^{12} / \text{cm}^2$. This is change in structure specification due to the different in size between silver ion and zinc ion, see table (2).

Table (2) the structure parameters.

Samples name	2 θ degree	FWHM	D_{avg} nm	microstrain	Dislocation density δ $\times 10^{11}/\text{cm}^2$	Number of crysted $\times 10^{11}/\text{cm}^2$
ZnO pure	25.45	0.0049	31	0.32	1.04	1.51
ZnO:5%Ag	25.48	0.0082	17	0.14	3.46	9.15
ZnO:10%Ag	25.49	0.0111	13	0.0076	5.91	20.48

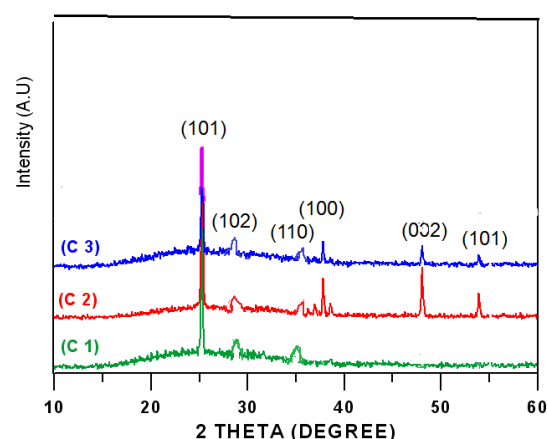


Figure (2) XRD analysis (c1) for ZnO pour , (c2) for ZnO:5%Ag and (c3) ZnO:10%Ag.

Figure (3) represented the image of the surface by AFM, the roughness, RMS, distribution grain size of thin films surface were measured. The image of AFM was in 3-Dimensional. The image showed the samples surface uniformly distributed and the distribution grain size in nanometer. Grain size decreases with increasing Ag content, this is decreasing belong to doping where the silver is enhancement of surface properties. Table (3) represents the parameters of measurements AFM

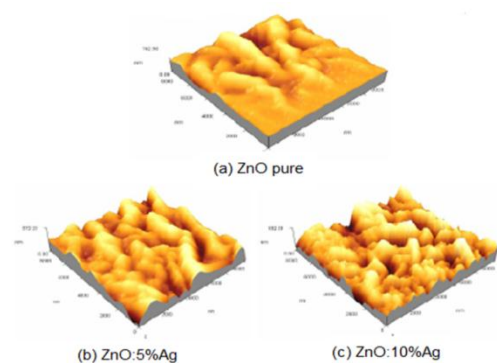


Figure (3) AFM analysis (a) ZnO pure, (b) ZnO:5%Ag, (c) ZnO:10%Ag.

Table (3) the results of AFM measurements.

Samples	Surface Roughness (nm)	RMS (nm)	Distribution grain size (nm)
S1	54.20	74.50	92.4
S2	26.40	33.90	81.56
S3	21.10	26.50	73.44

Figure (4) indicates the optical absorption for samples of ZnO:Ag thin films, the wavelength range was 270–700 nm. There are two regions; one is strong transmittance ($\lambda \leq 295$ nm) and other is strong transmittance region ($\lambda \geq 340$ nm). The first region, represented pure sample and second region represent doping phase. At visible region, the average transmittance of all samples is 80%. From figure (5) energy gap was calculated [9]. The energy band gap of ZnO thin films was 3.85 eV and other ZnO:Ag were 3.81 eV and 3.72 eV respectively. As the reported optical band gap value of ZnO thin film is less than the calculated value, this might be

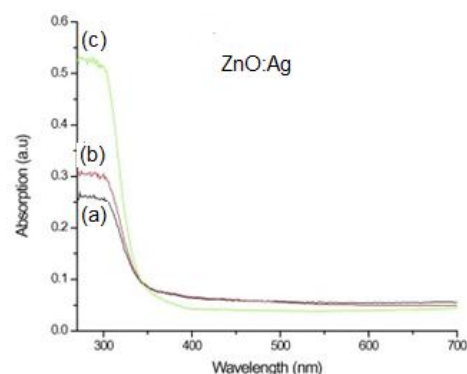
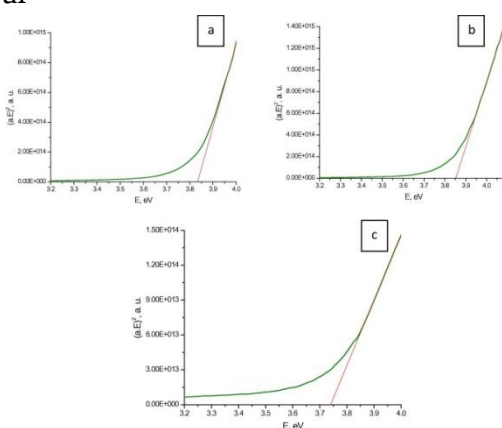


Figure (4) Optical absorption (a) ZnO, (b) ZnO:5%Ag, (c) ZnO:10%Ag.

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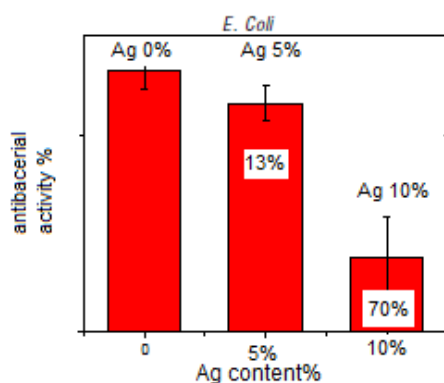


Figure(5)The energy gap of (a) ZnO, (b) ZnO:5%Ag, (c) ZnO:10%Ag.

For the antibacterial test, CUF counting method was used. The system used work by growth the bacteria *E. coli* on the films in special systems and leave it for a period of time and then calculated how much the bacteria kill around the films, figure (6) evaluated the process. However, the antimicrobial ratio of the three samples reaches up to 13% when 5% Ag was doping more than the ZnO pure and 70% killing when 10% Ag was doping more than effect of ZnO pure. Figure (7) documents the results of antibody bacterial for all samples.



Figure (6) represent CFU counting method



Figure(6) : *E.Coli* uncovered to ZnO thin films and ZnO:Ag at two Ag content

Conclusions

In this work a thin films of ZnO:Ag prepared by Sol-Gel technology was successfully as an antibacterial against *E-coli* bacteria. The addition of silver has improved the structural and optical properties of thin films prepared. The killing of bacteria has also improved to more than 13% when doping of silver was 5% and more than 70% when doping 10%Ag.

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