Direct Electrodeposition of Zno Nanosheets Film on Plastic Substrate

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Abstract. A novel and simple method to directly assemble nanostructures onto plastic substrate via a quasi-2D electrodeposition approach was proposed. It was demonstrated that such synthetic method was feasible for flexible electronics, as exemplified by the fabrication of ZnO nanosheets film photoresponse devise onto flexible transparent, polyethylene terephthalate (PET) substrate that can withstand bending. This direct assembly strategy is general to other nanostructures onto plastic substrate which can be electrodeposited.

Keywords. Electrodeposition; Flexible; Plastic substrate; ZnO nanosheet.

1. Introduction

In the recent years, flexible electronics have got considerable research enthusiasm because of their specific features and potential applications in flexible displays, sensors, electronic textiles, artificial skins and other wearable electronics, etc [1-5]. The academic hotspot in flexible electronics will continue to move forward, which is driven by the increased demand for electronics permitting light-weight design, portability, and low manufacturing cost as compared to their rigid substrate counterparts, and supported by techniques for the unceasingly miniaturization of individual ingredient in microelectronics [6-8]. With unique geometry, outstanding photoelectric properties, excellent mechanical flexibility and fine transparency, low-dimensional inorganic semiconductor nanomaterials facilitate significant insights and opportunities and favourable prospect for flexible electronics. In general, traditional flexible substrates include plastics, paper, metal foils, ultra-thin glass, etc. The keen interest in exploiting plastics as substrates for electronic applications is derived from their advantages of flexibility, transparency, insulation, biocompatibility, light weight, low cost, and roll-to-roll processing [9, 10]. As well known, by conventional electrochemical deposition, materials cannot be sedimentated directly onto insulating plastic substrate. Nevertheless, in ultrathin layers electrodeposition, the electrode and the substrate are disconnected, and the substrate definitely be insulating. Therefore, materials can be deposited on the plastic substrate straightforward. In previous reports about the ultrathin layers electrodeposition, the nanostructure materials were none exception deposited onto rigid substrates, such as glass or SiO₂ [11-21]. It gravely limits the application range of
the obtained nanostructured materials. The insulating polymer substrate, as opposed to the metallic substrates, enables the fabrication of electrical devices. In this communication, as an example, ZnO nanosheets film was deposited onto PET substrate. Furthermore, the electrical property under different bending condition has been implemented.

2. Experimental

2.1 Method of synthesis of ZnO nanosheets film onto PET substrate

All the chemicals were analytical grade reagents without further purification. The electrolyte solution of 0.05 M Zn(NO₃)₂ was prepared by Millipore water. The growth system consist of a growth chamber, a low temperature cycle water bath, a DC power supply (DF1731SB5A), an arbitrary function generator (AFG 310), an optical microscope (Leica Dmlm) and a CCD camera (A311f). The core part of growth chamber is shown in Figure 1. A Peltier element attached to DC power supply was fixed in the centre of the growth chamber, which was used to rapidly adjust the electrolyte temperature. The growth chamber temperature was controlled by low-temperature cycle water bath, and the growth potential was supplied by an arbitrary function generator. The growth process could be observed by optical microscope and CCD camera. Silicon substrates were cut into pieces about 20×20 mm² before they were successively cleaned with ethanol and water for 10 min, rinsed with Millipore water, and blown dry with high-purity nitrogen. Then the silicon wafer was placed on the Peltier element, afterwards two parallel electrodes made of 30 µm thick Zn foil were put on silicon substrates, and separated by a distance of approximately 8 mm. Then the electrolyte was dropped on the silicon substrate. Finally, a PET sheet was carefully put on the two electrodes, after that the electrolyte would fill the space between the PET wafer and silicon substrate. A uniform ultra-thin ice layer could be formed between the silicon and PET substrate by adjusting the temperature of the Peltier element and the low-temperature cycle water bath. After an ultra-thin ice layer was formed, we kept the growth chamber temperature constant for 30 min. The ultrathin liquid layer of concentrated electrolyte was formed between the ice layer and upper surface of silicon substrate, as well as the ice layer and lower surface of PET substrate. Electrodeposition was initiated when a constant voltage of 0.8 V was applied through the parallel electrodes. When the growth process ended, a slight increase in temperature was provided by the Peltier element to melt ice. Then the PET sheet was taken out, cleaned by the deionized water, and dried at room temperature.

The morphology, component and crystal structure of the ZnO nanosheets film were characterized by scanning electron microscope (SEM FEI Magellan-400), X-ray diffraction (Rigaku D/max-Ra) and transmission electron microscopy (TEM, JEOL JEM-2200FS).
2.2 Electrical devices fabrication and characterization

The samples onto the PET substrate were chosen as the test object. First, the sample was covered by a linear mask with a width of 50 µm. Two copper wires were fixed on both sides of the mask separately. Then the Au film was deposited on the glass by vacuum ion sputtering for 3 min. After that, the mask was taken away, and the sample was connected into the circuit. The schematic diagram of the fabricated electrical device is shown in figure 2(a). For photocurrent measurements, the 355 nm laser was used to irradiate the device while a source voltage was applied directly to the photoconductor and the DC current was read from a Keithley 2400 source meter. For bending experiments, photocurrent measurements were carried out on the ZnO devices grown onto PET substrates that were taped on the outer surface of glass vials with various radii (r=1.3, 1.6 and 2.1 cm), as shown in figure 2(b).

3. Results and discussion

The morphology, component and structure information of ZnO nanosheets film grown onto PET substrate were investigated by SEM, XRD and TEM, respectively. Figure 3 shows the SEM images of the obtained film at low and high magnification. As it can be seen, the film was composed of abundant nanosheets which were interwoven with each other. The thickness of the film is about 500 nm which is equal to the width of nanosheet. The thickness of the nanosheet is about 20 nm. Figure 4 shows the XRD pattern of the ZnO nanosheets film. All the diffraction peaks match to those characteristic of the wurtzite...
ZnO structure (JCPDS 036-1451). No characteristic peaks of other chemical compounds, such as Zn or Zn(OH)$_2$, were observed. The insets of figure 4 show the TEM (i) and HRTEM (ii) images of individual ZnO nanosheet. From the TEM image, it can be seen that there are a plenty of pores existed in the surface of the nanosheet. The pore size is less than 10 nm. The HRTEM analysis of an individual nanosheet reveals clear lattice fringes, with a lattice spacing of 0.26 nm corresponds well to the d-spacing of the (002) plane of the hexagonal wurtzite ZnO.

![Figure 3](image1.png)

**Figure 3.** (a) Low- and (b) high-magnification SEM images of the ZnO nanosheets film on PET substrate.

![Figure 4](image2.png)

**Figure 4.** XRD patterns of synthesized ZnO nanosheets film. The insets show the TEM image of individual ZnO nanosheet (i) and corresponding HRTEM image (ii).
During the electrodeposition process, \( \text{OH}^- \) formed on the electrode surface according to the reaction equation as \( \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \) [11], and meanwhile \( \text{Zn}^{2+} \) were constantly migrated to the cathode under an electric field. When the concentration of \( \text{Zn}^{2+} \) and \( \text{OH}^- \) reached the deposition condition of \( \text{ZnO} \), the nanosheet began to grow. Due to the hysteresis effect of ion transport in comparison to ion consumption, the ion concentration will decrease gradually in front of the deposit which result in the nanosheet stop grows temporarily [22]. With the gradually increasing of ion concentration, the next nanosheet growth began. In this way, \( \text{ZnO} \) nanosheets film was deposited periodically by self-oscillation.

![Figure 5](image)

**Figure 5.** Time dependent photo responses of a \( \text{ZnO} \) nanosheet film device onto PET substrate subjected to different radii of curvature.

As a flexible electrical device, its electrical performance should be stable under bending conditions. In order to investigate the flexibility and stability, the device was bent to different curvature radius to assess the optoelectronic performance of the device. Figure 5 shows the photoconductor response switching behavior of a representative \( \text{ZnO} \) photoresponse device at constant bias voltages (5 V) before, during, and after it was subjected to bending at various radii of curvature (r=1.3, 1.6 and 2.1 cm) by taping the PET substrates to common glass vials (as shown in figure 2). It can be observed that the photocurrent and response/recover characteristics of the device were nearly unchanged, which reveals that the performance of the device can be hardly affected by bending. It means that there is no significant device deterioration or obvious \( \text{ZnO} \) film cracking and nanosheets peeling in these bending tests. After the above study, we can draw that the nanosheets are strong adhesion to the PET substrate, making such kind of electrodeposition based assembly approach a viable route in fabricating flexible devices.

4. Conclusions

We report a simple and effective strategy to assemble nanostructures onto plastic substrate by using ultrathin layers electrodeposition technique; here as manifested by the fabrication of \( \text{ZnO} \) nanosheets film onto PET substrate using this method. We have exploited such assembled structures for flexible electronics by the fabrication of photoresponse device which show stable photoresponse under bending at various curvature radii (r= 2.1, 1.6 and 1.3 cm). This method can also be applied in other
nanostructures through electrodeposition, which can stimulate the development of low-cost, flexible and wearable technologies, limited not only to electrical devices but also to sensor applications, etc.

5. Conflict of interest
None.

6. References
[1] Liu Z, Xu J, Chen D and Shen G 2015 Che. Soc. Rev. 44 161-192
[2] Webb R, Bonifas A, Behnaz A, Zhang Y, Yu K, Cheng H, Shi M, Bian Z, Liu Z, Kim Y, Yeo W, Park J, Song J, Li Y, Huang Y, Gorbach A and Rogers J 2013 Nature Mater. 12 1078-78
[3] Hu P, Wang L, Yoon M, Zhang J, Feng W, Wang X, Wen Z, Idrobo J, Miyamoto Y, Geohegan D and Xiao K 2013 Nano Lett. 13 1649-54.
[4] Bai S, Wu W, Qin Y, Cui N, Bayerl D and Wang X 2011 Adv. Func. Mater. 21 4464-69
[5] Yang L, Wu L, Wu M, Xin G, Lin H and Ma T 2010 Electroch. Commun. 12 1000-03
[6] Kim B, Lee S, Kang M, Ahn J and Cho J 2012 ACS Nano. 6 8646-51
[7] Grimm D, Bof Bufon C, Deneke C, Atkinson P, Thurmer D, Schäffle F, Gorantla S, Bachmatiuk A and Schmidt O 2013 Nano Lett. 13 213-218
[8] Yuan L, Lu X, Xiao X, Zhai T, Dai J, Zhang F, Hu B, Wang X, Gong L, Chen J, Hu C, Tong Y, Zhou J and Wang Z 2012 ACS Nano 6 656-661
[9] Duan X, Niu C, Sahi V, Chen J, Parce J, Empedocles S and Goldman J 2003 Nature 425 274-278
[10] McAlpine M, Friedman R, Jin S, Lin K, Wang W and Lieber C 2003 Nano Lett. 3 1531-35
[11] Cui G, Gao L, Yao B, Wang S, Zhang P and Zhang M 2013 Electroch. Commun. 30 42-45
[12] Xiao C, Yang T, Chuai M, Xiao B and Zhang M 2018 Phys. Chem. Chem. Phys. 18 325-330
[13] Wu Z, Li H, Xiong X, Ma G, Wang M, Peng R and Ming N 2009 Appl. Phys. Lett. 94 041120
[14] Wang M, Zhong S, Yin X, Zhu J, Peng R, Wang Y, Zhang K and Ming N 2001 Phys. Rev. Lett. 86 3827-30
[15] Xiao C, Xiao B, Wang Y, Zhang J, Wang S, Wang P, Yang T, Zhao R, Yu H, Li Z and Zhang M 2015 Rsc. Adv. 5 17945-52
[16] Cui G, Li Z, Gao L and Zhang M 2012 Phys. Chem. Chem. Phys. 14 16321-25
[17] Wang K, Niu L, Zong Z, Zhang M, Wang C, Shi X, Men Y and Zou G 2008 Cryst. Growth & Design 8 442-445
[18] Zhang M, Wang M, Zhang Z, Zhu J, Peng R and Ming N 2004 Electrochimica Acta 49 2379-83
[19] Cui G L, Zhang M and Zou G 2013 Scientific Reports 3 1250
[20] Wang Y, Cao Y, Wang M, Zhong S, Zhang M, Feng Y, Peng R, Hao X, Ming N 2004 Phys. Rev. E 69 021607
[21] Liu T, Wang S, Shi Z, Ma G, Wang M, Peng R, Hao X and Ming N 2007 Phy. Rev. E 75 051606
[22] Zong Z, Zhang M, Lu H, Xu D, Wang S, Tian H, Liu C, Guo H, Gao H and Zou G 2010 Appl. Phys. Lett. 96 143113