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Fabrication of ZnO-Ag Nanocomposite and Their Antibacterial Activities

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Abstract

ZnO nanopowder was synthesized by a simple hydrothermal technique using zinc acetate and Triethanolamine (TEA) as surfactant agents. The resultant powder was annealed at 140 °C for 12 hours. The as – synthesized ZnO nanopowder was then mixed with AgNO3 to prepare ZnO-Ag nanocomposites. The structural, morphological, and optical properties were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV-Visible spectroscopy (UV-Vis). The results confirm that Ag nanoparticles (NPs) have been covered the ZnO hexagonal NPs, and show the redshift with the peak centered at 334 nm, because the interfacial electron coupling between ZnO and Ag NPs, the surface Plasmon peak centered at 403 nm was detected along with the excitonic peak of ZnO confirming the formation of ZnO-Ag nanocomposite. The antibacterial effect of ZnO - Ag nanocomposites was studied for Gram- negative (E.coli) and Gram– positive (Staphylococcus aureus), which showed that the diameter of the inhibition zone of pathogenic bacteria about 15 mm for E.coli and did not show any activity for Staphylococcus aureus.

Key words: ZnO-Ag nanocomposites, hydrothermal, TEA, antibacterial.

الخلاصة

في هذا العمل، تحضير جزيئات أوكسيد الخارصين بواسطة تقنية مائية حرارية بسيطة باستخدام خلات الخارصين و ثلاثي الايثيلامين كعامل مساعد للتفاعل. تم تلدين المسحوق الناتج عند 140 درجة مئوية لمدة 12 ساعة. ثم تم خلطها مع نترات الفضة لتحضير مركبات اوكسيد الخارصين- الفضة النانوية. وقد تم دراسة الخصائص الهيكلية وخصائص السطح والبصرية بحيود الأشعة السينية والمجهر الإلكتروني الماسح والأطياف المرئية للأشعة فوق البنفسجية حيث اكدت النتائج ان جسيمات الفضة المكعبة التركيب النانوية تغطي اوكسيد الخارصين ذو التركيب السداسي في حين تظهر نتائج الاشعة فوق البنفسجية انحياز نحو الاطوال الموجية الحمراء مقارنة مع اوكسيد الخارصين النقي وتم ملاحظة قمة البلازمون التي تؤكد تكوين المركبات النانوية. تم دراسة التاثير المضاد للبكتيريا لمركبات اوكسيد الخارصين - الفضة النانوية ضد بكتيريا جرام السالبة (الاشريكية القولونية) وبكتريا جرام الموجبة (المكورات العنقودية الذهبية), أظهرت النتائج أن قطر منطقة تثبيط البكتيريا المسببة للأمراض حوالي 15 ملم للإشريكية القولونية ولم تضهر اي نتيجة للمكورات العنقودية الذهبية.

Introduction

Nanotechnology, include manufacturing of materials at the atomic level to have unique properties, which can be applied for the desirable application [1]. Small organic and inorganic particles are getting wide attention in medical application because their ability to biological functionalization [2]. One of the most interesting areas of NPs is the fabrication of composites materials [3]. Nanocomposite materials including semiconductors and metals are important, due to their unique optical, electrical, biomedical, and catalytic properties [4]. Metal oxide nanostructure with controlled dimension are forming an essential foundation for making varied superstructures, which are scientifically important in chemical science, natural philosophy, textile science, biology and medicine [5][6]. Among nanocomposite structure, the ZnO-Ag has gained a great attention not only because ZnO is less toxic and desirable semiconductor but it's direct wide band gap 3.37 eV with large exciton binding energy of 60 meV. It's high chemical stability make it suitable for many applications. Furthermore, it is a bactericide and effective to inhibit both Gram- negative and Gram- positive bacteria [7][8]. Also silver nanoparticle has long been known to have strong toxicity to a wide range of micro- organisms; for this reason silver based compound has been used enormously in many bacterial applications [9].

Fabrication method such as microwave synthesis, sol-gel, hydrothermal, solid state, and pulsed laser ablation were used for synthesis of ZnO nanoparticles [10]. In this work, ZnO-Ag nanocomposite have been fabricated by hydrothermal technique using (TEA) as surfactant agent. Furthermore, the prepared nanocomposite was investigated for antibacterial activity using both Gram-negative and Gram- positive bacteria.

Materials and Methodology

Synthesis of Nano-Zinc Oxide via Hydrothermal Technique

Zinc oxide nanopowder was synthesized via hydrothermal technique. 1M aqueous solution of zinc acetate dehydrate was mixed with 1 ml TEA as surfactant agent and the solution PH was adjusted at 12 using 2.5 M sodium hydroxide. The solution reaction mixture transfer in a hydrothermal cell for 5 h at 200 ºC. The resulting ZnO nanopowder was washed several times with absolute ethanol to remove any residual salt and centrifuged at 4000 rpm for 15 min. Finally the resultant powders were dried under air Atmosphere.

Annealing of Prepared ZnO Nanopowders

ZnO nanopowder were annealed at 140 ºC for 12 h and using microwave assisted technology. Then, were allowed to cool down naturally to room temperature prior to characterization.

Preparation of ZnO-Ag nanoparticles

In typical synthesis, 0.3 g of the prepared ZnO nanopowder was dipresed in 10 ml of distilled water (DW) under magnetic stirrer for 30 min. After stirring, 0.3 g of $AgNO_3$ was dissolved in the above solution under constant stirring for 1 h. Then, the product was collected and washed with DW and redipresed in 15 ml of DW with 0.2 ml hydrazine hydrate as reducing agent under constant stirrer for 20 min, then collected and washed with DW and left to dry at 80 ºC for 1 hour.

Results and Discussion

Crystalline structure (X-ray diffraction analysis)

X- ray diffraction was studied to identify the crystal structure and phases of the synthesized ZnO NPs and ZnO-Ag nanocomposites. The XRD patterns of as – prepared ZnO NPs are shown in figure 1, where pattern A represent the ZnO peaks without annealing and pattern B represent the ZnO peaks annealed at 140ºC for 12 hours. The two patterns show several diffraction peaks were appeared in the pattern at 2θ (degrees) of 31.7º, 34.4º, 36.2º, 47.7º, 56.6º, 62.9º,67.8º, 69.1º, and 77.1º which correspond to the lattice planes of (100), (002), (101), (102), (110), (103), (112), (201), and (202), respectively for the wurtzite hexagonal phase of ZnO NPs. The diffraction peaks are matched with the (JCPDS card no. 36-1451) with lattice constant a= 0.325 nm and c= 0.524 nm. Diffraction peaks contain some impurities of metallic Zn are observed in the pattern which marked by (*). The peaks placed at 2θ= 38.11º, 44.3º, and 64.5º in C pattern are the characteristics of face- center- cubic structure of metal Ag (JCPDS card no. 04-0783). The diffraction peaks confirm that the nanocomposite consist of both Ag and ZnO NPs. However, the diffraction peaks of ZnO from nanocompsite are broader and weaker in intensity compared with ZnO NPs. This is due to ZnO NPs was encapsulated inside Ag NPs.

The crystal size (D) was calculated based on the width of the peak due to (101) for ZnO NPs and (111) for Ag NPs planes by using the Scherrer's formula [11]:

$$D = \frac{K\lambda}{\beta \cos\theta} \ldots\ldots (1)$$

Where k is a constant (k = 0.9), λ is the wavelength of X-ray used, β is the full-width at the half maximum (FWHM) of the diffraction peak and θ is the Bragg angle.

It was found that ZnO nanoparticles have an average crystallite size about 4 nm to 5 nm and changing with annealing temperature and 5.7 nm for Ag nanoparticles.

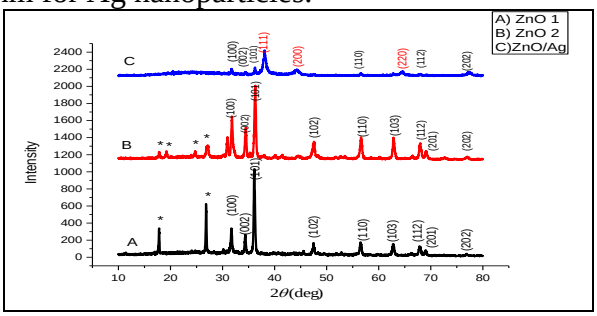

Figure 1. XRD patterns: A) ZnO without

annealing, B) ZnO annealed at 140°C for 12 h., C) ZnO-Ag nanocomposites.

Morphological Structure (FESEM) Analysis

FESEM was used to investigate the morphological structure of as – prepared ZnO NPs and ZnO - Ag nanocomposites. As seen in figure 2 (A) the morphology of ZnO NPs has unclear formation of nanoparticles, but by annealing ZnO at 140° C for 12 hours enhanced the formation to clear nanoparticles, some of them possess hexagonal phase with average particle size 113.53 nm as shown in Figure 2 (B) , while the morphological structure of ZnO-Ag nanocomposites in Figure 2 (C) illustrate the formation of ZnO NPs covered by small un uniform distributed Ag NPs with thickness about 40.51 µm as can be seen in Figure 2 (D) of the cross section.

UV−Vis Absorption analysis

UV-Vis analysis of ZnO and ZnO - Ag nanocomposites are shown in figure 3, where ZnO NPs without annealing have a strong peak at 381 nm and 361 nm for the annealed ZnO NPs. The presence of these peaks corresponds to the high crystalline nature of the nanoparticle with surface defects. ZnO - Ag nanocomposite show redshift with the peak centered at 334 nm, which isbecausethe interfacial electron coupling between ZnO and Ag NPs. The surface Plasmon peak centered at 403 nm detects along with the excitonic peak of ZnO confirming the formation of ZnO-Ag nanocomposite.

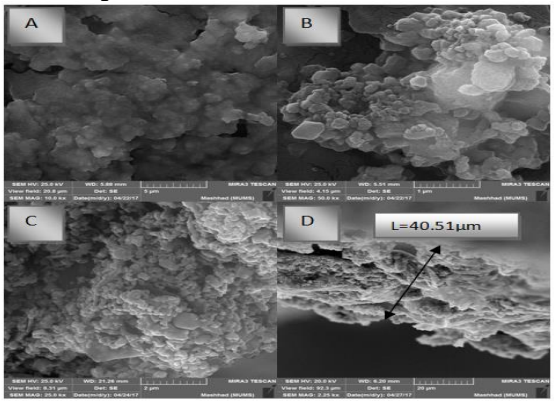

Figure 2. FESEM images of (A) ZnO without annealing, (B) ZnO annealed at 140 °C for 12 h, (C) ZnO -Ag nanocomposite, (D) cross section of ZnO -Ag nanocomposite.

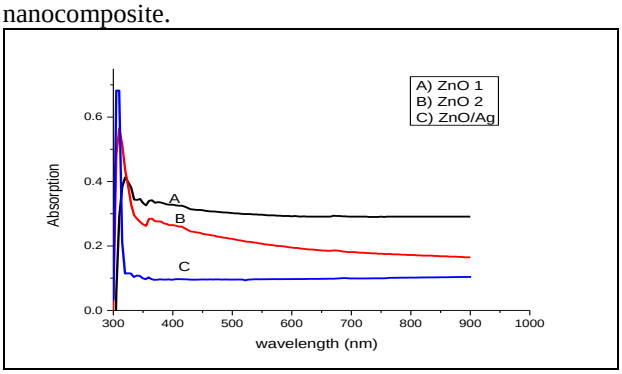

Figure 3. UV−Vis absorption spectra: A) ZnO Nps without annealing, B) ZnO NPs annealed at 140 °C for 12 h, C) ZnO -Ag nanocomposite.

Antibacterial activity

The bacterial growth on the nutrient agar surface of E.coli and staphylococcus aureus against certain concentration of ZnO -Ag nanocomposite is shown in Figure 4. It is obveous that the bacterial growth decreases for E.coli, which was measured and recorded in millimeter and found to be about 15 mm. In the case of staphylococcus aureus, there is no clear activity for ZnO-Ag nanocomposite. This difference due to structural and chemical compositional difference of the cell membrane of different kind of micro – organisms [12].

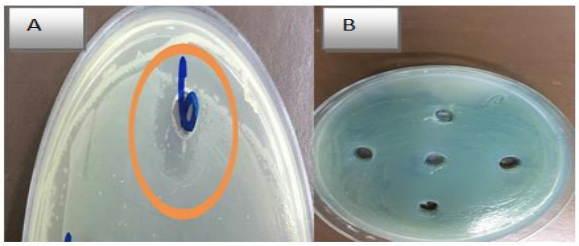

Figure 4. Inhibition zone photographs of ZnO-Ag nanocomposite against: (A) E.coli and (B) staphylococcus aureus.

Conclusions

Hydrothermal synthesis of ZnO-Ag nanocomposite revealed a good structural, morphological, and optical properties. The characterization result confirms the formation of cubic Ag NPs on the hexagonal structure of ZnO NPs. And optical properties show a red shift with the peak centered at 334 nm, which is due to the interfacial electron coupling between ZnO and Ag NPs. The surface

Plasmon peak centered at 403 nm detects along with the existence peak of ZnO confirming the formation of ZnO-Ag nanocomposite. However, the antibacterial activity of ZnO-Ag nanocomposite showed that the E.coli inhibition zone is higher than of staphylococcus aureus which has no activity at all. Antibacterial effect can be related to the destruction of cell membranes, which leads to leakage of cell contents and cell death.

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