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ZnO Nanoflakes on Pb Plates with Antibacterial Effects by Electrochemical and Hydrothermal Deposition

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Abstract: *ZnO nanoflakes were grown on the lead (Pb) plates using the electro- hydrothermal deposition methods. To investigate the influence of electrodeposition current, the ZnO seed layer was electrodeposited on the lead plates at a larger current of 160 mA (current density of 40 mA/cm^2) and a smaller current of 12 mA (current density of 3mA/cm^2), respectively. Then, ZnO nanoflakes were grown on top of the seed layer. Multiple analyses including field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), photoluminescence (PL) were performed on the ZnO nanostructures/Pb plates. Furthermore, surface contact angle measurements were conducted to study the hydrophobic properties and OD 600 antibacterial tests were used to investigate the antiseptic effects. Results indicate that the ZnO nanoflakes with the seed layer grown at a lower current of 12 mA exhibited good hydrophobic properties and strong antibacterial effects. ZnO nanoflakes/Pb plates show promising for future anti-radiation, antibacterial, and waterproof lead clothing applications.*

Keywords: ZnO nanoflakes, lead plates, seed layer, current, hydrophobicity, antiseptic

1. INTRODUCTION

ZnO [1] nanostructures have been receiving growing attention for their versatile applications. Recently, ZnO-related nanostrucutres have been proposed for electronic [2], optical [3], and biomedical devices [4]. Meanwhile, incorporating ZnO nanostructures on metal plates have been reported for material and biomedical analysis [5]. ZnO nanostructures on graphene/silicon substrates [6] and silver wires [7] have been demonstrated for their hydrophobic and antiseptic properties. In this research, we deposited ZnO nanostructures on top of the lead (Pb) plates, which were used for radiation protection [8], anti-corrosion applications [9], and batteries [10]. However, the lead plates integrated with ZnO nanostructures have not been clearly reported until now. In this study, we electrodeposited the ZnO seed layer with two different currents (a larger current of 160 mA and a small current of 12 mA [4][11]) on Pb plates. The electrodeposition current provided the electrons for the chemical reactions during the growth. If the current was too large, the growth might be too fast and inferior crystalline structures might be generated. On the other hand, if the current was too small, insufficient electrons might result in failure to growth. We chose two appropriate currents so that the nanostructures could be deposited on the Pb substrates and we investigate the relationship between the current and the nanostructure growth.

In our experiment, ZnO nanostructures were hydrothermally deposited on top of the seed layer. To examine the two types of the ZnO nanostructures on the lead plates, multiple analyses have been performed to investigate the material, optical, and antibacterial properties of ZnO nanostructures on Pb plates. Results indicate that the ZnO nanoflakes with the seed layer grown at a lower cur-

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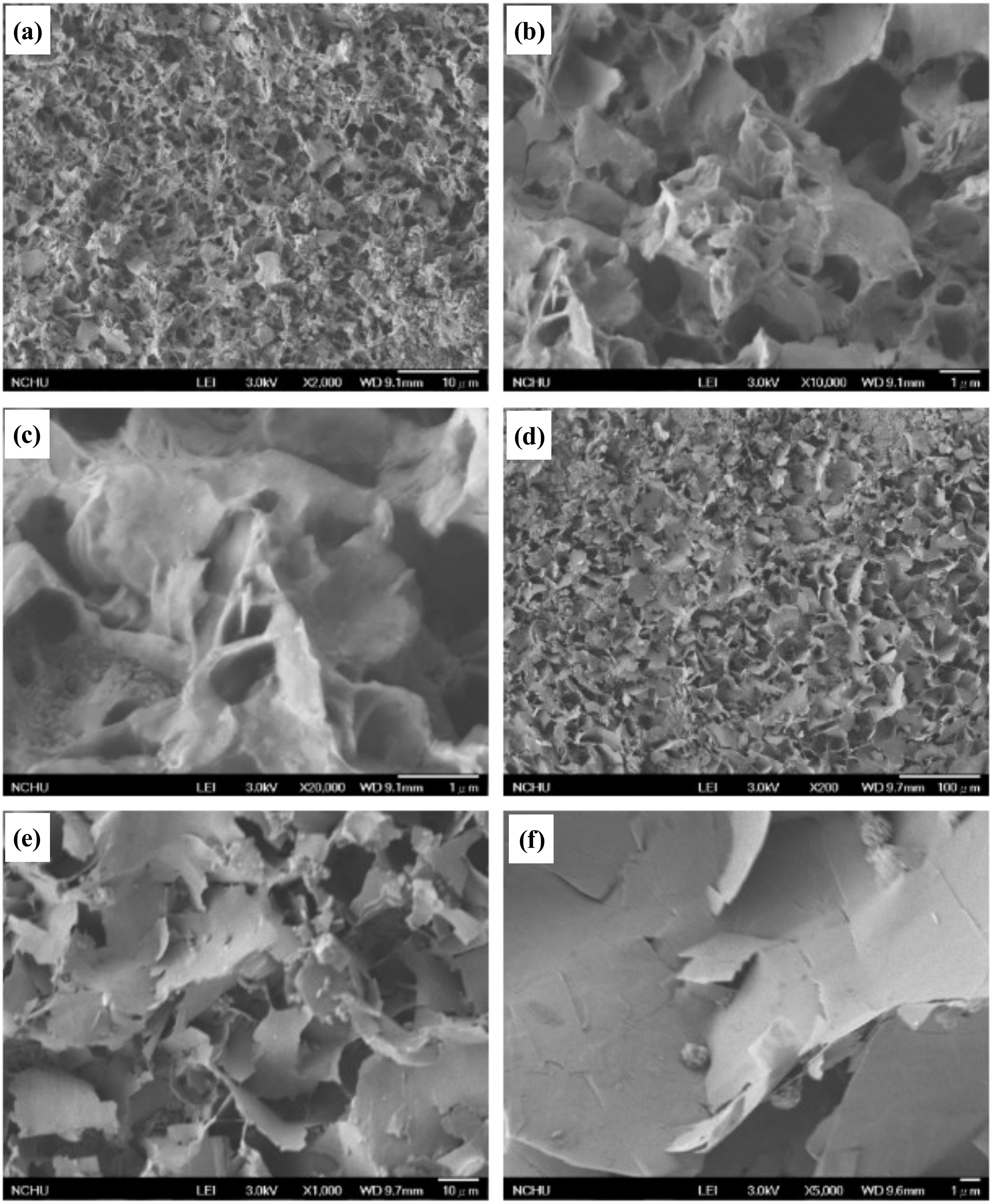

Figure 1. FESEM images of the ZnO nanoflakes with the seed layer grown at a larger current of 160 mA with a magnification rate of (a) 2000, (b) 5000, and (c) 10000. FESEM images of the ZnO nanoflakes with the seed layer grown at a smaller current of 12 mA with a magnification rate of (d) 200 , (e) 500 , and (f) 1000 FESEM.

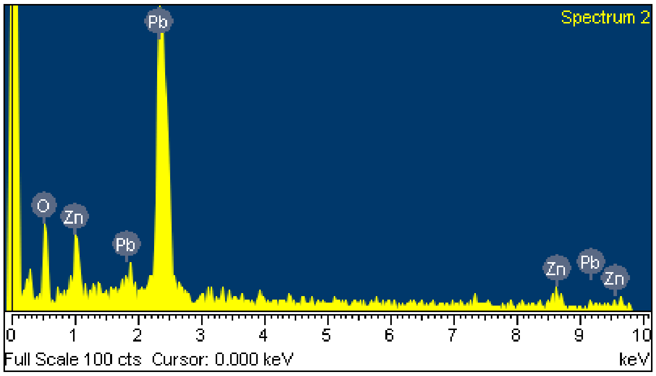

Figure 2. An EDX spectrum of ZnO nanoflakes on the lead plate.

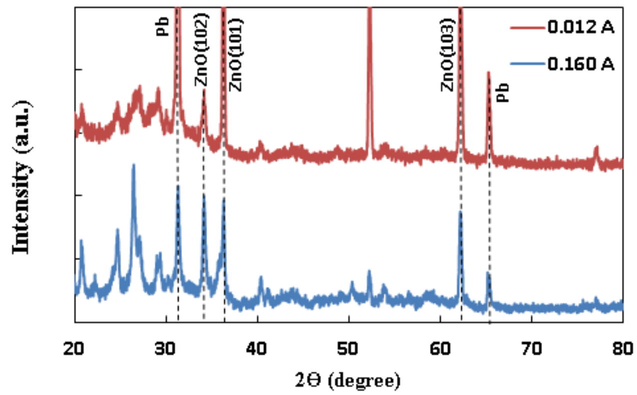

Figure 3. XRD of ZnO nanorods with the seed layers grown at a smaller current of 12mA and a larger current of 160mA.

rent of 12 mA possessed larger-sized uniformly-grown nanoflakes with good hydrophobic properties and strong antibacterial effects. On the other hand, the ZnO nanoflakes with the seed layer grown at a larger current of 160 mA obtained smaller-sized of irregular nanoflakes with hydrophilic properties and strong antibacterial effects. Moreover, the two types of the nanostructures exhibited different crystalline structures and optical properties. It is widely known that lead plates are used for medical clothing [12, 13] for their anti-radiative and anti-corrosion behaviors [14, 15]. For example, patients always have to wear lead clothing when undergoing dental X-ray examinations. ZnO nanoflakes on Pb substrates might be helpful to develop future medical anti-radiation clothing.

2. EXPERIMENTAL DETAIL

Lead plates with an area of 2 cm*2 cm were prepared as the substrate. The substrate polishing processes were as follows. We used sand paper # 200 to polish the Pb substrate. Then, we rotated the substrate for 90º and polished the substrate with #400 sand paper. Followed by rotation of the substrate for 90º, the substrate was polished by # 600. The same process was continued with #800 and #1000 sand papers. To deposit nanostructures on top of the lead substrate, the plates were first polished. Followed by polishing, the ZnO seed layer was grown on the polished substrate with the plating solution of $Zn(NO_3)_2$ and KNO_3. The electroplating solution consisted of $Zn(NO_3)_2 \cdot 6H_2O$ for 0.1M and KNO_3 for 0.1 M. The electrochemical deposition currents were set as a smaller current of 12mA and a larger current of 160mA, respectively. The area of the Pb substrate was 2cmX2cm ($4cm^2$). As the current was 160 mA, the current density was 40 mA/cm^2. While the current was 12 mA, the current density was $3mA/cm^2$. The temperature of the plating solution was set as 70ºC. Then, ZnO nanostructures were hydrothermally deposited on top of the seed layer for 1 hour with a deposition temperature of 80ºC. To observe the ZnO nanostructures on top of the lead plates, Field emission scanning electron microscopy (FESEM) was used to observe the surface morphologies and energy-dispersive X-ray spectroscopy (EDX) was measured to study the element compositions. Furthermore, X-ray diffraction (XRD) was used to study the crystalline structures and contact angle measurements were used to investigate the hydrophobic or hydrophilic properties on the surface of the ZnO nanostructures/Pb plates. Furthermore, photoluminescence (PL) was used to study the optical properties. To investigate the antibacterial property, OD 600 test was used to study bacterial suppression capability. Escherichia coli (E coli) bacterial were incubated in 16ml of lysogeny broth (LB) media for 4 hour. Each group of the samples was soaked with the bacterial solution. After the bacterial were incubated for various time with preirradiation by UV light. A spectrophotometer with OD 600 was used to evaluate density of bacteria.

3. RESULT AND DISCUSSION

To grow the ZnO nanostructures on top of the Pb plate, we electrochemically deposited a seed layer as an adhesion layer on top of the substrate. To investigate the influence of the seed layer, we grew the seed layer at a larger current of 160 mA and a smaller current of 12 mA, respectively. Then, ZnO nanostructures were hydrothermally deposited on the seed layer. To observe the surface morphologies of the ZnO nanorods grown in two different conditions, FESEM was used to view the morphologies of the ZnO nanostructures. As shown in Fig.1 (a), (b) and (c), the irregular or messy-like flake-like ZnO nanostructures can be seen on the images of the ZnO nanoflakes with the seed layer grown at a larger current of 160 mA. In the image with a lower magnification rate as shown in Fig.1 (a), nanoflakes well grown in a large area could be viewed. As the magnification rate increased, several irregular nanoflakes and flakes with various sizes could be clearly seen as shown in Fig.1 (b) and (c). As a comparison, ZnO nanostructures with the seed layer grown at a smaller electrodeposition current of 12 mA exhibited more arranged-like or regular nanoflakes as shown in Fig.1 (d) with a lower magnification rate. As the magnification rate increased, uniform-grown flakes and flakes with similar sizes can been seen as shown in Fig.1 (e) and (f). As the sizes of nanoflakes were compared, the nanoflakes with the seed layer electrodeposited at a smaller current were over 10 times larger than the flakes with the seed layer electrodeposited at a larger current.

To analyze the compositions of the ZnO nanostructures , EDX as shown in Fig.2 revealed the presence of Zn, O, and Pb element for the ZnO nanoflakes on the Pb plate. Since EDX was just a qualitative measurement and showed the existence of the elements on the sample, one EDX spectrum was shown.

To study the crystalline structures of the two types of the sam-

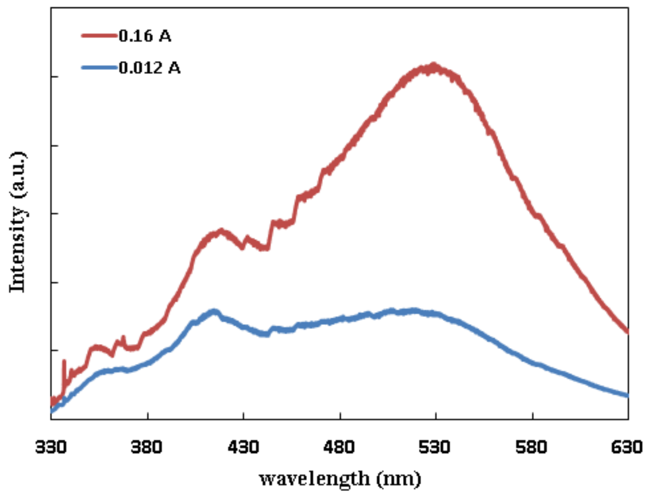

Figure 4. PL spectra of the ZnO nanorods with two types of the seed layer.

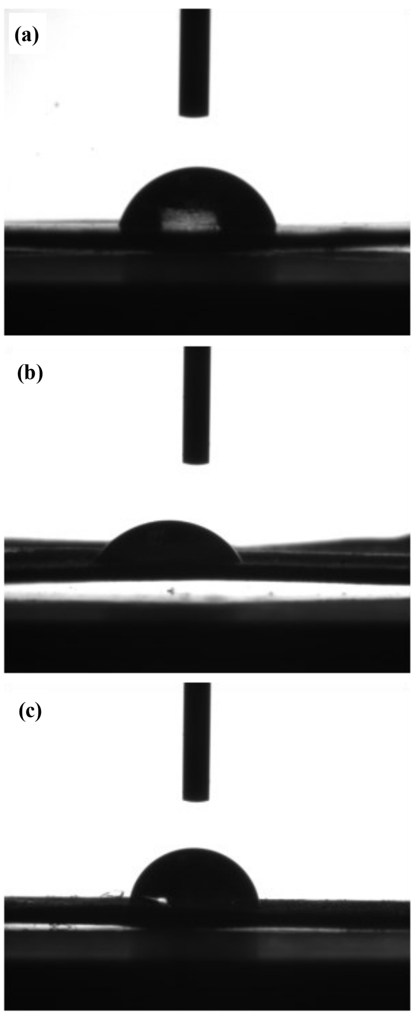

Figure 5. Contact angle measurements for (a) the Pb plate (b) the ZnO nanoflakes with the seed layer grown at a larger current of 160mA (b) the ZnO nanoflakes with the seed layer grown at a smaller current of 12mA

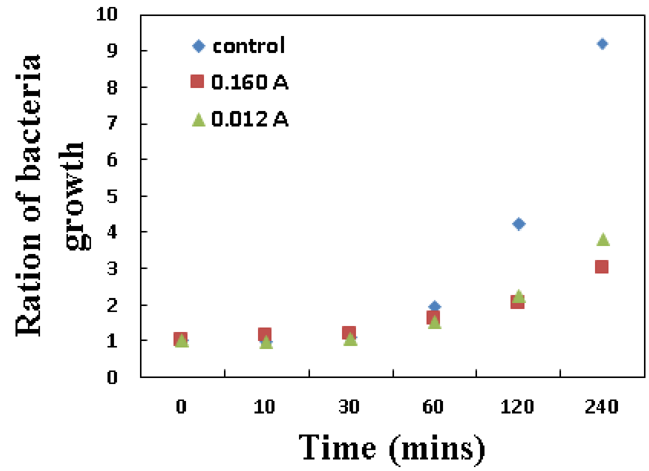

Figure 6. OD 600 antibacterial tests for the ZnO nanoflakes on the Pb plates.

ples, XRD spectra of the two samples are shown in Fig.3. Both of the XRD spectra show ZnO(102) , ZnO(101) , ZnO(103) and strong Pb signals. However, the ratios of the ZnO nanoflakes were different for the samples with the two types of the seed layer. The peak intensity for ZnO (102) , (101) , (103) were almost the same for the one with the seed layer grown at a larger current while the three peak intensities were quite different for the sample with the seed layer grown at a smaller current. Therefore, two types of crystalline structures can be observed for the samples with the seed layers grown in different currents.

To examine the optical properties of the two types of samples, photoluminescence (PL) measurements were performed as shown in Fig.4(a) and (b). Consistent with the FESEM images , the sample with the seed layer grown at a larger current showed stronger defect luminescence (around 530nm) while the sample with the seed layer grown at a smaller current showed weaker defect luminescence intensity. To study the hydrophobic properties of the ZnO nanostructures, surface contact angle measurements were conducted on the Pb plate and the two types of the samples as shown in Fig.5(a), (b) and (c). Results indicate that the contact angle for the lead plate without the nanostructure was 71^o, the contact angle for the sample with the seed layer grown at a larger current was 63^o, and the contact angle for the sample with the seed layer grown at a smaller current was 83^o. The plate with the messy-like nanostructure may decrease the hydrophobicity as the previous research indicated [6]. Therefore, the sample with the seed layer grown at a larger current might have inferior hydrophobic properties. On the other hand, the regular and uniform flake-like structure has higher density of nanoflakes. (Larger flakes and less void areas) Therefore, the higher density of nanoflakes might enhance the hydrophobicity, based on previous reports, higher density of ZnO nanostructures would result in higher hydrophobicity of the surface.

Finally, to examine the antibacterial capability, the OD 600 tests were performed on the two types of the samples. The tests show that both of the samples exhibited strong antibacterial capability (more than 50%) as the tested time lasted over 2 hours. Moreover, the sample with the seed layer grown at a larger current showed stronger antibacterial effects. The results were consistent with our previous research indicating more messy-like nanostructures might express stronger bacterial effects because of the larger surface contact area [6]. In addition, ZnO nanoflakes/Pb plates fabricated in two different conditions exhibited excellent bacterial suppression capability.

4. CONCLUSION

ZnO nanoflakes were grown on the lead plates. Two types of the samples with the seed layers deposited at a larger current of 160mA and a smaller current of 12 mA were fabricated. To compare the two types of the samples, multiple material characterizations including FESEM, EDX , and XRD were performed. Furthermore, surface contact angle measurements were conducted to study the hydrophobic effects of the nanostructures. Moreover, OD 600 tests were used to investigate the antiseptic properties of the samples. Results indicate that the ZnO nanoflakes/Pb plates exhibited excellent bacterial suppression capability. In addition, ZnO nanoflakes/Pb plates with the seed layer grown at a lower electrochemical deposition current of 12mA (current density of $3mA/cm^2$) could possess the hydrophobic effect. Inclusion of ZnO nanostructures on top of the lead plates as components of the lead clothing can further enhance the antiseptic and waterproof capability. Addition of ZnO nanostructures on Pb plates may further shield bacteria and water-attachment to form multi-protective (radiation, corrosion, bacteria, and water) medical clothing materials. The ZnO nanoflakes/ Pb plates may be useful for future lead clothing applications.

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